D-glucose diethyl dithioacetal, m.p. 137.0° (lit.[15] m.p. 134.0°), 6-deoxy-L-mannose diethyl dithioacetal, m.p. 134.5–136° (lit.[13] m.p. 136.5–137°), and 6-deoxy-L-galactose diethyl dithioacetal, m.p. 165.5° (lit.[16] m.p. 167–168.5°), were prepared from 0.5–1.0 g. of monosaccharide according to the procedure of Zinner.[13]

Acetylation of the Diethyl Dithioacetals.—D-Arabinose diethyl dithioacetal tetraacetate (I), m.p. 78–79° (lit.[17] m.p. 79–80°), D-galactose diethyl dithioacetal pentaacetate (VI), m.p. 77.5–78.5° (lit.[14] m.p. 77–78°), 2-deoxy-D-glucose diethyl dithioacetal tetraacetate (III), m.p. 76.5–77.0° (lit.[15] m.p. 77°), 6-deoxy-L-mannose diethyl dithioacetal tetraacetate (V), m.p. 59.5–60.0° (lit.[18] m.p. 60–62°), and 6-deoxy-L-galactose diethyl dithioacetal tetraacetate, m.p. 96.5–97.5° (lit.[19] m.p. 99–100°), were prepared from 0.1–0.6 g. of the diethyl dithioacetal by acetylating with acetic anhydride and pyridine at room temperature.

(15) J. L. Barclay, A. J. Cleaver, A. B. Foster, and W. G. Overend, *J. Chem. Soc.*, 789 (1956).

(16) E. Votoček and V. Veslelý, *Z. Zuckerind. Böhmen.*, **40**, 207 (1916).

(17) M. L. Wolfrom and M. R. Newlin, *J. Am. Chem. Soc.*, **52**, 3619 (1930).

(18) E. L. Patterson, R. Milstrey, and E. L. R. Stokstad, *ibid.*, **78**, 5868 (1956).

(19) M. L. Wolfrom and J. A. Orsino, *ibid.*, **56**, 985 (1934).

D-Arabinose Diethyl Dithioacetal Tetraacetate-d_{12}(II).—One-tenth gram of D-arabinose diethyl dithioacetal was dissolved by heating in 0.40 ml. of deuterium oxide. After the deuterium oxide was removed in a vacuum desiccator, the residue was acetylated with 0.20 ml. of acetic anhydride-d_6 and 0.10 ml. of dry pyridine; m.p. 78–79°.

2-Deoxy-D-glucose Diethyl Dithioacetal Tetraacetate-d_{12}(IV).—The procedure described for compound II was followed; m.p. 76.5–77.5°.

D-Fructose Diethyl Dithioketal Pentaacetate (VII).—*keto*-D-Fructose pentaacetate was prepared according to the procedure of Cramer and Pacsu[20]; m.p. 69.0–69.5° (lit.[21] m.p. 70°). The diethyl dithioketal pentaacetate was prepared[21] from the pentaacetate, m.p. 80–81° (lit.[21] m.p. 83°).

(20) F. B. Cramer and E. Pacsu, *ibid.*, **54**, 1697 (1932).

(21) M. L. Wolfrom and A. Thompson, *ibid.*, **56**, 880 (1934)

COMMUNICATIONS TO THE EDITOR

Mechanism of Electrochemical Reduction of Alkyl Bromides

Sir:

Although both ionic and free-radical mechanisms have been proposed for the electrochemical reduction of alkyl bromides at a mercury cathode,[1] the orientation of the carbon–bromine bond during the reduction has been discussed primarily in terms of the ionic mechanism. Regardless of whether carbon–bromine bond fission and electron uptake occur simultaneously or consecutively, it has been assumed that the bromine is as far as possible from the electrode surface and the carbon is as close as possible to the electrode surface so as to permit electron transfer directly to the carbon. While this spatial arrangement is an eminently reasonable one in view of the polarity of the carbon–bromine bond, the supporting evidence is sufficiently indirect[1,2] that it seemed desirable to test this feature of the mechanism more directly by investigating the reducibility of bridgehead halogen compounds, whose cage structures would make it impossible for the rear of the carbon–bromine bond to approach a mercury cathode.

