Electroorganic Chemistry. II.[1] Electroreduction of Vicinal Dibromides

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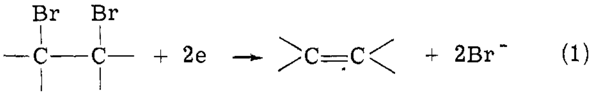
Received January 2, 1974

Electroreduction of vicinal dibromides at a stirred mercury cathode produces quantitative yields of olefins under very mild conditions. The resulting stereochemistry suggests that elimination from the trans-periplanar conformation is strongly preferred, if such conformation is accessible. Attempts to intercept a carbanionic intermediate were unsuccessful, indicating that the reductive elimination is either synchronous at both reacting centers or nearly so.

The reductive elimination of vicinal dibromides to produce olefins is a venerable reaction which has received limited attention,[2] inasmuch as the product olefin is usually also the starting point for the preparation of the dibromide. Reductive elimination involving zinc[3] has been exploited in steroid chemistry,[4] and more recently in the preparation of cyclobutadiene dimers.[5] Polarographic studies have shown a marked dependence of half-wave potential for the reduction of vicinal dibromides on the dihedral angle between the C–Br bonds,[6] and the product studies of this reaction[7] have shown that the overall process may be represented as follows.



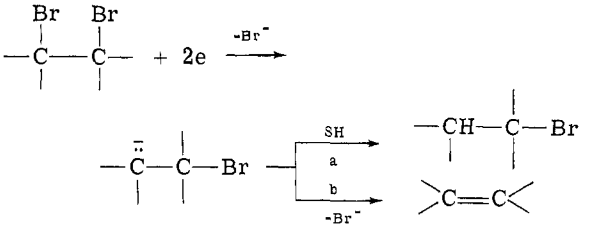
$$-\overset{\text{Br}}{\underset{|}{\overset{|}{C}}}-\overset{\text{Br}}{\underset{|}{\overset{|}{C}}}- + 2e \rightarrow \;>C{=}C<\; + 2Br^- \qquad (1)$$

However, the details of the electrochemical process illustrated in eq 1 were ambiguous. Elving and coworkers[8] reported that both *meso-* and *dl*-2,3-dibromosuccinate ethyl esters gave diethyl fumarate at all values of pH, whereas *meso*-2,3-dibromosuccinic acid gave fumaric acid, but *dl*-2,3-dibromosuccinic acid gave maleic or fumaric acid, depending upon pH. The lack of stereospecificity suggests the intervention of an intermediate carbanion or, alternatively,[9a] steric requirements which preclude the trans-periplanar conformation. Fry[9b] proposed that the reduction is concerted in cases for which the dihedral angle is favorable for p overlap in the transition state, but stepwise carbanionic in cases for which overlap of developing p orbitals is unfavorable. Free-radical intermediates have also been proposed to account for the products.[10] In one system studied which was particularly susceptible to carbanion formation (1,2-dibromo-1-chloro-1,2,2-trifluoroethene), Feoktestov[11] has reported two polarographic waves, the height of which depended upon the acid concentration, and which were interpreted as due to carbanion formation from the two stable conformers.

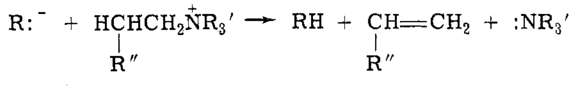
Electroreduction of 1,2-dibromides as a preparative method offered at attractive alternative to existing procedures, owing to the potential mildness of the reaction conditions and to the unique feature of electrochemistry, which places more reaction variable control in the hands of the experimenter.[12] It was the purpose of this investigation to establish the stereochemistry of this elimination process, to search for the intervention of possible carbanionic intermediates, and to assess the synthetic utility of this method.

