

anization at the end of the reaction path. A stable carbenic species is obtained. From this intermediate, reclosure is quite easy though not spontaneous. Thus, the eventuality of competing rearrangement processes must be taken into account, toward propyne or allene, for example.

(b) Photochemically, a striking difference is observed between singlet and triplet reactivities. In all cases, the low-energy $^3\pi\pi^*$ state is found to be unreactive and is therefore likely to lead to phosphorescence or bimolecular reactions such as (2 + 2) additions. If the first singlet state is populated, ring cleavage is observed through an overall synchronous opening and methylene rotation. We thus obtain a carbenic species possessing an excess of energy and which is able either to reclose (photochemical racemization) or to lead to further reactions. Side-chain cleavage may be observed if, at the same time, substituents are present on the double bond in order to lower the $^1\pi\pi^*$ energy and if a stabilizing group is attached to the C_3 position in order to stabilize the final diradical species.

(c) A word of caution must be added regarding the role of Rydberg states in *vapor-phase* reactions. These states are not likely to interfere with the low-lying triplet states,

but they may appear in the close vicinity of the first valence singlet state of alkyl-substituted cyclopropenes. Recent theoretical studies have shown that, for model reactions, the mixing of the Rydberg and the valence states ("derydbergization") is very easy and takes place at the beginning of the reaction.³² To a rough approximation these states might be considered as relatively low-energy reservoirs. Theoretical studies are in progress in this field.³³

(d) A very recent work by Padwa et al.³⁴ proposes a dissociation-reassociation mechanism to account for the formation of rearranged cyclopropenes upon photoexcitation. This mechanism is in very good agreement with our findings.

Registry No. Cyclopropene, 2781-85-3.

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Electrochemical Reduction of Bridgehead Iodides

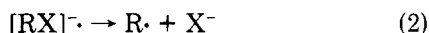
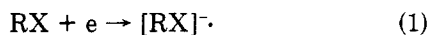
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Received December 10, 1980

Electroreduction of bridgehead iodides, 1-iodoadamantane, 1-iodobicyclo[2.2.2]octane, 1-iodobicyclo[2.2.1]heptane, 1-iodobicyclo[2.1.1]hexane, 6-iodotricyclo[3.1.1.0^{3,6}]heptane, iodocubane, and 1-iodotricyclo[4.1.0.0^{2,7}]heptane, at a mercury cathode is described. Polarographic studies of the iodides dissolved in dimethylformamide containing tetrabutylammonium perchlorate supporting electrolyte revealed that reduction is associated with a single two-electron wave in each case. Initially, the half-wave reduction potentials become progressively more negative as the s character of the bridgehead carbon exocyclic bonding orbital increases, but then there is a dramatic reversal of this trend. Several possible explanations are advanced to account for this behavior. Analysis of the product obtained from controlled-potential electrolysis of each iodide showed the corresponding hydrocarbon to be formed in moderate to high yield via a two-electron pathway.

The area of electroorganic chemistry has assumed increasing importance over recent years. One aspect which has generated considerable interest is that dealing with electroreduction of the carbon-halogen bond¹⁻⁵ for which the generally-accepted mechanism is that proposed some time ago by Elving and Pullman⁶ (eq 1-4).



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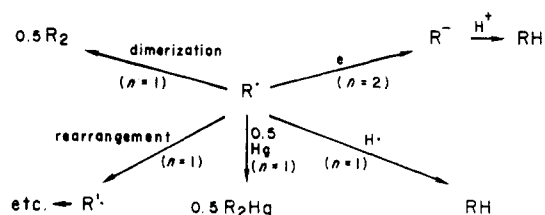
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Scheme I



For most haloalkanes, i.e., those in which the system does not lead to stabilization of the radical ion, $[\text{RX}]^-$, steps 1 and 2 are frequently assumed to be concerted;^{2,7} in other words, the radical anion can be regarded as a transition state rather than as an intermediate and in such cases the primary electron-transfer reaction is potential determining. At the same time, haloalkanes other than allyl, benzyl, and some tertiary halides generally display a single two-electron wave because reduction of the radical (eq 3) occurs at a less negative potential than that required

