needles from hexane: mp 56–57° (lit.[37] 53–55°); ir (CCl_4) 1718 cm^{-1} (C=O); nmr (CCl_4) δ 6.9–7.5 (5 H_m, aryl CH), 3.3–3.7 (1 H_m, benzylic CH), and 1.5–2.5 (8 H_m, aliphatic CH); mass spectrum *m/e* (rel intensity) 174 (48, M^+), 130 (100), 117 (49), 104 (30), and 91 (25). After 4.00 g (23 mmol) of 2-phenylcyclohexanone in 15 ml of CCl_4 had been brominated[36] with 3.85 g (24 mmol) of Br_2, a solution of the crude product in 80 ml of 2,6-lutidine was refluxed for 1 hr. The resulting mixture was concentrated under reduced pressure and then partitioned with Et_2O and aqueous HCl. The neutral ethereal layer was dried and concentrated and the residual brown oil (3.75 g) was chromatographed on SiO_2. From fractions eluted with 20% Et_2O in hexane was isolated 1.910 g (48%) of the crude unsaturated ketone **37**, mp 86–90°. Recrystallization from an Et_2O–hexane mixture afforded 692 mg (17.5%) of the pure enone **37** as white needles: mp 93–95° (lit. 95–96°,[38] 96–97°[39]); ir (CCl_4) 1685 cm^{-1} (conjugated C=O); uv$_{max}$ (95% EtOH) 221 (ϵ 12,500) and 262 mμ (2700); nmr (CCl_4) δ 7.2–7.5 (5 H_m, aryl CH), 6.92 (1 H_t, J = 4.4 Hz, vinyl CH), and 1.8–2.7 (6 H_m, aliphatic CH); mass spectrum *m/e* (rel intensity) 172 (100, M^+), 144 (53), 116 (39), and 115 (38).

Polarographic Measurements. The previously described[5,18,40] procedures were followed with a Heath polarograph (Model EU-402V) and a Leeds and Northrup Speedomax G recorder. The electrodes were a dropping Hg cathode, a Pt wire anode, and a saturated calomel reference electrode with intermediate salt bridges containing aqueous 1 *M* $NaNO_3$ and 0.5 *M* $Et_4N^+BF_4^-$ or $(n\text{-}C_4H_9)_4N^+BF_4^-$ in $(CH_3)_2NCHO$. The solvent and supporting electrolyte were purified[41] in $(CH_3)_2NCHO$ containing 0.50 *M* $(n\text{-}C_4H_9)_4N^+BF_4^-$.[42]

The $E_{1/2}$ values (*vs.* sce) and the αn values, obtained from plots of E *vs.* $\log [i/(i_d - i)]$, are listed in Table III. These are average values from two or more separate runs.

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[37] M. S. Newman and M. D. Farbman, *J. Amer. Chem. Soc.*, **66**, 1550 (1944).

[38] W. E. Bachmann and L. B. Wick, *ibid.*, **72**, 3388 (1950).

[39] D. Ginsburg and R. Pappo, *J. Chem. Soc.*, 516 (1951).

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[42] H. O. House, E. Feng, and N. P. Peet, *J. Org. Chem.*, **36**, 2371 (1971).

Electrochemical Reduction of Stereoisomeric Geminal Dihalonorbornanes[1,2]

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Abstract: The electrochemical reduction of 2,2-dichloronorbornane, 2-*exo*-bromo,2-*endo*-chloronorbornane, 2,-*exo*-chloro,2-*endo*-bromonorbornane, and 2,2-dichloronorbornane-2-*exo*-^{36}Cl was investigated in dimethylformamide under a wide variety of conditions. All dihalides gave the same mixture of *endo*-norbornyl chloride and nortricyclene when reduced under identical conditions. The fact that methanol and water appear to be much better proton donors than phenols or acetic acid toward an intermediate carbanion in the reduction is interpreted as a surface phenomenon. Analyses of the relative rates of heterogeneous electron transfer to the two bromo chlorides and of the isotopic label retained after reduction of the labeled dichloride indicate stereochemically preferred attack by the electrode upon the norbornane nucleus from the exo direction. Alkylmercury intermediates were shown not to be required to explain the unusual effects of proton donors. Finally, electrochemical reduction of a 2,2-dihalonorbornane in the presence of a dialkyl sulfide and phenol was found to produce norbornane, and a path to account for production of the latter hydrocarbon is proposed.

The stereochemistry of electrochemical reduction of alkyl halides has received a great deal of attention recently.[3-5] Most such studies have involved reduction of cyclopropyl halides.[4,5] It appears that the predominant stereochemical pattern in such systems is reduction with (partial) retention of configuration, although (partial) inversion has also been observed during reduction of 2,2-diphenyl-1-bromocyclopropanecarboxylic acid and its methyl ester.[5b] Reduction with a high degree of stereochemical inversion was reported for the electrochemical reduction of α-chloro-α-phenylpropionic acid.[5d,6] Since the studies upon cyclopropyl halides must proceed through cyclopropyl anions, which are known to possess considerable configurational stability,[7] stereochemical patterns observed with these compounds cannot be taken as representative of alkyl halides in general. Likewise, the fact that the presence of a carboxyl group can substantially affect the overall stereochemistry of reduction[5b] indicates that the high degree of stereochemical inversion reported[5d] for the electrochemical reduction of α-chloro-α-phenylpropionic acid, even if correct,[6] might not be typical of other alkyl halides. The present study was initiated to obtain information concerning

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[1] This research constituted part of the Ph.D. Thesis of R. G. R., Wesleyan University, 1971.

[2] Portions of these results have been described in preliminary form: (a) papers presented at the 21st Meeting of the International Society of Electrochemistry, Prague, Czechoslovakia, Sept 1970, and at the 139th National Meeting of the Electrochemical Society, Washington, D. C., May 1971; (b) A. J. Fry and R. G. Reed, *J. Amer. Chem. Soc.*, **93**, 553 (1971).

[3] A. J. Fry and M. A. Mitnick, *ibid.*, **91**, 6207 (1969).

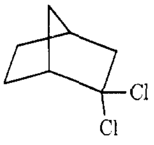
[4] J. L. Webb, C. K. Mann, and H. M. Walborsky, *ibid.*, **92**, 2042 (1970).

[5] (a) R. E. Erickson, R. Annino, M. D. Scanlon, and G. Zon, *ibid.*, **91**, 1767 (1969); (b) R. Annino, R. E. Erickson, J. Michalovic, and B. McKay, *ibid.*, **88**, 4424 (1966); (c) A. J. Fry and R. H. Moore, *J. Org. Chem.*, **33**, 1283 (1968); (d) B. Czochralska, *Chem. Phys. Lett.*, **1**, 239 (1967); (e) A. J. Fry and W. E. Britton, *Tetrahedron Lett.*, 4363 (1971).

[6] A reinvestigation of this report has, however, shown that the phenylpropionic acid formed in this reaction is essentially completely racemic: Professor R. E. Erickson and C. Fischer, private communication, Aug 4, 1971.

[7] H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3283 (1964).

the stereochemistry of reduction of alkyl halides of more representative structure than had previously been investigated, and also because it was of interest to investigate the possibility of interception, before equilibration, of stereoisomeric carbanions (**12**). The compounds investigated were 2,2-dichloronorbornane (**1**), 2-*exo*-chloro,2-*endo*-bromonorbornane (**2**), 2-*exo*-bromo,2-*endo*-chloronorbornane (**3**), and 2,2-dichloronorbornane-2-*exo*-^{36}Cl (**4**). Questions of particular interest were: (a) is there a preferred direction of approach by the electrode upon these electroactive species and (b) are dihalides **2** and **3** converted to a common intermediate during the reduction process? The experiments to be described herein not only provide answers to both of these questions but also have implications of importance for a number of other areas of organic electrochemical research. In addition, a new electrochemical reaction, exemplified by the formation of norbornane (**10**) during reduction of **2** in the presence of di-*n*-hexyl sulfide and phenol, was discovered during the course of these studies. Because previous studies have suggested that the stereochemical course of an electrode reaction is substantially dependent upon the nature of the experimental conditions,[5] reduction of **1**–**4** was studied under a wide range of experimental conditions.