Results and Discussion

Electroreduction of seven representative 1,2-dibromides was carried out in a compartmented cell of the design shown in Figure 1. The reductions were conducted at a stirred mercury cathode, using controlled potential electrolysis (cpe). For those reactions in which a gaseous product would be expected, the effluent gas stream was collected at −190°, fractionated using standard vacuum line techniques, and analyzed by gas–liquid phase chromatography. In all reductions the olefinic products formed in quantitative or nearly quantitative yields. The reactions were conducted at potentials which were normally 0.2 V or more negative than the half-wave potentials for the particular dibromide. Table I shows the results of these experiments. Most striking is the observation that excellent yields of olefins form at low negative potentials in all cases studied. The complete stereospecificity observed requires that elimination take place from the trans-periplanar conformation, when such a conformation is possible. This result suggests that the elimination may be concerted (entries 1–4, Table I). In order to test this possibility and to examine the possibility of a discrete anion intermediate (eq 2), a number of reductions were carried out in the presence of protonic substances known to be effective for anion capture during electroreduction of carbon–halogen bonds[10-14] (entries 5–9, 11, and 14, Table I). In no case was any product of proton capture obtained. This clearly implies the absence of a carbanion. Even those cases which should be most favorable to carbanion formation, 1,2-dibromo-2-phenylpropane (entry 9, Table I) and 1-bromo-*trans*-2-bromo-*trans*-4-*tert*-butylcyclohexane (entries 13 and 14, Table I), failed to yield any monobromide or saturated hydrocarbon. In the latter case, the Br-C-C-Br dihedral angle is approximately 65°, and should be unfavorable for concerted elimination. The present result with 1-bromo-*trans*-2-bromo-*cis*-4-*tert*-butylcyclohexane (entry 12, Table I) confirms a previously published account of the electroreduction of this compound,[15] in which reduction in dimethylformamide–5% water was found to yield no alkane. Olefins have been reported frequently as minor products from the Hofmann elimination reactions of tetraalkylammonium salts and presumed carbanions in electroreduction[11,16] (eq 3). The complete absence of Hofmann products in the present study is further evidence against a discrete carbanionic intermediate, and is consistent with current views of the process.[17] Moreover, reduction of 1,2-dibromoethane, which had been previously reported to give ethane,[7] in our hands (entry 8, Table I) failed to produce any trace of



(2)



$$R:^- + \underset{R''}{\underset{|}{HCHCH_2}}\overset{+}{N}R_3' \rightarrow RH + \underset{R''}{\underset{|}{CH}}{=}CH_2 + :NR_3' \qquad (3)$$

Table I
Electroreduction of Vicinal Dibromides

Registry no.	Entry	Compd, solvent	Potential −V, V[a]	Initial current, mA	Added proton source	Current[b] efficiency	Product(s) (yield, %)
5780-13-2	1	*meso*-2,3-Dibromobutane[c,d]	1.10	75	None	95	*trans*-2-Butene (quant)
	2	*meso*-2,3-Dibromobutane[d]	2.00	1000	None	95	*trans*-2-Butene (quant)
598-71-0	3	*dl*-2,3-Dibromobutane[d]	1.10	65	None	90	*cis*-2-Butene (quant)
	4	*dl*-2,3-Dibromobutane[d]	1.77	1000	None	95	*cis*-2-Butene (87)
	5	*dl*-2,3-Dibromobutane[d]	1.86	690	MeOH (10)[e]	79	*cis*-2-Butene (quant)
78-75-1	6	1,2-Dibromopropane[d]	1.50	375	MeOH (10)[e]	77	Propene:cyclopropane, 99.5:0.5[f] (95)
	7	1,2-Dibromopropane[g,h]	2.20	200[i]	H_2O[j]		Propene:cyclopropane, 99.6:0.4[f] (85)
106-93-4	8	1,2-Dibromoethane[g,h]	2.60	130[k]	H_2O[j]		Ethene (*ca.* 90)
36043-44-4	9	1,2-Dibromo-2-phenylpropane[d]	2.40[l]	450	AcOH (5)[m]		2-Phenylpropene (66)[n]
31734-61-9	10	1,2-Dibromo-4-*tert*-butylcyclohexane[d,o]	0.86	150	None	100	4-*tert*-Butylcyclohexene (quant)[p]
	11	1,2-Dibromo-4-*tert*-butylcyclohexane[d,q]	1.30	275	MeOH (10)[e]	87	4-*tert*-Butylcyclohexene quant)[r]
	12	1,2-Dibromo-4-*tert*-butylcyclohexane[d,s]	1.43	450	None	95	4-*tert*-Butylcyclohexene (94)
	13	1,2-Dibromo-4-*tert*-butylcyclohexane[d,t,u]	1.99	500	None	~75	4-*tert*-Butylcyclohexene (96)
	14	1,2-Dibromo-4-*tert*-butylcyclohexane[d,t,u]	1.90	375	MeOH (10)[e]	89	4-*tert*-Butylcyclohexene hexene (97)