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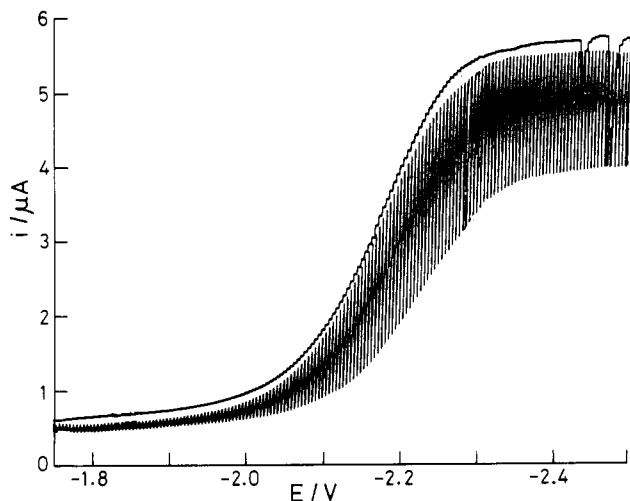
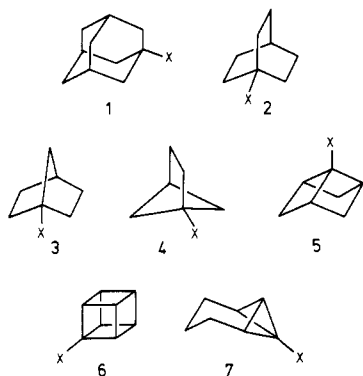


Figure 1. Polarogram of iodocubane.

for the initial charge-transfer reaction (eq 1).⁷

For reductions occurring at the mercury cathode, the original mechanism⁶ has been modified and further elaborated.⁸ Thus the fate of the radical generated in 2 is thought to depend on the relative importance of the various pathways depicted in Scheme I; this also accounts for the formation of products such as the dimers and organomercurials occasionally observed.

As Rifi¹ has pointed out, one of the important factors to be considered when discussing electroreduction of haloalkanes is the nature of the alkyl moiety. We initiated a study of the electrochemical reduction of the series of bridgehead iodides 1-7 (X = I) in order to determine to



what extent the variation in the structure of the alkyl group affects the ease of reduction in these caged molecules. Half-wave reduction potentials of 1-bromo-adamantane,^{16,17} 1-bromobicyclo[2.2.2]octane,¹⁶⁻¹⁸ and 1-bromobicyclo[2.2.1]heptane^{13,18} at mercury have been reported, and a detailed investigation¹⁰ has been made of the electrochemical reduction of 1-bromo and 1-iodobicyclo-

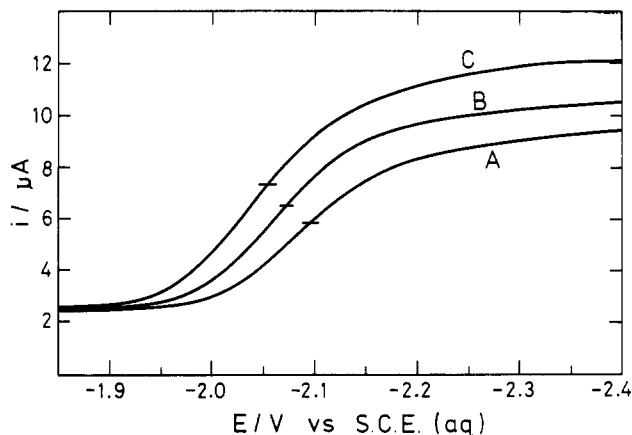


Figure 2. Variation of $E_{1/2}$ with drop time for the polarographic reduction of 1-iodobicyclo[2.2.2]octane; A = 0.5, B = 1.0, and C = 2.0 s.