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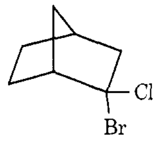

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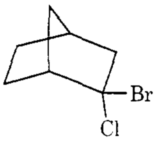

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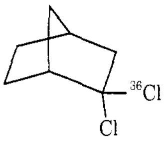

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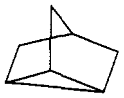
Results

Synthesis. The synthesis of compounds **2** and **3** has already been reported.[8] Synthesis of the labeled dichloride **4** took advantage of a previous observation that hydrochlorination of 2-chloronorbornene (**5**) proceeds rapidly, quantitatively, and regiospecifically to afford **1**.[9] Use of labeled hydrogen chloride in this reaction afforded **4**. The label was assigned the exo geometry, based upon stereochemical precedents in the hydrochlorination of other norbornenes[8–10] and upon the following conversions. Dehydrochlorination of **4** with potassium *tert*-butoxide in dimethyl sulfoxide resulted in the formation of **5** containing only 0.5% of the label; exo–cis dehydrohalogenation is known to be preferred in the norbornyl series.[11] Solvolysis of **4** in refluxing aqueous ethanol containing sodium acetate, *i.e.*, conditions favoring E1 elimination of hydrogen chloride,[9] yielded **5** containing less than 1% of the radioactive label. Exo loss is of course well known to be preferred over endo loss during ionization of norbornyl compounds.[12] Thus, it may be stated with confidence that at least 99% of the label is exo in **4**.[13]

Voltammetry and Coulometry. The polarographic behavior of dihalides **1**–**3** was investigated in dimethylformamide (DMF) containing 0.1 *M* tetraethylammonium bromide (TEAB). Each dihalide exhibited a single polarographic wave, distorted by a large polarographic maximum. Well-defined maxima-free polarographic waves could however be obtained with the aid of a mechanical drop timer (see Experimental Section). Dihalides **1**, **2**, and **3** had half-wave potentials of -1.54, -0.93, and -0.83 V,[14] respectively, when measured as 1 m*M* solutions in DMF–0.1 *M* TEAB, at a controlled polarographic drop time of 0.5 sec. Each compound consumed 2.00 ± 0.05 F/mol of dihalide when reduced at controlled potential at a mercury pool. The fact that **2** and **3** are reduced much more readily than **1** is as expected, based upon the well-known order of decreasing ease of reduction of alkyl halides: $RI > RBr > RCl$.[16]

All three compounds were investigated by cyclic voltammetry. In no case was there an oxidation peak upon scan reversal after the reduction peak, even at scan rates as high as 100 V sec^{-1}. No peaks other than the single reduction peak were observed either on the first or subsequent cycles. Thus, any intermediate(s) generated during reduction of the dihalides must be very short lived.

Controlled-Potential Electrolysis. Dihalides **1**–**3** were converted to a mixture of nortricyclene (**6**) and *endo*-2-chloronorbornane (**7**) upon controlled-potential electrochemical reduction at a mercury cathode. These were the only products observed, and typically accounted for 95 ± 5% of the starting material. Qualitative analysis of the electrolysis mixture by atomic absorption indicated the absence of organomercury



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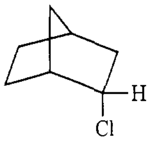

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[8] A. J. Fry, W. B. Farnham, B. J. Holstein, M. A. Mitnick, and L. C. Riggs, *J. Org. Chem.*, 34, 4195 (1969).

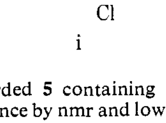
[9] A. J. Fry and W. B. Farnham, *ibid.*, 34, 2314 (1969).

[10] (a) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 89, 3901 (1967); (b) H. C. Brown and K.-T. Liu, *ibid.*, 89, 3898, 3900 (1967).

[11] J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, 88, 4922 (1966).

[12] P. D. Bartlett, "Non-Classical Ions," W. A. Benjamin, New York, N. Y., 1965.

[13] Solvolysis of 3-*exo*-deuterio-2,2-dichloronorbornane (i) under the



i

same E1 conditions[9] afforded **5** containing no detectable excess deuterium over natural abundance by nmr and low-resolution mass spectrometry.[8] Considered together, the solvolyses of **4** and i demonstrate that **1** undergoes a highly stereoselective (≧98%) exo–cis elimination of hydrogen chloride under ionizing conditions.

[14] These potentials are measured relative to the cadmium amalgam reference electrode of Marple.[15] This electrode is *ca.* -0.7 V relative to aqueous sce.

[15] L. W. Marple, *Anal. Chem.*, 39, 844 (1967).

[16] M. von Stackelberg and W. Stracke, *Z. Electrochem.*, 53, 118 (1949).

compounds after electrolysis.[17] No *exo*-norbornyl chloride was detected; a 2% yield of this compound would have been readily detected by the gas chromatographic analysis technique employed.

The relative proportions of **6** and **7** are highly dependent upon experimental conditions (*vide infra*). One variable which did *not* affect the ratio of **6** and **7**, however, is the nature of the dihalide: under identical experimental conditions **1**, **2**, and **3** each gave these products in the same ratio, suggesting that all three are converted electrochemically to a common intermediate. Since product ratios were found not to be dependent upon which dihalide is reduced, most of the subsequent experiments were carried out upon only one or two of the three dihalides, usually **2**, which is readily prepared,[8] and is more easily reduced than **1**, hence permitting a wider range of electrolysis conditions.

Stereoselectivity of Attack. It was of interest to determine whether or not there exists a preferred direction of approach of these dihalides toward the electrode. This question was investigated in two ways. The first method involved measurement of the amount of labeled chlorine-36 remaining in **7** isolated (preparative vpc) from electrochemical reduction of **4**. This proportion amounted to only 7 ± 1% of the original label. This value was independent of the cathode potential over the range -1.5 to -2.0 V, and was unaffected by added proton donors (1.0 M H_2O and 1.0 M hydroquinone). This result indicates a substantial preference for removal of the exo chlorine in the reduction. If the rates of heterogeneous reduction of exo and endo chlorine are designated as $k_{\mathrm{h,exo\,Cl}}$ and $k_{\mathrm{h,endo\,Cl}}$, respectively, 93 ± 1% removal of the label corresponds to a value of $k_{\mathrm{h,exo\,Cl}}/k_{\mathrm{h,endo\,Cl}}$ of 13 ± 2.

The second method for determining the relative ease of removal of exo and endo halogens involved comparison of the rate constants for heterogeneous electron transfer to **2** and **3**. This was done in the following way. Electrochemical cleavage of the carbon–halogen bond is a totally irreversible process (*cf.* the cyclic voltammetry data), and hence the current for reduction of an alkyl halide should increase exponentially with increasingly negative potentials so long as the rate of mass transfer is much higher than the rate of electron transfer. Specifically the polarographic current for a totally irreversible reduction process should increase exponentially with increasing negative potential, at the foot of the polarographic wave for that process, where the concentration of electroactive substance at the electrode surface may be assumed equal to its bulk concentration.[19] The latter assumption is valid for polarographic currents less than one-tenth of the diffusion-controlled limiting current for the totally irreversible process.[19] Under these conditions the polarographic current i (at the end of the drop-life) is given by

$$i = n\mathfrak{F}AC^0k^0_{\mathrm{f,h}} \exp[-\alpha n\mathfrak{F}(E - 0.46)/RT] \qquad (1)$$