[a] Potentials were measured *vs.* saturated calomel electrode. [b] Per cent calculated as $10^2 \times$ millifaradays required for a two-electron process/millifaradays passed. [c] Usually 5 mmol. [d] Dimethylformamide, with 0.2 *M* tetra-*n*-butylammonium fluoroborate. [e] 10 *M* methanol added to solvent. [f] Starting dibromide contained traces of 1,3-dibromopropane, and this product may be an artifact. [g] Dioxane–water (3:1 v/v). [h] Supporting electrolyte 0.05 *M* tetraethylammonium bromide. [i] Potential increased after 45 min to produce 450 mA. [j] See footnote *g*. [k] Potential increased after 45 min to produce 300 mA. [l] Vitreous carbon cathode. [m] 5 *M* acetic acid added to solvent. [n] Substantial amount of unidentified white solid in catholyte. [o] 75:25 mixture of diaxial:diequatorial dibromide, respectively. [p] 25% of pure diequatorial dibromide was recovered unreacted. [q] 60:40 mixture of diaxial:diequatorial dibromide, respectively. [r] 40% of pure diequatorial dibromide was recovered unreacted. [s] Pure diaxial isomer. [t] Pure diequatorial isomer. [u] Supporting electrolyte 0.2 *M* tetraethylammonium fluoroborate.

ethane using a dioxane–water solvent. Our conditions would have permitted the detection of as little as 0.3% of the saturated hydrocarbon. This previous report has given rise to speculation about a carbanion intermediate[18] which is no longer tenable.

Hence, the technique of electroreduction affords a superior method for the reductive elimination of vicinal dibromides, leading to the product of exclusively trans elimination, if the appropriate conformation is possible. The product appears to be formed in a synchronous two-electron transfer from the shape of the chronoamperometric (potentiostatic) curve,[19] and the process can be conducted in a highly protonic medium without deleterious results. It is noteworthy that, owing to the sensitivity of the reduction potential to the dihedral angle between vicinal C–Br bonds in rigid 1,2-dibromides, it is possible now to synthesize otherwise inaccessible isomers by selective destruction of the more easily reduced partner in a mixture. One example of this is seen in Table I (entries 10 and 11), in which the diequatorial dibromide could be recovered cleanly from the cpe of a mixture of the diaxial and diequatorial isomers. To our knowledge, the present procedure represents the only reduction procedure suitable for such a selective reduction. In addition, the mildness and variety of reduction conditions suggest this to be the method of choice for the synthesis of sensitive olefins from the dibromide. A recent example of this was reported recently in the preparation of benzocyclobutadiene dimer in 90% yield from 1,2-dibromobenzocyclobutene.[20]

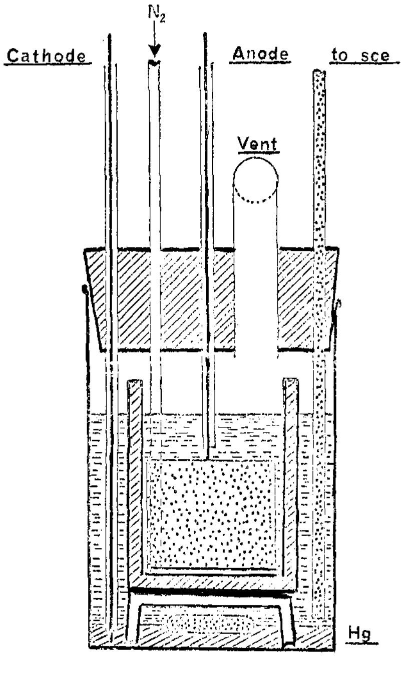


Figure 1.

Experimental Section

General. Boiling points are uncorrected. Nmr spectra were recorded on a Varian A-60 spectrometer using carbon tetrachloride solutions with internal tetramethylsilane. Analytical glpc was performed using a Porapak Q, 80–100 mesh, 3 m × 0.125 in. column at 80° for gases. Liquids were analyzed on a Carbowax 20M column, 15%, 10 ft × 0.25 in., using a Varian Model 90P chromatograph.

