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ELECTROCHEMICAL PREPARATION OF SMALL RING COMPOUNDS II,[1] MECHANISM OF CARBON-HALOGEN BOND CLEAVAGE

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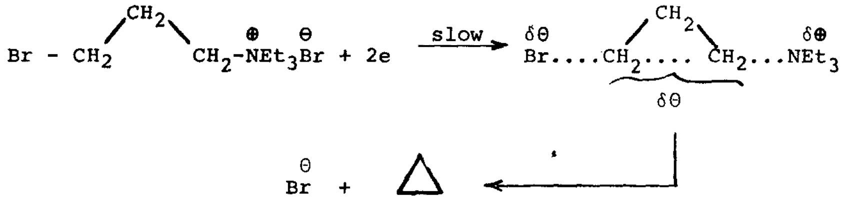
The electrochemical cleavage of carbon-halogen bonds in mono and dihalocarbons has been explored in detail.[2-6] While the general mechanism proposed involves the addition of one electron in the rate determining step, the addition of two electrons in the slow step has also been postulated.[4,6]

In the electrochemical reduction of dihalohydrocarbons, the half wave potential depends on the proximity of the two halogen atoms. This dependency has been explained as due to the torsional angle (in vicinal dihalides) between the two carbon-halogen bonds,[4] and to inductive effects in nonvicinal dihalides. These explanations which are based mostly on polarographic data and do not include product analysis cannot be disregarded. However, our data on the reduction of dihalides, which were obtained from polarographic, coulometric and product analysis are discussed in terms of the transition state of these reactions.

An examination of the half wave potentials of several α,ω-dibromides, Table I, reveals that those dibromides which give cyclic products upon electrolysis, (with the exception of 1,3-dibromo-1,3-dimethylcyclobutane) have a more positive value than those which give open chain hydrocarbons. This lower, but reproducible value is considered to be an indication of a concerted mechanism in the formation of cyclic compounds. Furthermore, it was found in the present study that, in the propane series, replacement of one of the halide groups with a quaternary ammonium group lowers the half wave potential considerably. For example, 3-bromopropyltriethyl-ammonium bromide reduced at a potential 0.57 v. more positive than did the 1,3-dibromopropane and 0.79 v. more positive than the 1,6-dibromohexane. Such a difference corresponding to 13-16 k.cal./mole is too high to be accounted for on the basis of inductive effects. Furthermore, since torsional angles of carbon-halogen bonds are not as effective in non-vicinal dihalides as they are in vicinal dihalides, this large difference in potential strongly suggests a transition state with a low activation energy and is consistent with a concerted mechanism in which the transition state resembles the cyclic product. Such a transition state is, of course, of lower activation energy because of the partial formation of a carbon-carbon bond. How well such a bond is developed, will be reflected in the $E_{\frac{1}{2}}$ value, as can be seen from Table I.



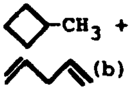
The electrolysis of 1,3-dibromopropane in the presence of water affords cyclopropane as the only product. This may be an indication of a concerted mechanism where the additional bond in the transition state is not as well developed as in the case of the 3-bromopropyltriethylammonium bromide shown above. Alternatively the reaction may proceed through the bromopropyl anion which cyclizes at a rate faster than proton capture.

The formation of cyclobutane and n-butane in the electrolysis of 1,4-dibromobutane is considered to proceed via a stepwise anionic mechanism where proton capture from the reaction medium becomes important.

In the electrolysis of 1,3-dibromo-1,3-dimethylcyclobutane, it was found that the cis and trans isomers reduce at the same potential and afford the same product, (see Table I). Furthermore, this potential is nearly the same as those of the dibromides which do not afford cyclic products. These observations are consistent with a stepwise mechanism whereby both isomers pass through a common intermediate i.e., an anion which equilibrates prior to cyclization.

TABLE I

Half Wave Potentials of Dihalides [DMF/n-Bu_4NClO_4]

Dihalide	$E_{1/2}$ (s.c.e.)	Cyclic Product	Straight Chain Hydrocarbon	αn
1,2-Dibromoethane	-1.38	Ref. (5)	Ref. (5)	0.323
1,3-Dibromopropane	-1.91	Cyclopropane	-	0.263
1,4-Dibromobutane	-1.99	Cyclobutane 25%	*n*-Butane 75%	0.233
1,5-Dibromopentane	-2.14	-	*n*-Pentane	-
1,6-Dibromohexane	-2.13	-	*n*-Hexane	-
1,3-Dibromo-1,3-dimethylcyclobutane (cis and trans)	-2.02	1,3-Dimethylbicyclobutane 90%	-	0.246
3-Bromopropyltriethyl ammonium bromide	-1.34	Cyclopropane	-	0.430
1-Bromo-3-bromomethyl cyclobutane[a]	-2.08	-	 $-CH_3$ + (b)	-

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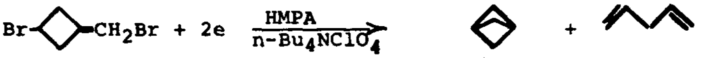
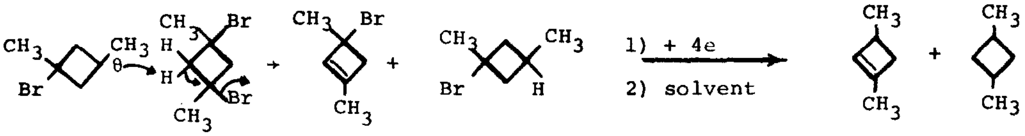
[a] Kindly supplied by Dr. K. B. Wiberg and V. Williams, Yale University.

[b] When the reaction was carried out in hexamethylphosphoramide, the desired bicyclo [1.1.1] pentane was obtained and was identified from its n.m.r. spectrum.[7]



Further indication of a stepwise mechanism for the electrochemical reduction of 1,3-dibromo-1,3-di-methylcyclobutane was provided by the dependency of the yield of 1,3-dimethylbicyclobutane on the concentration of the starting material. At concentrations of 1.0M or below, the yield of the bicyclic compound exceeded 90%. However, at concentrations of above 1.0M, the yield drops drastically and the formation of 1,3-dimethylcyclobutene and 1,3-dimethylcyclobutane is observed. These observations are rationalized by the following mechanism:



<u>Polarographic Results:</u> In an attempt to calculate (αη) values for the dihalides recorded in Table I, the following was observed: (a) Those compounds with more positive values of $E_{\frac{1}{2}}$ had the highest values of (αη); (b) Compounds which gave cyclic products upon electrolysis exhibited diffusion currents approximately half as large as those which gave open chain hydrocarbons.

While correlation between reaction mechanism and values of (αη) has been made,[8] we feel that such values ought to be used with caution as it is generally difficult to determine whether variations in (αη) values are due to variations in values of (α) or (η). However, we feel that since in the dibromides recorded in Table I, the cleavage of carbon-bromine bond is common to all compounds, it is quite likely that (η) is constant and that variations in values of (αη) are due to variations in values of (α). These values then give information concerning the position of the transition state, on an energy diagram, with respect to product and starting material. The higher the value of (α), the closer is the transition state to product. This is consistant with experimental results where the dihalides which afforded cyclic products exhibited higher values of (αη) that those which afforded linear products.

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