where n is the number of electrons transferred per molecule in the potential-determining step, $\mathfrak{F}$ is Faraday's constant, A is the area of the mercury drop $k^0_{\mathrm{f,h}}$ is the rate constant for heterogeneous electron transfer at a potential of 0 V *vs.* the normal hydrogen electrode, E is the electrode potential relative to the cadmium chloride|cadmium amalgam reference used in the present work,[15] α is the transfer coefficient, C^0 is the bulk concentration of electroactive material, A is the area of the electrode, and R and T have their usual significance. A plot of log i *vs.* potential, therefore, will afford a straight line of slope $-2.303\alpha n\mathfrak{F}/RT$ and intercept (at 0 V) equal to log $n\mathfrak{F}AC^0k^0_{\mathrm{f,h}}$. It was found that plots of log i *vs.* potential for the reduction of **2** and **3** are indeed linear when restricted to potentials at the foot of the wave. Furthermore, the two lines are parallel, demonstrating, not surprisingly, that αn is identical for the two compounds. If the polarographic currents for reduction of **2** and **3** are designated i_2 and i_3, respectively, and the electron-transfer rate constants are designated $k^0_{\mathrm{h,endo\,Br}}$ and $k^0_{\mathrm{h,exo\,Br}}$, respectively, and the reasonable assumptions are made that (a) under the experimental polarographic conditions for reduction of **2** and **3** (identical capillary, mercury flow rates, and drop times) the area of the drop is identical in both experiments, and (b) judged from the similarities in their polarographic, cyclic voltammetric, coulometric, and large-scale electrolytic behavior, n is identical for the two substances, eq 1 simplifies to

$$\frac{k^0_{\mathrm{h,exo\,Br}}}{k^0_{\mathrm{h,endo\,Br}}} = \frac{i_3C_2^0}{i_2C_3^0} \qquad (2)$$

Since the two lines are parallel, the ratio i_3/i_2 may be measured at any potential. The ratio $k^0_{\mathrm{h,exo\,Br}}/k^0_{\mathrm{h,endo\,Br}}$ was found to be equal to 3.[20] Considering the approximations involved, this is in reasonable agreement with the value of 13 ± 2 determined from the measurements made upon **4**. Note also that since αn identical for the two compounds, this ratio is independent of potential; the ratio $k_{\mathrm{h,exo\,Cl}}/k_{\mathrm{h,endo\,Cl}}$ for the reduction of **4** was also found experimentally to be independent of electrode potential (*vide supra*).

Effects of Proton Donors. It is well known that many organic electrode reactions carried out in aprotic solvents are affected greatly by the addition of proton donors.[21] In the present context it was of particular interest to investigate the effects of added proton donors upon the reduction of dihalides **1**–**3** in order to determine whether carbanionic intermediates might be intercepted. The proton donors investigated were methanol, several phenols (phenol, hydroquinone, and 2,4,5-trimethylphenol), water, and acetic acid.

Addition of increasing amounts of water to the electrolysis solution enhanced the yield of **7** at the expense of **6** up to a value of 80% **7** at *ca.* 1.0 M water (Figure 1). It is known, however, that water is actually a relatively poor proton donor toward aromatic radical anions in DMF.[22,23] It has been postulated that this is due to the high degree of association between water and DMF (demonstrated by both the very large heat of mixing of DMF and water and the

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(17) Organomercury compounds have been detected by this technique after electrochemical reduction of 1-methyl-2,2-diphenylcyclopropyl[4] and *n*-hexyl[18] halides.

(18) J. W. Sease and R. C. Reed, unpublished observations.

(19) L. Meites, "Polarographic Techniques," 2nd ed, Wiley, New York, N. Y., 1965, pp 232–239.

(20) To our knowledge this is the first time that eq 1 has been used to determine relative rates of electron transfer to two organic species.

(21) G. J. Hoijtink, *Advan. Electrochem. Electrochem. Eng.*, 7, 221 (1970).

(22) D. L. Maricle, *Anal. Chem.*, 35, 683 (1963).

(23) J. R. Jezorek and H. B. Mark, Jr., *J. Phys. Chem.*, 74, 1627 (1970).

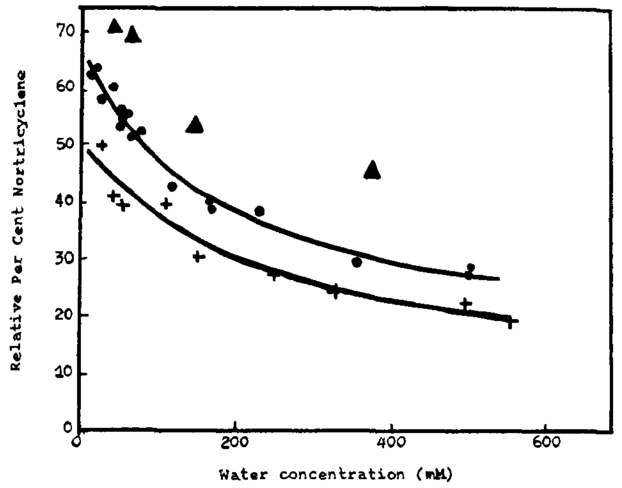

Figure 1. Dependence of products of the reduction of *exo*-2-chloro,*endo*-2-bromonorbornane in dimethylformamide upon water content and mode of reduction: ●, electrochemical reduction; +, reduction by naphthalene radical anion; ▲, electrochemical reduction in the presence of 0.2 *M* *n*-octyl sulfide.

Table I. Effects of Added Proton Donors upon the Electrochemical Reduction of Geminal Dihalonorbornanes[a,b]

Dihalide	Proton donor	Concn of proton donor, m*M*	% **6**	% **7**
1	Water	16	63	37
1	Water	75	52	48
2	Water	10	58	42
2	Water	13	62	38
2	Water	15	60	40
2	Water	26	57	43
2	Water	45	52	48
2	Water	65	48	52
2	Water	110	42	58
2	Water	160	38	62
2	Water	350	29	71
2	Water	500	27	73
2	Water	1000	20	80
2	Water	2000	20	80
2	Water	5000	20	80
2	Methanol[c]	1000	27	73
2	Acetic acid[c]	1000	32	68
2	2,4,5-Trimethylphenol[c]	1000	50	50
2	Hydroquinone[c]	1000	40	60
3	Water	66	51	49
3	Water	225	38	62
3	Water	1000	23	77

[a] Electrolyses were conducted upon a 0.02 *M* solution of the dihalide in dimethylformamide containing 0.1 *M* tetraethylammonium bromide. [b] Cathode potential was maintained at −1.8 V for **1** and −1.1 V for **2** and **3**. [c] Water content = 30–40 m*M*.

increased viscosity of the resulting solutions relative to the individual components).[23] On the other hand, water and acetonitrile are not strongly associated, and water is indeed a much better proton donor in acetonitrile than in DMF. Likewise, methanol and DMF are not strongly associated, and methanol, even though less acidic than water, is much superior to water as a proton donor in DMF.[23] It is also known that phenols and carboxylic acids are much more efficient proton donors toward aromatic radical anions in DMF than are water or alcohols.[23,24] For all of these reasons it was expected that the ratio of **6** to **7** would be affected much more by the addition of phenols or carboxylic acids than by the addition of water or methanol. To our surprise, it was actually found that added water and methanol enhance the ratio of **7** to **6** noticeably more efficiently than do acetic acid or phenols (Table I). From the data in Figure 1 and Table I, it may be seen that 0.1 *M* water is about as efficient a proton donor as is 1.0 *M* phenol (both reduce the nortricyclene yield to 42%). By way of contrast, a 0.001 *M* solution of phenol in DMF is about as efficient at intercepting naphthalene radical anion as is 1.0 *M* water.[23] The data also show that acetic acid, which also ought to be far superior to water as a proton donor,[24] is not as efficient as water, although the difference is not as marked as with phenol. Solutions containing high concentrations of both water and acetic acid or phenol afforded **6** and **7** in the same ratio as did solutions of the same water concentration alone.

There is a further indicator of unusual proton donor phenomena in this system. Electrolyses at low concentrations of water resulted in the evolution of ethylene, identified by its vpc retention time. Ethylene is undoubtedly generated by a Hoffmann elimination upon the supporting electrolyte (tetraethylammonium bromide) by a base generated in the electrolysis (*vide infra*).[4] It was observed that ethylene formation is not completely quenched by addition of phenols or acetic acid (1.0 *M*), indicating that tetraethylammonium ion competes favorably as a proton donor with the latter species under our conditions. Water completely quenches ethylene formation, and hence is again seen to be superior as a proton donor to phenols or acetic acid.