[2.2.1]heptane. However no meaningful comparisons of the various results can be drawn owing to the different conditions employed. It is known¹⁻³ that the ease of reduction of haloalkanes is in the order RI > RBr > RCl > RF, and in the limited number of examples of reduction of bridgehead bromides examined, it is found that in some cases the reduction potentials are so negative that the polarographic waves are deformed by background decomposition.^{10,13,16-18} Accordingly, we chose iodine as the halogen appropriate to this work in order to provide the maximum range of operation.

Results and Discussion

Polarography. Preliminary experiments using DMF as solvent were conducted with three different supporting electrolytes, viz., tetramethylammonium perchlorate (TMAP), tetraethylammonium perchlorate (TEAP), and tetrabutylammonium perchlorate (TBAP). Although it has been demonstrated¹³ that, relative to the other tetraalkylammonium salts, TBAP causes a shift of the half-wave potential to more negative values, for compounds 1-7 (X = I) it proved to be less capricious and produced well-defined polarographic waves free of absorption maxima in the diffusion-controlled region (see, e.g., Figure 1). An investigation of the variation of $E_{1/2}$ with the mercury drop time t (Figure 2) showed that electroreduction of the carbon-iodine bond in the iodides 1-7 (X = I) was indeed irreversible.^{1,3,4,13,18} The polarographic waves in all cases were shown by standard methods to be associated with the transfer of two electrons.¹⁹

At the foot of the wave where the current is determined by the rate of electron transfer (i.e., where $i < 0.1 i_d$), the concentration of the electroactive substance at the electrode surface can be assumed to be equal to the bulk concentration (C^0).^{19,20} For a totally irreversible process under these conditions, the current i (at the end of the drop life) is related to the potential, E (in volts vs. SCE), by eq 5,²⁰ where n is the number of electrons transferred

$$i = nFAC^0 k_{t,h}^0 \exp \left[\frac{-anF(E + 0.24)}{RT} \right] \quad (5)$$

per molecule in the potential-determining step, F the Faraday constant, A the area of the mercury drop, $k_{t,h}^0$ the rate constant for heterogeneous electron transfer at a po-

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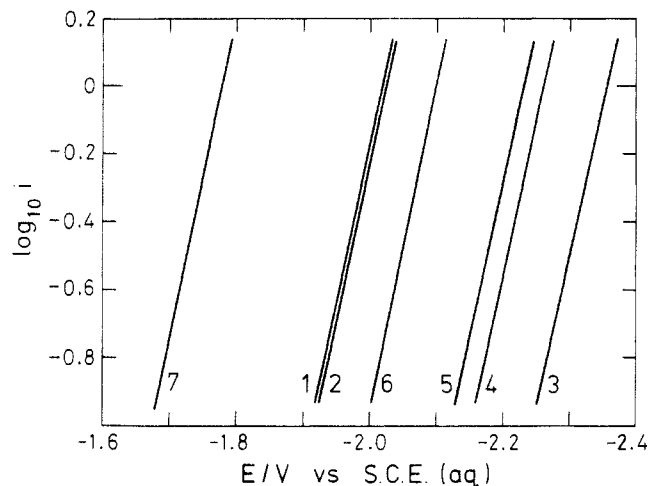


Figure 3. Plots of $\log i$ vs. E for values of $i < 0.1i_d$ from polarograms of compounds 1-7 ($X = I$).

tential of 0 volt vs. NHE, and α is the transfer coefficient. Equation 6, which is in the form of the Tafel equation,²¹ follows from eq 5.

$$E = \frac{RT}{\alpha nF} \left[2.303 \log_{10} (nFAC^0 k_{f,h}^0) - \frac{0.24\alpha nF}{RT} \right] - \left[\frac{2.303RT}{\alpha nF} \right] \log_{10} i \quad (6)$$

