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ELECTROCHEMICAL REDUCTION OF THE STEREOISOMERIC 2,4-DIBROMOPENTANES TO CYCLOPROPANES. EVIDENCE FOR A STEPWISE MECHANISM

Albert J. Fry and Wayne E. Britton
Hall-Atwater Laboratories of Chemistry
Wesleyan University, Middletown, Connecticut 06457

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The electrochemical reduction of 1,3-dihalides to cyclopropanes is a reaction of considerable generality.[1] Rifi has favored a concerted mechanism for this process, that is, a mechanism in which both carbon-bromine bonds have begun to break, and the new carbon-carbon bond has begun to form, in the transition state for electron-transfer.[1a,b] This proposal is novel, and, if correct, of great theoretical importance in view of the paucity of well-authenticated concerted 1,3-eliminations in the organic chemical literature.[2] We report herein evidence that this reaction (a) is in fact a stepwise process, and (b) proceeds via a highly efficient intramolecular cyclization of an intermediate bromocarbanion.

We investigated the electrochemical reduction of the diastereomeric 2,4-dibromopentanes (**1**)[3]. If the reduction is indeed concerted, each isomer of **1** should be converted stereospecifically to a single isomer of 1,2-dimethylcyclopropane (**2**). The products of controlled-potential electrolyses of the individual isomers of **1** in dimethylsulfoxide (DMSO) containing 0.1 F tetraethylammonium bromide (TEAB) are listed in Table I.

Table I

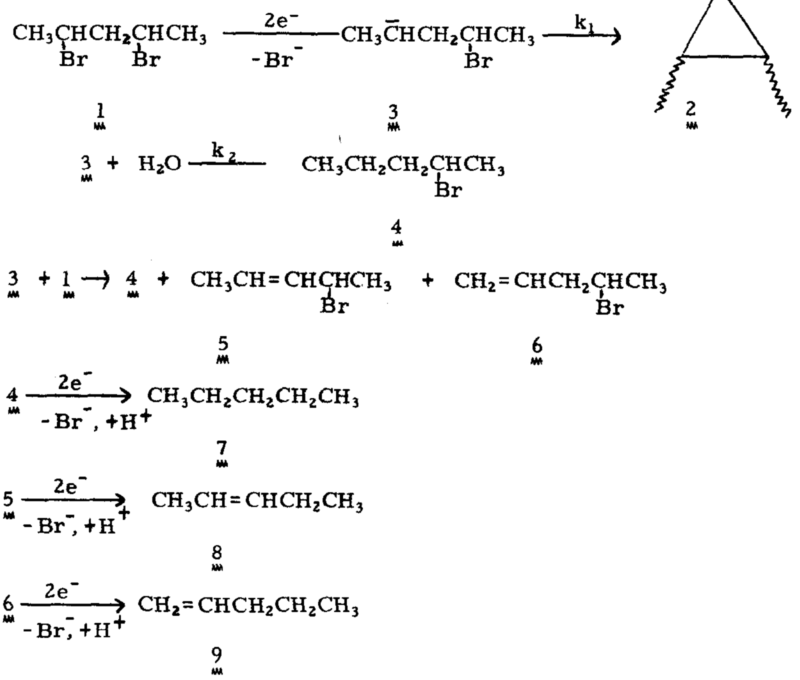
Electrochemical Reduction of the Diastereomeric 2,4-Dibromopentanes

Dibromide	Products (Relative yield,%)[a-c]					
	trans-**2**	cis-**2**	**7**	trans-**8**	cis-**8**	**9**
dl-**1**	39.5	44	3	9	4.5	trace
meso-**1**	45	41	6	5.5	2.5	trace
meso-**1**[d]	49.5	41.5	6	2.5	1	0

[a] Electrolysis at -2.2V (vs s.c.e.) in DMSO containing 0.1M TEAB. Similar results were obtained in dimethylformamide. [b] Total (absolute) yields: 100 ± 5%. [c] Controlled-potential coulometry indicated a consumption of 2.0 ± 0.1 Faradays/mole of **1**. [d] Solution contained added water (1.0M).