A number of electrolyses were performed using electrolytes other than TEAB. Within experimental error (±2–3%), the ratio of **6** to **7** was the same (at equal water concentrations) whether lithium bromide or TEAB was the electrolyte (Table II). Phenol appears to be a much better proton donor when lith-

Table II. Effects of Electrolytes and Proton Donors upon the Electrochemical Reduction of 2-*exo*-Chloro,2-*endo*-bromonorbornane[a]

Electrolyte[b]	Water concn, m*M*	% **6**	% **7**
LiBr	75	52	58
TEAB	75	53	47
LiBr	350	35	65
TEAB	350	30	70
LiBr	1000	25	75
TEAB	1000	22	78
LiBr[c]	17	13	87
TEAB[c]	15	39	61
LiBr[c]	155	11	89
TEAB[c]	100	41	59
LiBr[c]	500	10	90
TEAB[c]	500	28	72
LiBr[c]	1000	11	89
TEAB[c]	1000	23	77
TBAI	150	26	74
TBAP	200	38	62
Et_3NHBr	15	8	92

[a] Electrolysis conditions same as in Table I. [b] TEAB = tetraethylammonium bromide; TBAI = tetrabutylammonium iodide; TBAP = tetrabutylammonium perchlorate. [c] Solution contained 1.0 *M* phenol.

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(24) M. E. Peover, *Electroanal. Chem.*, **2**, 1 (1967).

ium bromide is the electrolyte than when the electrolyte is TEAB. Table II also shows that the anion of the supporting electrolyte has little effect upon the electrolysis (*cf.* the results with TEAB, TBAP, and TBAI, which suggest that only iodide ion affects product ratios). When the cation of the electrolyte is changed from tetraethylammonium to triethylammonium, the ratio of **7** to **6** is, however, considerably higher (92:8) than that observed (38:62) when the electrolyte is TEAB.

Search for Alkylmercury Compounds. Since alkylmercury compounds have been identified by several investigators as intermediates and/or products during the electrochemical reduction of alkyl halides,[4,18,25] it was deemed advisable to search for such species in our experiments. This search involved several kinds of experiments. First of all, a plot of the logarithm of the electrolysis current with time was prepared and was found to be a straight line. Nonlogarithmic decay of current with time had previously been invoked as evidence for an alkylmercury intermediate.[4] Secondly, examination of the electrolysis solution by atomic absorption after electrolysis indicated the absence of detectable amounts of mercury-containing species. This procedure had been shown previously to produce positive results when mercury-containing products are formed in electrolyses.[4,18] Coulometry provided a third means of demonstrating that alkylmercury intermediates do not build up in solution during electrolysis. The sum of the absolute yields of products **6** and **7** was measured as a function of time during a typical electrolysis; the amount of current passed in the electrolysis was recorded simultaneously. Throughout the experiment complete "current balance" was attained; that is, the total current passed at any point during the electrolysis was just enough to account for the amount of products formed, assuming the previously established coulometric value of 2 F/mol of dihalide. As Mann, Webb, and Walborsky have pointed out, electrolyses involving buildup and decay of appreciable amounts of alkylmercury intermediates will not exhibit a current balance.[4] Instead, at the beginning of electrolysis, current will be consumed faster than product appears, and *vice versa* near the end of the electrolysis.

All of the above lines of evidence demonstrate that alkylmercury compounds are neither products of the electrolysis nor formed in substantial quantities during electrolysis, but they do not eliminate the possibility that organomercury compounds might be intermediates present at low steady-state concentrations. Two other types of experiments afforded information on the latter possibility, however. Both experiments involve reduction of **2** in the absence of mercury. In the first of these, electrolysis of **2** was carried out at a platinum cathode in the presence of known amounts of water; the relative and absolute yields of **6** and **7** were the same as in electrolyses at mercury under the same conditions.[26] In the second type of experiment, naphthalene was reduced electrochemically to its radical anion, and the geminal halide **2** was then added to the resulting solution after the electrical current had been interrupted. The products were **6** and **7**, as in the direct electrolytic reduction of **1** and **2**. Because of the slowness of reaction between naphthalene radical anion and water in DMF, it was possible to generate the radical anion in solutions whose water content ranged as high as 0.5 *M*, although such solutions did decay rather rapidly. The dependence of the relative yields of **6** and **7** upon the concentration of water was roughly the same as in the direct electrochemical reduction of **1**–**3**, except that the relative yield of **6** was generally lower for a given concentration of water in these experiments than in the direct reduction (Figure 1).

Addition of Sulfides. Suspicion that the unusual response of this system to the addition of proton donors arose from effects operating in the electrical double layer at the electrode surface (see Discussion) prompted experiments designed to test the response of the system to deliberate perturbations of the structure of the double layer. (The experiments described above involving changes in the nature of the supporting electrolyte were in fact prompted by this consideration.)

Addition of surface-active substances, *i.e.*, substances adsorbed at the electrode–solution interface, is known to affect the course of many electrochemical reactions.[27] Many organic sulfur compounds are strongly adsorbed upon mercury.[28] The effect of addition of various organic sulfides upon the electrochemical reduction of **2** was therefore investigated. The polarographic behavior of **2** was found to be unaffected by the addition of *n*-hexyl or *n*-octyl sulfides (0.2 *M*). Preparative scale electrolysis of **2** in DMF–TEAB containing 0.2 *M* alkyl sulfides and varying amounts of water afforded, as usual, **6** and **7**. These electrolyses differed in two respects from identical experiments carried out in the absence of sulfides however. First, the relative yield of nortricyclene **6** was always greater in the presence of sulfide than when it was omitted (Figure 1). More surprising was the decrease in the absolute yields of **6** and **7**. Electrolyses conducted in the presence of octyl, phenyl, and hexyl sulfides resulted, for the first time in this investigation, in a situation in which the sum of the absolute yields of **6** and **7** was not extremely high (95–100%). Electrochemical reduction of **1** in the presence of hexyl sulfide, for example, produced **6** and **7** in 23 and 42% yields, respectively. No other volatile products (vpc) were produced in these electrolyses.

Since (a) sulfur compounds are often adsorbed strongly on mercury, and (b) it was felt (see Discussion) that the poor proton donor ability of phenols and carboxylic acids in this system lay in their exclusion from the inner layer at the electrode surface, it was decided to examine the effect of addition to the electrolysis solution of sulfur-containing proton donors. The expectation was that adsorption would enhance the concentration of these substances in the inner layer. The additives selected were thiophenoxyacetic acid (**8**) and 4-methylthio-3-methylphenol (**9**). These proton donors indeed increased the ratio of **7** to **6**. At the same time, however, a more striking phenomenon

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(25) J. Grimshaw and J. S. Ramsey, *J. Chem. Soc. B*, 60 (1968).

(26) Phenol could not be investigated as a proton donor due to interference from hydrogen discharge (reduction of phenol to hydrogen and phenolate ion) at platinum.

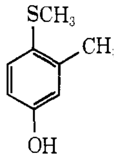
(27) (a) J. Heyrovsky and J. Kuta, "Principles of Polarography," Academic Press, New York, N. Y., 1966, Chapter 16; (b) L. Holleck, B. Kastening, and R. O. Williams, *Z. Electrochem.*, **66**, 396 (1962).

