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ELECTRODE-CATALYZED [2+2]CYCLOREVERSION REACTION OF PHENYLATED BIS-HOMOCUBANES[1)]

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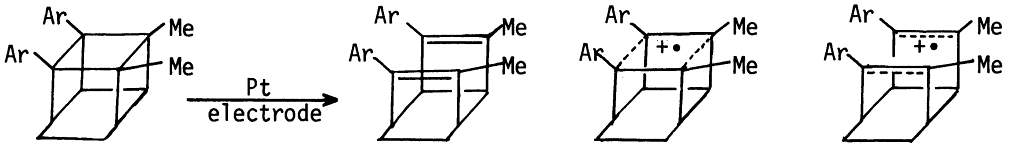
The constant potential anodic oxidation reaction of phenylated bis-homocubanes involved the [2+2]cycloreversion to give the dienes via a radical chain mechanism.

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 **1** to **2**, the cation radicals ($\mathbf{1}^{+\cdot}$) and ($\mathbf{2}^{+\cdot}$) were suggested to serve as key intermediates to achieve the radical chain formation of **2** from **1**.[2)] The structural elucidation of $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ by CIDNP technique revealed their important roles for a chain process, providing that $\mathbf{1}^{+\cdot}$ has a shallow but discreat energy minimum and irreversiblly cyclorevertes to $\mathbf{2}^{+\cdot}$ much faster than the isomerization of $\mathbf{2}^{+\cdot}$ to $\mathbf{1}^{+\cdot}$.[3)]



1 2 $1^{+\cdot}$ $2^{+\cdot}$

a: Ar=C_6H_5
b: Ar=p-$MeOC_6H_4$

In order to gain further insight into the reactivities of $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$, we investigated the constant potential anodic oxidation of **1**. Herein we report that the anodic oxidation of **1** also involves the facile cycloreversion to **2** via a chain mechanism. The electrolyses of **1a** and **1b** were conducted at 200 mV anodic site to each oxidation potential ($E_{1/2}^{ox}(\mathbf{1a})$=+1.41 V and $E_{1/2}^{ox}(\mathbf{1b})$=+1.09 V vs. SCE)[2)] by using a platinum gauze electrode. When a solution of **1** 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 **2** in high yields as shown in Table 1. The anodic oxidation of **2**, however, did not afford **1** under the same conditions, indicating the irreversible rearrangement of **1** to **2**.

It should be noted that **1** rearranges to **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

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

Substrate	[**1**]a)	Yield/% b)		Time	Theoretical coulombs	Coulombs passedc)	Average chain lengthd)
	M	**2**	recovery	min	C	C	
1a	0.02	99	0	10	38.6	8.0	3.8
1a	0.005	81	3	10	9.65	7.2	0.3
1b	0.02	88	2	2	38.6	2.3	15.8
1b	0.005	74	0	2	9.65	1.8	4.4

a)20 ml of 0.1 M solution in Et_3NClO_4 in acetonitrile. b)Determined by NMR.
c)Obtained by current vs. time plots. d)Defined as average chain length= (theoretical coulonmbs to consume **1**/coulombs passed)-1.

plausible mechanism can be proposed as shown in Scheme 1. The initial electron-transfer on the electrode generates $\mathbf{1}^{+\cdot}$ which very facilely isomerizes to $\mathbf{2}^{+\cdot}$.3) Although **2** can be directly formed from $\mathbf{2}^{+\cdot}$, the second electron-transfer from **1** to $\mathbf{2}^{+\cdot}$ 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** ($E^{ox}_{1/2}$(**2a**)=+1.40 V and $E^{ox}_{1/2}$(**2b**)=+1.09 V 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 $\mathbf{1}^{+\cdot}$.

$$\begin{aligned} 1 &\longrightarrow 1^{+\cdot} \\ 1^{+\cdot} &\longrightarrow 2^{+\cdot} \\ 1 + 2^{+\cdot} &\longrightarrow 1^{+\cdot} + 2 \\ 2^{+\cdot} &\longrightarrow 2 \end{aligned}$$

Scheme 1 .

References

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