Plots of E vs. $\log_{10} i$ ($i < 0.1i_d$) for the substrates 1-7 ($X = I$) (Figure 3) gave a series of parallel lines of approximate slope 120 mV/decade, which is consistent with a mechanism involving a one-electron irreversible rate-determining step in each case.²¹

In view of the fact that the slopes are essentially identical (constancy of αn) and that n is similar²⁰ for all the iodides 1-7 ($X = I$), it follows that at any chosen potential E (Figure 3) the relative value of the current i_E for each substrate can be regarded as a measure of the relative rate of electron transfer to the respective compound. Thus, for a pair of iodides A and B, eq 7 is valid provided $C_A^0 = C_B^0$

$$\frac{k_{f,h}^0(A)}{k_{f,h}^0(B)} = \frac{i_E(A)}{i_E(B)} \quad (7)$$

and external conditions such as capillary size, mercury flow rates, drop area (A), drop time (t), temperature (T), and scan rate (ν) are held constant. Alternatively, under these same experimental conditions, and further assuming that adsorption effects are similar, the half-wave potentials can be considered to be a measure of the activation energy of heterogeneous electron transfer (eq 1).²

Table I lists the $E_{1/2}$ values as well as the observed relative rates of electron transfer in the electroreduction of the iodides 1-7 ($X = I$). The one-bond coupling constants, $^1J(^{13}\text{C}-\text{H})$, of the bridgehead carbon in the parent hydrocarbons 1-7 ($X = \text{H}$) are also included as a measure of bridgehead strain. It is interesting to note that initially the values of $E_{1/2}$ become more negative, but beyond 1-iodobicyclo[2.2.1]heptane (3, $X = I$) the trend is reversed; i.e., reduction becomes easier from 3-7 ($X = I$). In comparing the rates of electron transfer to isobutyl and *tert*-butyl bromides, Fry and Krieger¹³ suggest that the observed rate ratio reflects the relative stabilities of the halogen-free radicals. If it is similarly assumed that the

Table I. Polarographic Analysis of Iodides 1-7 ($X = I$) in DMF

compd ($X = I$)	$E_{1/2}$ ^a mV	rel rates of electron transfer	$^1J(^{13}\text{C}-\text{H})$ ^b
1	-2085	1.5×10^3	133.5
2	-2120	1.1×10^3	134
3	-2370	1	140
4	-2320	7.2	150
5	-2300	14	157
6	-2175	3.0×10^2	154
7	-1983	2.4×10^5	240

^a ± 5 mV vs. SCE; [substrate], 10^{-3} M; [TBAP], 10^{-1} M.

^b One-bond coupling constant of the bridgehead carbon in the hydrocarbons 1-7 ($X = \text{H}$). (For these data see Della et al., ref 32).

stability of the species, $(\text{RX})^\cdot$ is a reflection of the relative stability of the corresponding bridgehead radical, the values of $E_{1/2}$ would have been expected to become progressively more negative along the series 1-7 ($X = I$). On the other hand, this assumption may be invalid in the case of iodides 1-7 ($X = I$), especially for the more highly strained systems. As Table I shows the magnitude of $^1J(^{13}\text{C}-\text{H})$ involving the bridgehead carbon increases along the series 1-7 ($X = \text{H}$), and this is associated with an increase in the s electron density of the carbon orbital. Enhancement of the s character of the exocyclic bonding orbital of the bridgehead carbon has been demonstrated²² to significantly improve its ability to sustain a negative charge; i.e., the carbon displays increased electronegativity. Perhaps the radical anion, which is a hybrid of the forms $\text{R}\cdot\text{X}^- \leftrightarrow \text{R}^-\cdot\text{X}$, is actually stabilized in the more constrained systems (where the bridgehead carbon is more electronegative) because of the greater importance of the latter contributor. There is evidence to support this contention, particularly in the case of organic iodides.²³ Calculations suggest, for example, that in iodoethyne the carbon-iodine bond is polarized in an opposite direction ($\text{HC}\equiv\text{C}-\text{I}^+$) to that expected.^{23a}