Accordingly, half-wave potentials of a number of alkyl bromides have been determined (Table I) under experimental conditions similar to those of Lambert and Kobayashi.[2] Our use of a silver–silver bromide anode as well as more concentrated solutions of alkyl bromides and tetraethylammonium bromide led to values which are 0.45–0.50 v. more positive than those reported by Lambert and Kobayashi, but otherwise in excellent agreement.

(1) (a) P. J. Elving, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **14**, 99 (1953); (b) P. J. Elving and B. Pullman, *Advan. Chem. Phys.*, **1**, 1 (1960).

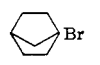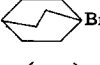(2) F. L. Lambert and K. Kobayashi, *J. Am. Chem. Soc.*, **82**, 5324 (1960)

The observed reduction of 1-bromobicyclo[2.2.2]-octane and 1-bromobicyclo[2.2.1]heptane could not have taken place by any mechanism which involved back-side attack on carbon, and such a process is therefore excluded in the case of these compounds. While reductive attack on carbon from the bromine side is conceivable, a more attractive alternative would be a displacement on bromine to give an alkyl free radical and a bromide ion, the latter located immediately next to the mercury surface. This process would require the transfer of electrons *through* the bromine atom *from* the cathode *to* the carbon atom, a direction opposite to that encountered in the S$_N$2 displacement reaction; the intermediate would be very similar to the "bridged activated complex" proposed by Taube[3] for the reduction of certain metal halide complex ions.

Similar arguments apply to the reduction of 1-bromotriptycene, which also cannot occur by direct back-side attack on carbon. Furthermore, an indirect back-side attack on carbon, in which electrons are relayed through a benzene ring to the carbon atom of the carbon–bromine bond, seems highly improbable, since it could hardly be expected to take place more readily than a direct reductive attack on an aliphatic carbon–bromine bond. The only reasonable possibility seems to be reduction from the bromine side of the bond, the strained free radical formed at the bridgehead carbon atom being stabilized to a considerable extent by the three benzene rings. Although the effect of the rings is large enough to make bromotriptycene more easily reducible than the acyclic alkyl bromides, it is nevertheless much smaller than that encountered in benzyl bromide (Table I), which has a single ring free to assume the optimum

(3) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 24 (1959).

conformation for resonance stabilization of the free radical.

TABLE I
POLAROGRAPHIC HALF-WAVE POTENTIALS

Halide	$E_{1/2}{}^a$ (volts $vs.$ Ag–AgBr)	Halide	$E_{1/2}{}^a$ (volts $vs.$ Ag–AgBr)
⬡Br	−2.17	$C_6H_5CH_2Br$	−0.82
		$CH_3(CH_2)_{15}Br$	−1.79
⬡Br	−1.79	$CH_3(CH_2)_7Br$	−1.81
		$CH_3(CH_2)_5Br$	−1.81
(⬡)₃ CH CBr	−1.42	$CH_3(CH_2)_3Br$	−1.77
		CH_3CH_2Br	−1.70

^{a} Solutions 0.002 F in alkyl halide and 0.03 F in Et_4NBr.

The nature of the stabilization in the bromotriptycene reduction is not clear at this time. Conjugation with the aromatic systems is apparently excluded because of the unfavorable orientation of the rings, while a negative inductive effect[4] could facilitate the reduction only if the potential-determining step involved a negatively charged transition state which led to such products as a carbanion, or a bromide ion plus a free radical.

The evidence now available for the reduction of non-bridgehead compounds does not distinguish between front-side attack on bromine and back-side attack on carbon. The difference of about 0.15 v. between the half-wave potentials of the acyclic compounds and that of 1-bromobicyclo[2.2.2]octane may be a consequence of mechanistic changeover. On the other hand, all reductions may occur via reductive attack on bromine, the more negative half-wave potentials for the bicyclo compounds being simply the result of steric strain in transition states leading to nonplanar free radicals. The difference of 0.1 v. between the half-wave potentials of 1-bromobicyclo[2.2.2]octane and 1-bromoadamantane reported by Lambert and co-workers[5] agrees with this view, if it is assumed that an adamantyl free radical is slightly less strained than a bicyclooctyl free radical. The determination of half-wave potentials of less strained bicyclo compounds having one or more three-carbon bridges in addition to two-carbon bridges should be helpful in settling this point.