(28) (a) R. S. McKinney and S. Rosenthal, *J. Electroanal. Chem.*, **16**, 261 (1968); (b) E. Blomgren, J. O'M. Bockris, and C. Jesch, *J. Phys. Chem.*, **65**, 2000 (1961); (c) I. M. Kolthoff, W. Stricks, and N. Tanaka, *J. Amer. Chem. Soc.*, 77, 4739 (1955).

was observed, *i.e.*, the formation of a third volatile product, norbornane (**10**). The sum of the absolute yields of **6**, **7**, and **10** was 100 ± 5%. When [H_2O] = 110 m*M*, for example, the yields of **6**, **7**, and **10** were 42, 58, and 0%, respectively, while in the presence of **8** (0.2 or 1.0 *M*), they are 10, 54, and 36%, respectively. When [H_2O] = 70 m*M*, the ratio of **6** to **7** is 48:52; when [**9**] = 0.2 *M*, the yields of **6**, **7**, and **10** are 22, 72, and 6%, respectively. At [**9**] = 1.0 *M*, these yields become 18, 77, and 5%, respectively. Electrolysis of **2** in the presence of an alkyl sulfide *and* a phenol does result in formation of norbornane, and in amounts sufficient to provide a satisfactory material balance: **6**, **7**, and **10** are produced in yields of 23, 42, and 35% in the reduction of **2** in a solution containing 1.0 *M* phenol and 0.2 *M* *n*-hexyl sulfide; recall (*vide supra*) that in a similar electrolysis not containing phenol these yields were 23, 42, and 0%.

$C_6H_5SCH_2CO_2H$

8



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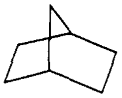


10

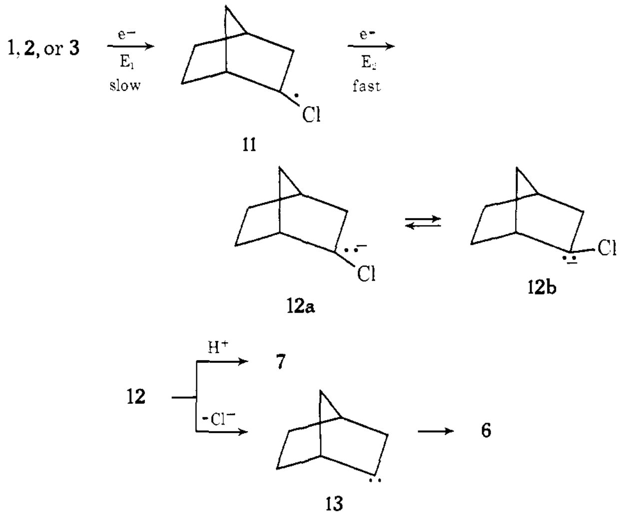
At present not enough is known concerning the nature of the reaction(s) leading to formation of norbornane to permit any definitive mechanistic proposal. (This process is being studied intensively by us.) In the present context it will suffice to describe results which permit a phenomenological description of the process. First of all, **10** does not arise from simply direct reduction of either **6** or **7**; these substances are not reducible even at the most negative potentials accessible in DMF–TEAB, irrespective of the presence or absence of dialkyl sulfides or dialkyl sulfides plus phenol. The following experiments serve to suggest the approximate sequence of events leading to **10**. The electrolysis of a mixture of **2** and hexyl sulfide was allowed to proceed until the formation of **6** and **7** was complete (10 min). The current was then turned off, and phenol was added. No norbornane was formed over the next 20 min. If the electrical current was turned on, either at the end of this interval or immediately after addition of phenol, norbornane formation began and continued until it had reached its final value. If the current was interrupted during the latter process, norbornane production stopped; it resumed, however, when the current was turned back on. It is noteworthy that norbornane formation is slow; formation of **6** and **7** was normally complete in 10–15 min, either in the presence or absence of added sulfide, while norbornane formation always continued over a period of 30 min or more.

These results permit the following description of the reaction. Dialkyl sulfides intercept an intermediate X in the reduction of **2**, forming a new intermediate Y. Although Y is not reducible electrochemically, it can be protonated by phenol, however, to afford a new species, Z, which *is* electrochemically reducible to norbornane. Z is reduced slower than the starting dihalide; this would be true if its reduction potential were negative of that of **2**. The identity of X, Y, and Z is the subject of speculation in the Discussion.

Discussion

Mechanism of Reduction. A plausible mechanistic scheme to account for the observed products is shown in Scheme I. Initial electron transfer to **1**, **2**, or **3** should cleave the carbon–halogen bond and generate radical **11**. We presume that the reduction potential E_2 of the radical **11** is quite positive of the potentials (E_1) at which initial cleavage of the carbon–halogen bond of **1**–**3** takes place (−1.5 V for **1** and *ca.* −0.9 V for **2** and **3**). This presumption is based both upon the evidence against mercury compounds as intermediates or products (*vide supra*) and upon the potential independence of the product distribution. It is not unreasonable that **11** should be easier to reduce than a simple alkyl radical, in view of the presence of the electronegative chlorine atom. Reduction of **11** would afford the anion **12**. Protonation of this species from the less hindered exo direction would then afford **7**. Ejection of chloride ion from **12** would on the other hand afford carbene **13**, which is known to undergo transannular insertion to afford **6**.[29]

Scheme I



A number of investigators[4,30] have written the initial step in the electrochemical reduction of alkyl halides not as

$$RX + e^- \longrightarrow R\cdot + X^- \qquad (3)$$

but as a composite of two steps, *i.e.*

$$RX + e^- \longrightarrow \underset{\mathbf{14}}{[RX]\cdot^-} \qquad (4a)$$

$$\mathbf{14} \longrightarrow R\cdot + X^- \qquad (4b)$$

We have no firm evidence bearing on the question of whether eq 3 represents a single step or a composite of two steps. The results from fast scan (100 V/sec) cyclic voltammetry indicate, however, that if a species analogous to **14** is an intermediate, its lifetime must be no more than a few milliseconds. We prefer therefore to regard eq 3 as a single step, in the absence of any data to the contrary. In general, the resolution of this question ought to be extremely difficult. Species analogous to **14** have been suggested as intermediates

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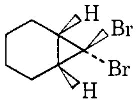
[29] W. G. Dauben and F. G. Willey, *J. Amer. Chem. Soc.*, **84**, 1497 (1962).

[30] (a) L. W. Marple, E. I. Hummelstedt, and L. B. Rogers, *J. Electrochem. Soc.*, 107, 437 (1960); (b) N. S. Hush and G. A. Segal, *Discuss. Faraday Soc.*, No. 45, 23 (1968).

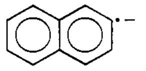
in the reaction of alkyl halides with solvated electrons,[31,32] and their lifetimes are far too short for measurement by standard electrochemical techniques.

Stereochemical Preference for Exo Reduction. Several years ago we suggested that the first stage in the electrochemical reduction of **15** and some related compounds was stereoselective removal of the less hindered halogen atom, *i.e.*, the one which is cis to the two hydrogen atoms at the ring juncture.[5c] This suggestion was subsequently disputed by Erickson, *et al.*, who suggested instead a mechanism for reduction of such compounds involving indiscriminate removal of either halogen atom.[5a] While we feel that the mechanistic scheme proposed by Erickson is unnecessarily complicated compared with the one originally proposed by us, we choose not to comment further upon it. The experiments conducted by us upon the extent of radioactive label removed from **4** upon reduction and upon the relative rates of reduction of **2** and **3** do, however, clearly indicate that in the norbornyl system an electrode can indeed discriminate between two sites of differing stereochemical accessibility. This may well be a fairly general phenomenon. Kabasakalian and McGlotten studied the polarographic reduction of several keto steroids and found the ease of reduction to be correlated with the degree of steric hindrance about the carbonyl group (the least hindered ketones being easiest to reduce),[33] and Schenck and Kirchhof reduced the less hindered carbonyl (at C-3) of a diketo steroid selectively on a preparative scale many years ago.[34] Lambert observed that *exo*-norbornyl bromide is substantially easier to reduce than the endo bromide.[35] He ascribed the difference to the relative ease of ionization of the two bromides, but it would also be consistent, of course, with the relative steric accessibilities of the two halogens.[36]



