Curve Crossing in the Cyclic Voltammetric Oxidation of 2-Phenylnorbornene. Evidence for an ECE Reaction Pathway

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Abstract: The preparative electrooxidation of 2-phenylnorbornene (**1**) leads to the formation of a dienic oxidative coupling product **2**. Analysis of the anodic behavior of **1** by cyclic voltammetry indicates a novel curve crossing, the first such experimental observation in an electrooxidation. An ECE mechanism with significant redox cross reaction is suggested as an explanation for this unusual observation.

Introduction

The recent recognition of the importance of ion radicals in a wide range of chemical transformations has prompted a rejuvenation of interest in characterizing the competing reaction pathways available to such intermediates. Investigations within our laboratory of the fate of cation radicals generated at the surface of irradiated semiconductor powders[1] had led us to examine whether intramolecular rearrangements of cation radicals might be kinetically competitive with intermolecular reactions and/or deprotonation. A few cation radical rearrangements are known,[2-5] but the structural features necessary for efficient rearrangement have not yet been experimentally verified. Since electrochemical techniques offer a convenient and definitive method for obtaining the required data, we have examined the electrooxidative behavior of 2-phenylnorbornene (**1**) by cyclic voltammetry. We describe

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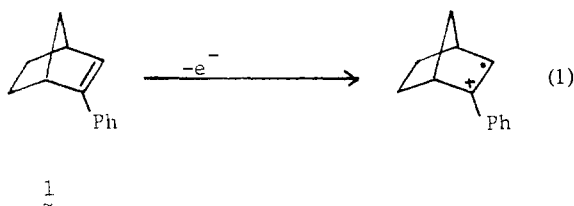
here a novel curve crossing that establishes the operation of a catalytic ECE reaction pathway initiated by electrochemical oxidation (eq 1) of this substituted olefin. This route nearly completely supersedes skeletal rearrangement as a fate for the electrogenerated olefinic cation radical.

Results

An unusual cyclic voltammetric curve crossing is observed when **1**, at concentrations $>10^{-3}$ M, is oxidized at platinum under argon in acetonitrile or in methylene chloride containing tetrabutylammonium perchlorate (TBAP), Figure 1. Thus, an anodic scan shows the presence of an irreversible wave at ca. +1.1 V (vs. Ag/AgNO₃: exact position depends on scan rate). On scan reversal, the curve does not return to the base line but rather crosses the anodic scan, exhibiting an oxidative peak at ca. +0.9 V. In the presence of small quantities of methanol or oxygen, this curve crossing disappears and normal appearing irreversible waves are observed, e.g., Figure 2. The peak current intensity

(i_p^{ox}) depended on scan rate (v), and a plot of $i_p^{ox}/\sqrt{v}$ vs. log v,[6] Figure 3, was characteristic of electrode processes in which chemical reaction and further electron transfer follow the initial electrooxidation.

If the applied potential is held at a value slightly negative of i_p^{ox}, the current continues to increase after a short (1–2 s) induction period. If the initial concentration of the olefin were increased, the duration of the induction period decreases and eventually disappears. This current growth could also be seen in cyclic voltammograms obtained at slow scan rates, e.g., Figure 4. At very fast scan rates, the curve crossing disappears. Even at such rapid scan rates, the oxidative wave remains completely irreversible.

On repeated scans (up to 50 cycles), a new oxidation peak appears that has a less positive peak potential than the starting material (Figure 5). Preparative controlled-potential electrolysis of **1** (just positive of i_p^{ox}) in acetonitrile gave rise to the product distribution shown in eq 2. Coulometric measurements obtained