The reduction of **1** to **2** is clearly nonstereospecific. We formulate the reduction mechanism as follows (Scheme I):

Scheme I



The isomeric cyclopropanes 2 are believed to arise via intramolecular cyclization of bromo-carbanion 3. Dehydrohalogenation of starting material by 3 would generate 2-bromopentane (4) and three unsaturated bromides (*cis* and *trans*-5, and 6); all four monobromides would then undergo further reduction to the observed by-products, pentane (7) and the three pentenes (*cis* and *trans*-8, and 9). In fact, when the electrolysis was monitored by vpc, it was possible to detect the buildup and subsequent decay of 2-bromopentane 4 and two other compounds of similiar retention time, presumably *cis* and *trans* -5 (6 should be present in much smaller amounts, and must escape detection). The relative yields of 7, 8, and 9, increase during the electrolysis, as the three bromides disappear toward the end of the reaction. Carbanions generated by electrochemical reduction of 4, 5, and 6 no doubt contribute to olefin formation, but in a minor way, since the concentration of these bromides is never very high during the electrolysis. Hydroxide generated by reaction of 3 with traces of water in the solvent no doubt also serves as a base toward 1.

While added water does tend to suppress the yields of 8 and 9, cyclopropane formation is largely unaffected. Thus for $[H_2O] = 1.0M$, the ratio $k_1/k_2\ [H_2O]$ must be much greater then unity. This must be related in part to the high degree of structure in water-DMSO solutions, as a consequence of which water is a rather poor proton donor in DMSO.[4,5] Cyclization of 3 to 2 is nevertheless surprisingly efficient. We prefer not to comment at this time upon the interesting difference in the *cis*-*trans* ratio of cyclopropanes from *meso* and *dl*-1, other than to note that it also implies rapid cyclization of 3.[10]

The fact that 1,3-dibromopropane is easier to reduce by *ca.* 0.2V than 1,5-dibromopentane or 1,6-dibromohexane was adduced as evidence for concerted reduction of 1,3-dibromides.[1] This difference in reduction potentials was assumed to reflect a lower energy transition state for electron-transfer via the concerted path *vis-a-vis* the transition state energy for reduction of an alkyl monobromide. Although this argument is plausible, we find that *meso* and *dl*-**1**, which are not reduced concertedly, are also reduced easier than a related monobromide, 2-bromopentane (**4**), by *ca.* 0.2V [$E_{1/2}$(vs s.c.e.): *dl*-**1**, -1.91V; *meso*-**1**, -1.90V; **4**, -2.09V]. We believe that this difference is simply due to the inductive effect of the γ-bromine in **1**; this conclusion is based on Lambert's comprehensive study of substituent effects upon reduction potentials of alkyl bromides.[6]

It is not possible at this time to determine the sterochemistry of the conversion **3**→**2**. Two extreme geometries, termed semi-W and semi-U by Nickon and Westiuk,[7] must be considered. This question, and a number of other problems related to the sterochemistry of reductive 1,3-eliminations in general,[3b,8] could be examined using optically active 2,4-dibromopentane of known absolute configuration. The synthesis of this substance is in progress.

Other dihalides claimed in the literature to be reduced concertedly are probably also reduced in stepwise fashion. A notable example, the electrochemical reduction of the stereoisomeric 1,6-dibromocyclodecanes,[9] is being reinvestigated by us.

Acknowledgement

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10) A referee has suggested that our results may also be explained if each isomer of **1** is reduced via two conformations, each of which is reduced concertedly and stereospecifically to a different isomer of **2**. We feel that the mechanism outlined in Scheme I is much simpler than a scheme involving parallel concerted reactions, and therefore, we invoke Occam's Razor as grounds for rejection of the latter proposal.