Another factor worth considering is that the ease of reduction of the halides may be determined to a significant extent by steric effects,^{4,9,10,13} as suggested some time ago by Lambert.²⁴ Contrary to earlier suggestions,^{6,11,25} cathodic reduction of haloalkanes is now believed to proceed with the carbon-halogen bond axis oriented perpendicular to the electrode surface such that the halogen is closer to the electrode.^{3,10,15,18,26} An examination of molecular models of the substrates employed in this work suggests that the iodine atom is less sterically hindered by the substituted β -carbon as the system becomes more constrained. As a result the electrode would be expected to become more accessible to those compounds in which the iodine is more exposed (5-7, $X = I$); i.e., these substrates become less difficult to reduce. This kind of steric phenomenon may well be augmented in the presence of the bulky tetrabutylammonium ions whose concentration is reasonably high in the vicinity of the cathode.¹⁰ Indeed, if this steric hypothesis is correct, the observed "reversal" effect would be expected to be progressively smaller with tetrabutylammonium, tetrapropylammonium, tetraethyl-

(22) (a) See Lansbury and Sidler (*Tetrahedron Lett.* 1965, 691) for the relative stabilities of some of the bridgehead carbanions. (b) See Luh and Stock (*J. Am. Chem. Soc.* 1974, 96, 3712) for the relative acidity of cubane. (c) See Closs and Larrabee (*Tetrahedron Lett.* 1965, 287) for the relative acidity of 7 ($X = \text{H}$).

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Table II. Controlled Potential Electrolysis of Iodides 1-7 (X = I) at Mercury in DMF

compd (X = I)	V, mV ^a	"n" ^b	product ^c (X = H), % yield
1	-2350	1.92	1, 78
2	-2350	1.65	2, 72
3	-2550	1.85	3, 80
4	-2530	1.62	4, 70
5	-2500	1.95	5, 68
6	-2360	1.88	6, 65
7	-2190	1.70	7, 70

^a Applied potential; [substrate], 10^{-2} M; [TBAP], 10^{-1}

M. ^b Coulometric *n* value (based on starting material) calculated from integration of the *i/t* curve for reduction.

^c Yields of products determined by GLC analysis.

ammonium, and tetramethylammonium ions. Unfortunately, the difficulties encountered with maxima in the polarograms of the latter were such as to preclude any reliable data.

Controlled Potential Electrolyses. Product analyses were carried out by semimacro scale electrolysis of the iodides (1-7, X = I) at constant potentials chosen in the diffusion region of the respective polarographic waves (Table II). In each case, the hydrocarbon (1-7, X = H) was obtained in moderate to high yield, indicating that cleavage of the carbon-iodine bond results from the steps following the initial electron transfer. Coulometric *n* values for the overall process lie between 1.62-1.95 for the various compounds, suggesting a two-electron path to account in large part for the formation of the hydrocarbon via a carbanionic intermediate (R⁻). No dimeric products or organomercurials were isolated. It should be noted that the product distribution of an electrolysis may vary with the chosen potential,^{10,12,27} and it has been suggested that the formation of organomercury compounds is more efficient at potentials positive with respect to the current maximum.^{10,12,28} Thus, for example, Carroll and Peters¹⁰ found that the reduction of 1-iodobicyclo[2.2.1]heptane (3, X = I) in DMF with TBAP as supporting electrolyte yielded measurable quantities of bis(1-bicyclo[2.2.1]heptyl)mercury (2-6%) at potentials more positive than -2.35 V (vs. SCE). However, when electrolyses were conducted at more negative potentials, no organomercurials were observed. Since the potentials employed in our study were well into the diffusion region (Table II), it is not surprising that detectable amounts of organomercurials were not observed among the final products.