15

Effects of Proton Donors. The effects of proton donors upon the electrochemical reduction of dihalides **1**–**3** are undoubtedly unusual. A very substantial literature exists to support the generalization that in DMF water is a much poorer proton donor than phenols or carboxylic acids. We find (Figure 1 and Table I), however, the reverse order to hold in our system. Is there an inconsistency here? We think not. We believe the difference in relative proton donor abilities to arise from the differences in basicity of the species being protonated. All previous studies involving measurement of relative effects upon electrochemical behavior of adding different proton donors have involved aromatic radical anions, *e.g.*, **16**, **17**, or **18**. The negative charge in such species is highly delocalized. By contrast, the negative charge in anion **12** is localized on one carbon atom. The basicity of **12** should for this reason be *much greater* than that of **16**–**18** or other radical anions. There is ample precedent for this premise. Bank and Bockrath have recently shown very clearly that carbanion **19** is orders of magnitude more basic (kinetically) toward water than is **16**.[40] Likewise, we have pointed out that the extent of delocalization in radical anions of aromatic imines (Schiff bases) is directly related to their lifetimes in DMF.[41] One would expect that in general kinetic basicities of electrochemically generated bases ought to be inversely proportional to the extent to which the negative charge is dispersed in such species. An analogous generalization has in fact already been proposed with respect to the reactivity of electrochemically generated aromatic radical cations.[42]



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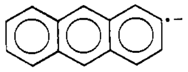
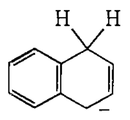


17

$(C_6H_5)_2CO^{\cdot -}$

18



19

The chemical composition of the highly structured region of solution near the electrode surface known as the electrical double layer can differ very substantially from the composition of the bulk solution.[43] It is in this region that electrochemically generated intermediates are initially produced. We propose the following generalization: highly reactive, short-lived intermediates generated at an electrode surface may undergo chemical reaction faster than diffusion out of the electrical double layer; if so, their reactions may not be characteristic of reactions occurring in the bulk of solution. Conversely, species which are long lived relative to the time necessary to diffuse out of the double layer will react normally in bulk solution. The unusual proton donor effects observed by us can be understood if carbanion **12** is reacting in the electrical double layer and if the composition of that region is unrepresentative of the bulk composition of the solution. We conclude that water and methanol are constituents of the inner layer, and that phenols and carboxylic acids are present in the inner layer in much lower amounts than their bulk concentrations. Only in this way can we account for the fact that the latter substances, although much more acidic than water or methanol, are relatively inefficient at capturing **12**. The fact that Hoffmann elimination upon tetraethylammonium ion to afford ethylene is suppressed by added water but not by added acetic acid, even when the ratio of acetic acid to tetraethylammonium ion is 10:1, demonstrates this inefficiency very dramatically.

It follows from the above line of reasoning that in

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(31) (a) M. Anbar, *Advan. Phys. Org. Chem.*, **7**, 115 (1969); (b) M. Anbar and E. J. Hart, *J. Phys. Chem.*, **71**, 3700 (1967).

(32) Methyl iodide radical anion, $[CH_3I]^{\cdot -}$, has been estimated to have a lifetime of *ca.* 10^{-7} sec in aqueous solution at 25°: J. K. Thomas, *ibid.*, **71**, 1919 (1967).

(33) P. Kabasakalian and J. McGlotten, *Anal. Chem.*, **31**, 1091 (1959).

(34) M. Schenck and H. Kirchhof, *Z. Physiol. Chem.*, **163**, 125 (1927).

(35) F. L. Lambert, A. H. Albert, and J. P. Hardy, *J. Amer. Chem. Soc.*, **86**, 3155 (1964).

(36) Sease and coworkers have shown that ionization does not occur in the transition state for electrochemical reduction of benzyl bromides.[37] Initial ionization to a carbonium ion[38] cannot be operating in the reduction of **2** and **3**. Under ionizing conditions[9] **2** eliminates both hydrogen chloride and hydrogen bromide, but *chlorine* loss is preferred (HCl:HBr $\simeq$ 2:1).[39] If reduction of **2** involved initial ionization, norbornyl bromide would be one of the products.

(37) J. W. Sease, F. G. Burton, and S. L. Nickol, *J. Amer. Chem. Soc.*, 90, 2595 (1968).

(38) P. J. Elving, *Rec. Chem. Progr.*, **14**, 99 (1953).

(39) B. J. Holstein and A. J. Fry, unpublished results.

(40) S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, **93**, 430 (1971).

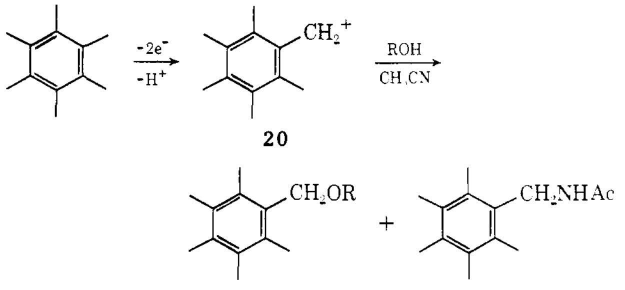
(41) A. J. Fry and R. G. Reed, *ibid.*, **91**, 6448 (1969).

(42) (a) L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *ibid.*, **89**, 5766 (1967); (b) R. N. Adams, *Accounts Chem. Res.*, **2**, 175 (1969).

(43) D. M. Mohilner, *Electroanal. Chem.*, **1**, 241 (1966).

order to affect the behavior of a very reactive carbanion, a proton donor must be present in substantial concentration in the inner layer. It is known that tetraalkylammonium ions are specifically adsorbed at mercury;[43] hence an acidic ammonium ion would be expected to be an efficient trap for reactive carbanions. Indeed, when tetraethylammonium bromide was replaced as supporting electrolyte by the stronger acid triethylammonium bromide, the ratio of **7** to **6** rose from 38:62 to 92:8. Triethylammonium ion (pK_a = 9.2 in DMF) is a stronger acid than acetic acid (pK_a = 13.5 in DMF),[44] but the important feature here is suggested to be its incorporation into the inner layer.[45] Availability, rather than acidity, of a proton source appears to be the more important feature where reactive anions are concerned. The results obtained using the sulfur-containing proton donors **8** and **9** support the hypothesis that the ratio of **7** to **6**, *i.e.*, the efficiency with which **12** is trapped, is related to proton availability in the inner layer. Like other sulfur compounds, **8** and **9** ought to be adsorbed on mercury. Thus, these compounds should be present in higher concentration in the double layer than are simple phenols and carboxylic acids, and they should therefore have a greater effect upon the ratio of **7** to **6** than do the latter. This is indeed the case.

The data of Table II indicate that phenol is a better proton donor when lithium bromide is the electrolyte than when the electrolyte is TEAB. The ability of water to protonate **12** is apparently independent of the nature of the supporting electrolyte, however. The effect of lithium might be due to its small size, which would produce a steeper potential gradient in the inner Helmholtz layer, and hence possibly affect the pK_a of phenol by a Wien effect.[46] It is also possible that lithium ion is strongly solvated by phenol, thus leading to artificial incorporation of this proton donor into the double layer in fashion akin to that observed with **8**, **9**, and triethylammonium ion. An analogous proposal has been made in anodic chemistry by Nyberg and by Eberson and Olofsson.[47] Nyberg studied the electrochemical oxidation of hexamethylbenzene, a reaction known to involve the pentamethylbenzyl cation **20** as an intermediate, in acetic acid–acetonitrile mixtures.[47a] The products are acetate **21a** and amide **22**, depending upon whether **20** undergoes nucleophilic attack by acetic acid or by acetonitrile (the latter initiates a Ritter reaction involving traces of water in the solvent). The ratio of **21a** to **22** in 99:1 acetonitrile–acetic acid is 16:84 and 22:78 when the electrolyte is sodium perchlorate and tetrabutylammonium perchlorate, respectively, but is 81:19 when the electrolyte is tetrabutylammonium tetrafluoroborate.[47a] It was argued that **21a** predominates over **22** in the presence of tetrafluoroborate ion because the latter is preferentially solvated by acetic acid. Since the anion should be present in excess in the inner Holmholtz layer at anodic potentials, the local concentration of acetic acid at the electrode surface would therefore be higher than in bulk solution. Exactly analogous results were obtained by Eberson and Olofsson, and the same rationale was presented, for the electrochemical oxidation of hexamethylbenzene in acetonitrile–water solutions.[47b]

