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ELECTRODE-CATALYZED [2+2]CYCLOREVERSION REACTION OF PHENYLATED BIS-HOMOCUBANES¹⁾

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The constant potential anodic oxidation reaction of phenylated bis-homocubanes involved the [2+2]cycloreversion to give the dienes via a radical chain mechanism.

The photoinduced [2+2]cycloaddition of olefins and the photoinduced [2+2]cycloreversion of cyclobutanes to olefins have been demonstrated in many cases to involve a variety of key intermediates.

In our studies on the photosensitized electron-transfer [2+2]cycloreversion of l to 2, the cation radicals (l^{\ddagger}) and (2^{\ddagger}) were suggested to serve as key intermediates to achieve the radical chain formation of 2 from l^{2} . The structural elucidation of l^{\ddagger} and 2^{\ddagger} by CIDNP technique revealed their important roles for a chain process, providing that l^{\ddagger} has a shallow but discreat energy minimum and irreversiblly cyclorevertes to 2^{\ddagger} much faster than the isomerization of 2^{\ddagger} to 1^{\ddagger} .



In order to gain further insight into the reactivities of l^{\ddagger} and l^{\ddagger} , we investigated the constant potential anodic oxidation of l. Herein we report that the anodic oxidation of l also involves the facile cycloreversion to l^{\ddagger} via a chain mechanism. The electrolyses of l_{a} and l_{b} were conducted at 200 mV anodic site to each oxidation potential $(E_{1/2}^{ox}(l_{a})=\pm1.41 \text{ V}$ and $E_{1/2}^{ox}(l_{b})=\pm1.09 \text{ V}$ vs. SCE)²⁾ by using a platinum gauze electrode. When a solution of l in 20 ml of dry acetonitrile containing 0.1 M tetraethylammonium perchlorate was subjected to electrolysis, the [2+2]cycloreversion efficiently took place to give l in high yields as shown in Table 1. The anodic oxidation of l^{1} , however, did not afford l^{1} under the same conditions, indicating the irreversible rearrangement of l_{1} to l_{2} .

It should be noted that $\frac{1}{2}$ rearranges to $\frac{2}{2}$ with less electricity than a theoretical one required for a one-electron oxidation process. This observation indicates the operation of a chain process, the efficiency of which can be assessed by calculating an average chain length (Table 1).⁴) From the results shown in Table 1, a

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					Theoretical	Coulombs	Average chain
Substrate	[l] ^{a)}	Yi	eld/% ^{b)}	Time	coulombs	passed ^{c)}	length ^{d)}
	M	2	recovery	min	C	C	
łą	0.02	99	0	10	38.6	8.0	3.8
la	0.005	81	3	10	9.65	7.2	0.3
lþ	0.02	88	2	2	38.6	2.3	15.8
lþ	0.005	74	0	2	9.65	1.8	4.4

Table 1. Electrode-catalyzed [2+2]cycloreversion of 1 to 2

a)20 ml of 0.1 M solution in Et₃NClO₄ in acetonitrile. b)Determined by NMR. c)Obtained by current vs.time plots. d)Defined as average chain length= (theoretical coulonmbs to consume <u>l</u>/coulombs passed)-l.

plausible mechanism can be proposed as shown in Scheme 1. The initial electrontransfer on the electrode generates $1, \frac{1}{2}$ which very facilely isomerizes to $2, \frac{1}{2}, \frac{3}{2}$. Although 2 can be directly formed from $2, \frac{1}{2}$, the second electron-transfer from 1 to $2, \frac{1}{2}$ operates as a major pathway to form 2 and completes a radical chain process. This mechanism can be supported by the facts that the oxidation potentials of 2a and 2b $(E_{1/2}^{0x}(2a)=+1.40 \text{ V} \text{ and } E_{1/2}^{0x}(2b)=+1.09 \text{ V} \text{ vs. SCE})^{2}$ are nearly equal to those of 1a and 1b, respectively, and that a decrease in the concentration of 1 resulted in a decrease in an average chain length. The electrolytic results shown here accord with the fact that the photo-sensitized cycloreversion of 1 to 2 occurs with the limited quantum yield over unity and thus further confirm a radical chain mechanism induced by an initial electron-transfer generation of $1, \frac{1}{2}$.



Scheme 1.

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