Chemicals. Mercury was Bethleham instrument grade. It was recycled by washing three times with 50% nitric acid, flooding with water, washing three times with 95% ethanol, and finally washing three times with ether. It was dried and degassed at room temperature under vacuum (*ca.* 0.1 mm) for more than 24 hr. Dimethylformamide was purified by stirring for at least 48 hr over calcium hydride and distilling under vacuum, and the fraction boiling at 64° (30 mm) was collected, stirred with phthalic anhydride, and redistilled under the same conditions. Tetra-*n*-butylammonium fluoroborate was prepared[21] from tetra-*n*-butylammonium hydrogen sulfate (Aldrich Chemical Co.) and sodium tetrafluoroborate (Alfa Chemical Co.). Tetraethylammonium fluoroborate (Southwest Analytical Chemicals) and tetraethylammonium bromide (Eastman Chemical Co.) were commercial and were used without further purification. 1,2-Dibromopropane was commercial and was distilled, the fraction of bp 32° (0.1 mm) being collected. *meso*- and *dl*-2,3-dibromobutane were prepared from *trans*- and *cis*-2-butene, respectively, by the method of Young,[22] and the fractions boiling at 28.5° (0.1 mm) and 27° (0.15 mm) were collected. 4-*tert*-Butylcyclohexene was prepared according to Sicher and coworkers,[23] bp 34° (2 mm), and converted to 1-bromo-*trans*-2-bromo-*cis*-4-*tert*-butylcyclohexane in 98% isomeric purity using pyridinium hydrobromide perbromide,[24,25] bp 105° (1.5 mm) [lit.[15] bp 78–80° (1 mm) and lit.[26] bp 68° (0.3 mm)]. 1-Bromo-*trans*-2-bromo-*cis*-4-*tert*-butylcyclohexane was converted to a mixture of geometric isomers (ratio diaxial:diequatorial normally *ca.* 3:2) by heating the neat liquid in the dark under nitrogen for 48 hr.[26]

1,2-Dibromo-2-phenylpropane.[27] α-Methylstyrene (2.84 g, 24 mmol) in 15 ml of chloroform was treated with a solution of 4.5 g (28 mmol) of bromine in 20 ml of chloroform at 0°. When the addition was complete, the mixture was washed with cold aqueous sodium sulfite, cold aqueous sodium bicarbonate, and finally water. It was dried over anhydrous calcium chloride, filtered, and concentrated. The residual oil was distilled to give a pale yellow liquid, bp 95–97° (0.07 mm), nmr 2.28 (3, s, $-CH_3$), 4.20 (2, q, $-CH_2Br$), 7.2–7.6 ppm (5, m, $-C_6H_5$).

Electrolysis Experiments. The electrolysis cell used in this work is shown schematically in Figure 1. It consisted of an unjacketed 150-ml cylinder (54 mm i.d. × 90 mm height) equipped with a magnetic stirring bar. The cathode was a *ca.* 5-mm depth pool of mercury placed in the bottom of the cell. Electrical connection was made by a small piece of platinum, sealed in glass and immersed in the mercury. A platinum anode (44 × 24 mm foil) was placed in a clean,[28] porous ceramic bucket (45 mm o.d.) that was supported in the cell by a glass tripod. The apparatus was fitted with a five-hole rubber stopper. Two holes were used for the cathode and anode connections, one for an agar bridge which was in contact with an external saturated calomel electrode (sce), one for the nitrogen inlet, and one for the outlet. The outlet hole was fitted with a ball joint that could be connected directly to a cold trap. During controlled potential electroreduction, achieved by means of a potentiostat,[29] a constant stream of nitrogen was passed through the cell, and the volatile products were collected in a cold trap at liquid nitrogen temperature. The trap was so designed that the contents could be pumped directly into a high-vacuum line after electrolysis was completed. For reactions in which no volatile products were expected the cold trap was replaced by a drying tube. All components of the cell were dried in an oven overnight at 110° prior to use. The ceramic bucket was dried at least three days after extraction.[28]

In a typical run, the substrate (1–5 mmol) was added to the catholyte and the system was purged with dry nitrogen. Typical catholyte and anolyte charges were 75 and 25 ml, respectively. Current yields were calculated by cut and weigh methods, using the data from an amperometric strip chart recorder connected as a coulometer.[30] Gaseous products, after transfer to a high-vacuum line, were fractionated at the appropriate temperatures to remove solvent, and the amount of gas was measured volumetrically. Yields were calculated from low-pressure samples using the gas law. A homogeneous gas sample was removed and analyzed by glpc, and the identity of various peaks was established by comparison to authentic samples of candidate compounds. Nmr and ir identification confirmed the structural assignment of all compounds. Nongaseous products were purified by extraction of the catholyte. Typically, the catholyte was diluted with 100 ml of water and extracted with 3 × 50 ml of ether. The combined organic extracts were washed with saturated salt solution (3 × 25 ml) and water (3 × 25 ml), then dried over anhydrous sodium sulfate. The extract was examined directly by glpc, then concentrated under vacuum (if appropriate) and analyzed by nmr and glpc. All runs were repeated several times to ensure reproducibility.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation, Undergraduate Research Participation Program, for support of this work.

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