$$\text{(2)}$$
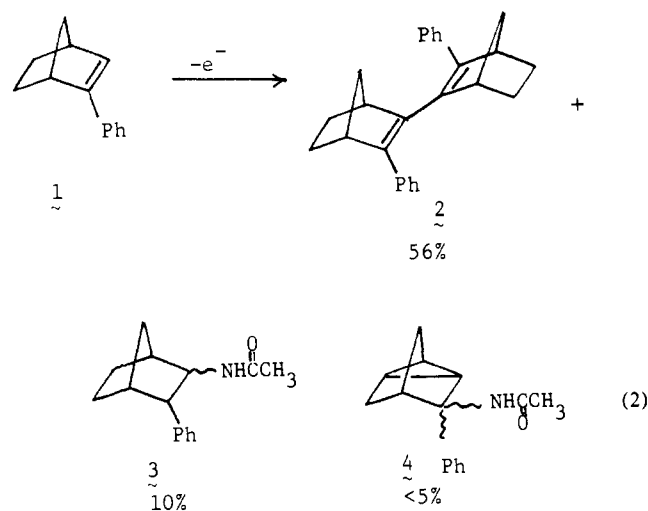
in early stages of the electrolysis showed that one electron had been taken up for each molecule of **1** reacting. Although an attempted catalytic controlled-potential oxidation (at a potential one-quarter of the height of the peak potential) was too slow to be useful synthetically, monitoring the uptake of coulombs at the oxidative peak potential showed that the rate of oxidation increases, after a short induction period, before slowly declining as starting material was consumed. That the new peak can be attributed to the major product **2** of the electrolysis (dimer) was established by comparing its cyclic voltammogram, Figure 6, with that described above, Figure 5. (By comparison, irreversible oxidative

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(2) Jones, G., II; Chiang, S. H.; Becker, W. G.; Greenberg, D. P. *J. Chem. Soc., Chem. Commun.* **1980**, 681. Roth, H. D.; Schilling, M. L. M.; Jones, G., II *J. Am. Chem. Soc.* **1981**, *103*, 1246.
(3) Jones, G., II; Chiang, S. H. *Tetrahedron* **1981**, *33*, 3397.
(4) Fox, M. A.; Campbell, K. A.; Hunig, S.; Berneth, H.; Maier, G.; Schneider, K. A.; Malsch, K. D. *J. Org. Chem.* **1982**, *47*, 3408. Bock, H.; Roth, B.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 2131.
(5) Rearrangements of cation radicals in the gas phase have been extensively studied by mass spectroscopists.

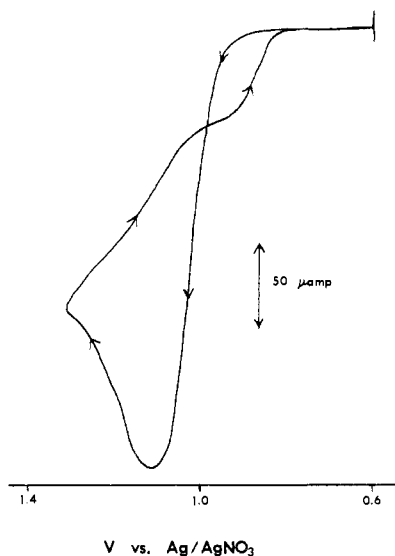(6) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 190.

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Figure 1. Cyclic voltammogram for the electrooxidation of **1** (3.64 mM **1**, Pt, CH$_3$CN, 0.1 M TBAP, room temperature, under 1 atm of Ar, scan rate = 200 mV/s).

Figure 3. Dependence of the oxidative peak current intensity on scan rate.
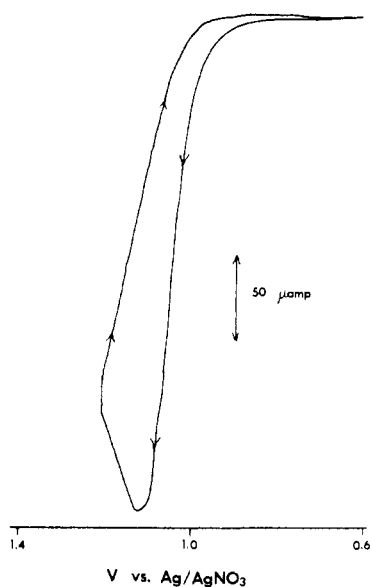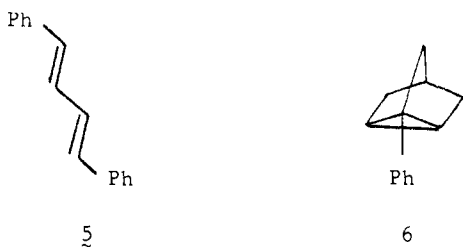