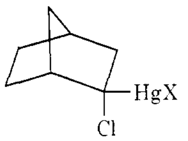


20

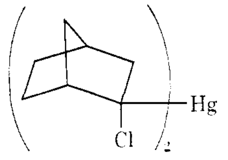
21a, R = Ac
b, R = H

22

Alkylmercury compounds have sometimes been identified as intermediates or products of electrochemical reduction of alkyl halides at mercury cathodes.[4,18,25] The possibility therefore existed that the apparently anomalous order of proton-donating efficiency ($H_2O \sim CH_3OH >$ phenols or carboxylic acids) observed in this system arises because the step leading to **7** is not protonation of **12** but protonolysis of an alkylmercury intermediate, *e.g.*, **23** or **24**. The Results summarize several experiments which demonstrate that alkylmercury compounds are not products of the electrolyses, and if intermediates, must be present in no more than low steady-state concentrations. It is clear, furthermore, from the fact that similar results were obtained during reduction of **2** either electrochemically at a platinum cathode or in homogeneous solution by naphthalene radical anion, that no evidence exists compelling the postulate of such intermediates at all during reductions at mercury. A final strong argument against such intermediates comes simply from their known chemistry. It could be argued that protonolysis of **23** or **24** could produce **7**, while thermal fragmentation of these species into carbene **13** could lead to **6**. Since the electrolyses were complete in 15 min at room temperature, both of these processes would have to be rapid. In fact, protonolysis of organomercury compounds usually requires considerably more vigorous conditions,[48a] and compounds analogous to **23** and **24** are known to be thermally stable in the absence of added catalysts.[48b] Bis(bromomethyl)mercury, $Hg(CH_2Br)_2$, is recovered unchanged in 99% yield after 20 days in refluxing benzene, for example.[48b] Bromomethylmercuric bromide, $BrCH_2HgBr$, is even more stable toward methylene transfer than is bis-



23, X = Cl or Br



24

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[44] I. M. Kolthoff, M. K. Chantooni, Jr., and H. Smagowski, *Anal. Chem.*, **42**, 1622 (1970).

[45] Horner has reached a similar conclusion from a study of the effects of proton-donating electrolytes, *e.g.*, dimethylammonium ion, upon the hydrodimerization of ethyl cinnamate in methanol: L. Horner and H. D. Ruprecht, *Tetrahedron Lett.*, 2803 (1970).

[46] (a) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1958, p 138 ff; (b) A. Vincenz-Chodkowska and Z. R. Grabowski, *Electrochim. Acta*, **9**, 789 (1964).

[47] K. Nyberg, *Chem. Commun.*, 774 (1969); (b) L. Eberson and B. Olofsson, *Acta Chem. Scand.*, **23**, 2355 (1969).

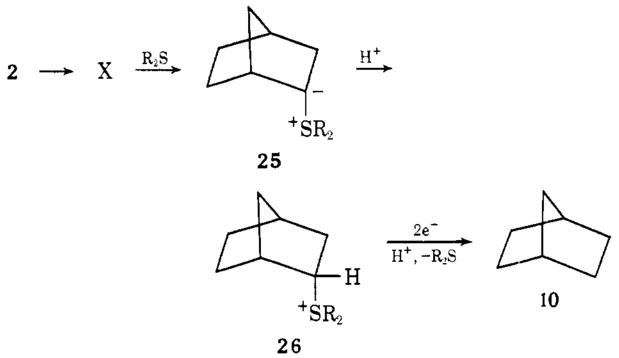
[48] (a) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968; (b) D. Seyferth, P. M. Turkel, M. A. Eisert, and L. J. Todd, *J. Amer. Chem. Soc.*, **91**, 5027 (1969).

(bromomethyl)mercury: the latter undergoes slow reaction with cyclohexene to afford norcarane over an 8-day interval at 80° in benzene, but bromomethylmercuric bromide can be recovered from this reaction.[48b]

The experiments involving reaction between **2** and electrochemically generated naphthalenide ion also provide convincing evidence that alkylmercury compounds need not be invoked as intermediates. It is well known that the reaction of alkyl halides with naphthalenide ion involves reduction of the alkyl halide to a carbanion; hence it is entirely reasonable that anion **12** should be generated in this reaction.[49,50] The ratio of **7** to **6** exhibits about the same trend with increasing water concentration as in the direct electrochemical reduction of **2**, except that for a given water concentration the ratio of **7** to **6** is always larger in the direct reduction than with naphthalenide ion (Figure 1). This may indicate that even the concentration of water at the electrode surface, while not zero, is less than its bulk concentration. This would be consistent with both the formation of ethylene during reductions in the presence of as much as 0.2 *M* water and recent electrocapillary data on DMF–water solutions.[51] It would also be reasonable, since metals are "soft" acids, while water is a "hard" base and DMF is "soft." All of the anions known to be strongly specifically adsorbed on mercury are also soft bases.[52] While we are unable at present to present a definitive rationalization of the fact that water concentrations in the double layer in DMF appear to be much higher than those of phenols or carboxylic acids, this finding does have major implications for organic electrochemical experimentation. Phenols or carboxylic acids are often added to aprotic solvents to trap electrochemically generated carbanions. Our results suggest that failure to affect a reaction in a major way through addition of one of these acidic proton donors does not necessarily demonstrate that the reaction does not involve carbanionic intermediates. Quenching of anions by phenols or carboxylic acids ought to be particularly inefficient when the negative charge on the anion is localized on a single carbon atom. We have recently encountered a situation where even water is not a very efficient proton donor because the carbanion has a rapid intramolecular reaction available to it.[5e]

Addition of Sulfides. The results obtained by addition of **8** and **9** suggest that adsorption of these compounds on the electrode surface through their sulfur functionality constitutes a method of enhancing proton donor concentrations in the double layer. The challenging question remains of describing the mechanism by which norbornane **10** is formed during the reduction of **1** or **2** in the presence of **8** or **9** or a mixture of dialkyl sulfide and phenol. The experiments described in the Results demonstrate the existence of more than one intermediate in the reduction. A possible mechanism is outlined in Scheme II. In this scheme, the electroinactive intermediate Y is sulfur ylide **25**, which is protonated by phenol to afford sulfonium salt **26** (Z). Reduction of the latter would then lead to norbornane. There are precedents for several of the individual steps in this scheme. It is known that sulfur ylide **27** is not reducible electrochemically at mercury. The corresponding sulfonium salt **28**, is, however, reduced cleanly to acetophenone at a mercury cathode.[53] A number of other simple sulfonium salts have been reduced electrochemically with cleavage of the carbon–sulfur bond, although the mechanisms of such reductions are unclear.[54] A question exists as to the identity of the intermediate X which is intercepted by the alkyl sulfide. Possible candidates are radical **11**, carbanion **12**, and carbene **13**. Reactions of dialkyl sulfides with radicals, carbanions, and carbenes have in fact all been observed at one time or another.[55] The fact that the yields of both **6** and **7** are diminished by the addition of sulfur compounds suggests, however, that it is not the carbene **13** but an earlier intermediate, *i.e.*, **11** or **12**, which is actually being intercepted. Experiments, including the synthesis of **25** and **26**, are underway to elucidate the mechanism of the process producing norbornane.[56]

Scheme II



$C_6H_5CO\overset{-}{C}H\overset{+}{S}(CH_3)_2$ **27**

$C_6H_5COCH_2\overset{+}{S}(CH_3)_2$ **28**

A final parenthetical comment regarding our synthetic route to authentic **6** is in order here. Addition

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(49) J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, **88**, 4260 (1966).

(50) Isolation of nortricyclene, derived from **13**, from these reactions constitutes the first example of formation of a carbene product from reduction of a geminal dihalide with naphthalenide ion. Further reduction of **7** to norbornane was minimal under these conditions because an excess of **2** was added to the solution of naphthalenide.