Experimental Section

Chemicals. The supporting electrolytes, tetra-*n*-butylammonium perchlorate (TBAP), tetraethylammonium perchlorate (TEAP), and tetramethylammonium perchlorate (TMAP) were purchased from G. Frederick Smith Chemical Co. and were used without further purification. Spectroscopic grade dimethylformamide was distilled twice from calcium hydride and stored under nitrogen over molecular sieves (Linde 4A). Cell solutions were deoxygenated by using high-purity nitrogen which was previously passed through columns of activated copper turnings and molecular sieves.

1-Iodoadamantane (1, X = I) was prepared from the corresponding alcohol (1, X = OH) as described.²⁹ The iodides 2-6

(X = I) were synthesized by decarboxylative iodination of the corresponding carboxylic acids 2-6 (X = COOH) as recently reported.³⁰ 1-Iodotricyclo[4.1.0.0.2⁷]heptane (7, X = I) was obtained from the parent hydrocarbon (7, X = H) following the procedure outlined by Szeimies and co-workers.³¹ An authentic sample of adamantane was available commercially. The remaining hydrocarbons 2-7 (X = H) were prepared as described.³²

Instrumentation and Procedures. Polarograms were obtained by using a Princeton Applied Research (PAR) Model 174A polarographic analyzer equipped with a PAR Model 174/70 drop timer head and a Houston Omnigraphic Model 2000 XY recorder. The counter electrode was a platinum coil, and the reference electrode was a saturated calomel electrode with a remote junction contact. Solutions of the iodides 1-7 (X = I), 10^{-3} M in DMF containing TBAP (10^{-1} M), were used for all polarographic measurements which were carried out at constant temperature (25 °C). A potential scan rate of 10 mV s⁻¹ and a drop time of 0.5 s were used.

Controlled potential electrolyses were performed with the aid of a PAR Model 173 potentiostat/galvanostat. A two-compartment H-cell of conventional design,³³ with the working compartment (capacity 40 mL) containing a mercury pool cathode and the auxiliary compartment (capacity 20 mL) containing a platinum gauze counter electrode, was used in conjunction with the saturated calomel reference electrode. Coulometry was performed by recording the voltage drop across a standard resistor (1 ohm) in series with the cell using a Rikadenki Model B161 recorder. Each electrolysis was preceded by a blank electrolysis of a deoxygenated solution of TBAP (10^{-1} M) in DMF at -2600 mV. When the current decayed to ca. 200 μA, known amounts of the iodide 1-7 (X = I) and phenylcyclohexane (internal standard)¹⁰ were injected into the working compartment, which was maintained under an atmosphere of nitrogen, and the electrolysis was performed at the chosen potential (Table II) until the current reached the background level. The catholyte was diluted with cold water and extracted with pentane. The combined pentane extracts were washed with cold water, dried (MgSO₄), and analyzed (GLC). Essentially the sole product detected in each case was the corresponding hydrocarbon 1-7 (X = H). The identity of the hydrocarbon was established by comparison of GLC-MS spectra with those of authentic specimens. Yields were determined by measuring the area under each hydrocarbon peak relative to that of the internal standard, phenylcyclohexane, in each GLC trace and then applying a correction to this ratio according to predetermined GLC response factors for the particular substances.

The presence of organomercury compounds was investigated both by GLC/MS and by the iodination procedure described by Carroll and Peters.¹⁰ Although traces of mercury-containing compounds were detected by mass spectrometry, their presence was not confirmed by chemical analysis.¹⁰

Acknowledgment. We thank Dr. S. Fletcher for valuable discussions.

Registry No. 1 (X = I), 768-93-4; 1 (X = H), 281-23-2; 2 (X = I), 931-98-6; 2 (X = H), 280-33-1; 3 (X = I), 930-80-3; 3 (X = H), 279-23-2; 4 (X = I), 74725-75-0; 4 (X = H), 285-86-9; 5 (X = I), 74725-76-1; 5 (X = H), 51273-50-8; 6 (X = I), 74725-77-2; 6 (X = H), 277-10-1; 7 (X = I), 65131-65-9; 7 (X = H), 287-13-8.

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