Acknowledgment.—The authors wish to thank Professor Paul D. Bartlett for a sample of 1-bromotriptycene, Professor C. A. Grob for a sample of bromobicyclooctane, and Professor Kenneth B. Wiberg for a sample of bromobicycloheptane.

(4) G. Wittig and W. Tochtermann, $Ann.$, **660**, 23 (1962).
(5) F. L. Lambert, A. H. Albert, and J. P. Hardy, $J. Am. Chem. Soc.$, **86**, 3155 (1964).

DEPARTMENT OF CHEMISTRY   JOHN W. SEASE
WESLEYAN UNIVERSITY   PATRICIA CHANG
MIDDLETOWN, CONNECTICUT   JOYCE L. GROTH

Polarography of Organic Halogen Compounds.
II. Sterically Hindered Alicyclic Bromides[1]

$Sir:$

The polarographic reduction of three bridgehead bromides[2] might appear to vitiate any fundamental

(1) Part I: F. L. Lambert and K. Kobayashi, $J. Am. Chem. Soc.$, **82**, 5324 (1960).
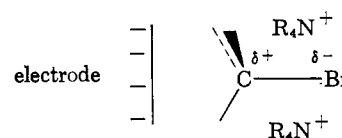(2) J. W. Sease, P. Chang, and J. L. Groth, $ibid.$, **86**, 3154 (1964).

basis for the correlation of polarographic half-wave potentials of organic bromides with their classic displacement rates.[1,3a] Further, Sease and co-workers[2] are led by their results to postulate the electroreduction of R–Br compounds as involving a displacement on bromine.

However, parallel work in our laboratories (Table I) indicates that the electrochemical reduction of bridgehead and hindered bromides supports our use of Elving's basic mechanism for the electrode process.[3]

Briefly stated: as the R–Br compound diffuses toward the immediate vicinity of the negative electrode, the bromine end of the C–Br dipole should be oriented away from the electrode surface.[3b] The electrostatic field of the electrode acts to increase the polarization of the carbon–halogen bond as this C–Br portion of the molecule nears the electrode.

The reaction point just prior to the transition state is[3]

Depending on several factors[4] the actual potential-determining step for an R–Br compound may involve direct ionization to form R^+ and Br^- (S_N1-like) or may involve adding an electron to a σ^* to form $(R \dot{-} Br)^-$ $i.e.$, an S_N2-like step.

The behavior of the bridgehead bromides provides an illuminating test of this basic picture of the reduction mechanism. Steric interference by the bulky rings of the bridgehead compounds hinders close approach of the back side of the C–Br to the electrode. This should effectively prevent direct addition of an electron to a σ^* to form $(R \dot{-} Br)^-$ in an S_N2-like process. Such steric interference to close approach should also decrease the polarizing influence of the electrode's field on the relatively distant C–Br group. Thus, because formation of neither an anion radical nor a carbonium ion can occur readily, reduction should not—and does not—take place at moderate potentials.

However, as the electrode potential is made more negative, a correspondingly greater polarization of the C–Br bond toward $C^{\delta+}$–$Br^{\delta-}$ occurs. If the polarization proceeds far enough, $i.e.$, if the electrode potential is negative enough, ionization might be expected to occur, and to occur at potentials in an order determined by the relative ease of formation of the carbonium ions from the bridgehead compounds.[5] The reduction potentials do follow this order, indicating that an ionic process of dissociation to carbonium ions[3] (an S_N1-like electrode process) may be the potential-determining step.[6]

(3) (a) P. J. Elving and B. Pullman [$Advan. Chem. Phys.$, **3**, 1 (1961)] reiterate Elving's valid cautions about using terms which are derived from homogeneous reaction kinetics (S_N1, S_N2) to apply to the heterogeneous electrode process. However, it would be profitable to use S_N1-$like$ or S_N2-$like$ if these terms describe potential-determining steps which are experimentally indicated as different by consistent correlation of $E_{1/2}$ values with homogeneous reaction rates. (b) $Ibid.$, **3**, 14 (1961).
(4) $E.g.$, steric influences in the R of RBr, polar effects in R, resonance stabilization of groups in R, bond strength of R–X, and the nature of the supporting electrolyte.
(5) P. von R. Schleyer and R. D. Nicholas, $J. Am. Chem. Soc.$, **83**, 2700 (1961).