(51) R. Payne, *Advan. Electrochem. Electrochem. Eng.*, **7**, 1 (1970).

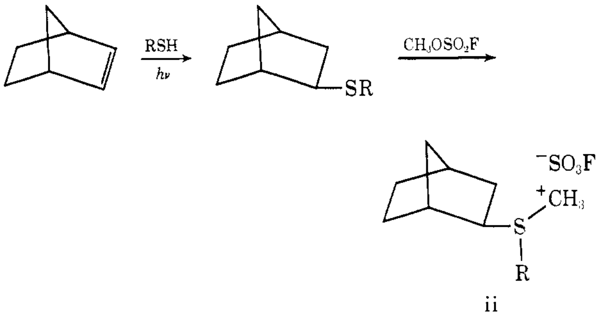
(52) D. J. Barclay, *J. Electroanal. Chem.*, **19**, 318 (1968).

(53) (a) P. Zuman and S.-Y. Tang, *Collect. Czech. Chem. Commun.*, **28**, 829 (1963); (b) J.-M. Saveant, *C. R. Acad. Sci.*, **258**, 585 (1964).

(54) (a) P. S. McKinney and S. Rosenthal, *J. Electroanal. Chem.*, **16**, 261 (1968); (b) M. Finkelstein, R. C. Petersen, and S. D. Ross, *J. Electrochem. Soc.*, **110**, 422 (1963); (c) W. A. Bonner, *J. Amer. Chem. Soc.*, **74**, 5078 (1952).

(55) (a) Radicals, U. Schmidt, A. Hochrainer, and A. Nikiforov, *Tetrahedron Lett.*, 3677 (1970); (b) carbanions, B. M. Trost and S. Ziman, *Chem. Commun.*, **181** (1969); (c) carbenes, W. Kirmse and M. Kapps, *Chem. Ber.*, **101**, 994 (1968).

(56) Compound ii has been synthesized by the indicated route as a



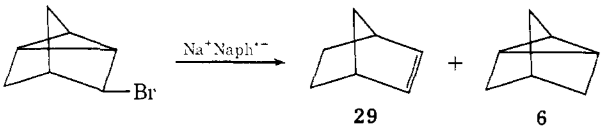
ii

(mixture of diastereomers)

R = *n*-hexyl

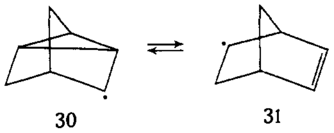
model compound for **26**. Electrochemical cleavage of ii is slow (30–50 min) at the potentials used to reduce **2**; norbornane is the major hydrocarbon produced, along with a trace of hexane: L. L. Chung, unpublished results.

of a 2.1 *M* solution of sodium naphthalenide in triglyme to a solution containing nortricyclyl bromide produced a 2:1 mixture of **6** and norbornene (**29**),



29 **6**

presumably *via* the interconverting pair of radicals **30** and **31**.[57] Under these conditions the first intermediate, **30**, undergoes rearrangement to **31** at a rate competitive with further electron transfer to form the corresponding carbanion. Electrochemical reduction of nortricyclyl bromide in DMF (−2.5 V *vs.* sce) resulted, however, in quantitative formation of **6**, unaccompanied by **29**. Presumably at the electrode surface reduction of **30** to the corresponding anion occurs faster than its rearrangement to **31**.



30 **31**

Experimental Section

Apparatus. Polarography and cyclic voltammetry at a hanging mercury drop were carried out with the aid of a Princeton Applied Research (PAR) Model 170 electrochemistry system. Polarographic drop times were controlled at 0.5 sec with the PAR Model 172 drop timer. Controlled-potential electrolyses were performed using a potentiostat based upon a Kepco KS-120-2.5 programmable power supply. Coulometry was performed by recording the voltage drop across a standard resistor in series with the cell on a Leeds and Northrup Speedomax H recorder equipped with Disc integrator and the digital printer accessory for the integrator. Preparative gc was carried out on a Varian Model 90-P3; analytical gc was carried out on a Varian Model 1200, with flame ionization detector.

Chemicals. Dimethylformamide (DMF) was purified by reflux over 4A molecular sieve, followed by distillation *in vacuo* from molecular sieve. The water content of each electrolysis mixture was checked by gc analysis (5 ft × $^1/_4$ in., Porapak Q, 210°) immediately before electrolysis was begun. Electrolytes were purified by standard procedures,[58] dried overnight in a vacuum desiccator, and then stored in the desiccator. Triethylammonium bromide was prepared by reaction between 40% hydrobromic acid and the amine at 0°, evaporation to dryness, and recrystallization from ether, mp 254°.

Scintillation Counting. 2,2-Dichloronorbornane-*exo*-^{36}*Cl* (**4**) and its reduction product *endo*-norbornyl chloride-^{36}*Cl* were analyzed by scintillation spectrometry. A weighed sample (1–10 mg) was dissolved in 15.00 ml of scintillation grade toluene containing Packard Permablend I. These solutions, contained in low-potassium glass vials, were counted in a Packard Tricarb liquid scintillation spectrometer Model 3003 equipped with automatic sample changer and printer.

Materials. Dihalides **1–3** were prepared according to published procedures. *exo*-Norbornyl chloride was prepared by hydrochlorination of norbornene. *endo*-Norbornyl chloride and nortricyclene were characterized through isolation of the products of an electrolysis by preparative-scale vpc and comparison of their nmr spectra with literature data. Nortricyclene was also prepared by electrochemical reduction of nortricyclyl bromide in DMF at −1.8 V (*vs.* cadmium amalgam); gc analysis revealed the absence of norbornene (**29**).

2,2-Dichloronorbornane-*exo*-^{36}*Cl* (4). H^{36}Cl (0.34 ml; 2.35 *N*) (specific activity 3.5 mCi/g) (New England Nuclear) was dissolved in 5 ml of concentrated hydrochloric acid. 2-Chloronorbornene was hydrochlorinated using this solution in the Brown[2] hydrochlorinator. The specific activity of the resulting dichloride after purification by preparative scale gc was 2.0 μCi/mmol.

Gc Analyses. Electrolysis products were analyzed using a 25 ft × $^1/_8$ in. column of 8% Zonyl E-7 on Chromosorb G in series with a 25 ft × $^1/_8$ in. column containing 5% Zonyl E-7 on Chromosorb G. At 75° and a nitrogen carrier flow rate of 25 ml/min, relative relation retention times were **10**, 9.8 min, norbornene, 10.2 min, **6**, 11.0 min, **7**, 60.4 min, and *exo*-norbornyl chloride, 65 min. A mixture of norbornane and norbornene was not resolved. The three hydrocarbons could be separated more efficiently on a 25 ft × $^1/_8$ in. column of 5% tricresyl phosphate on Chromosorb W at 50°; retention times: **10**, 17.8 min; norbornane, 16.8 min; and **6**, 20.0 min. Peak heights and areas were both proportional to concentration; the former were used for analysis. New calibration charts for conversion of peak heights to actual amounts of **6** and **7** were constructed whenever carrier gas tanks were changed.

Electrolysis Procedure. The electrolysis cell has been described.[59] A 0.1 *M* solution of tetraethylammonium bromide (4.90 ml) in dimethylformamide was degassed for 15 min by a nitrogen stream saturated with dimethylformamide. The solution was then pre-electrolyzed at the potential to be used for electrolysis, until the background current had dropped to a constant value. A solution of 0.1 mmol of the appropriate dihalide in 0.10 ml of dimethylformamide was injected, a 5-μl aliquot was removed for water analysis, and the electrolysis was then allowed to proceed until the current had returned to background level, *ca.* 15 min. Product analysis by gc was performed immediately upon completion of the electrolysis.

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[57] (a) C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966); (b) S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, **90**, 2832 (1968).

[58] C. K. Mann, *Electroanal. Chem.*, **3**, 57 (1969).

[59] A. J. Fry, M. A. Mitnick, and R. G. Reed, *J. Org. Chem.*, **35**, 1232 (1970).