Figure 2. Cyclic voltammogram for the electrooxidation of **1**. As in Figure 1, except saturated with oxygen.

waves at +0.88 and +1.46 V, respectively, are observed for compounds **5** and **6**.)

Analogous oxidation of **1** in methanol gave rise to a mixture of mono- and dimethoxylated products. The yield of the monomethoxylated product diminished dramatically if the electrolysis were conducted in the presence of pyridine.

Discussion

   Radical Cation Rearrangement. The isolation of a major product incorporating the intact, unrearranged norbornenyl skeleton implies that intermolecular dimerization is much faster than any of several
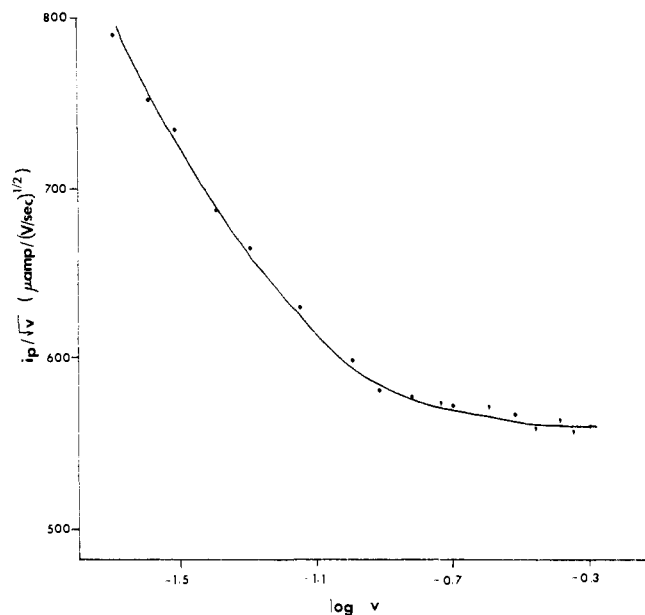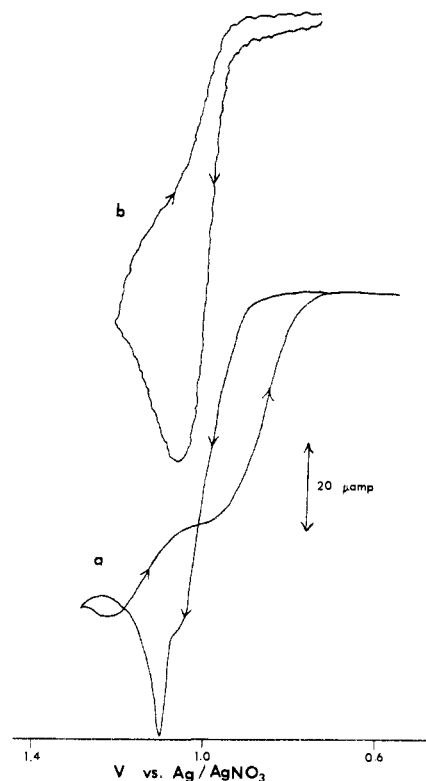

Figure 4. Cyclic voltammogram for the electrooxidation of **1** as a function of scan rate. As in Figure 1, except (a) scan rate = 20 mV/s. (b) scan rate = 50 V/s.

possible intramolecular rearrangements of the radical cation derived from **1**. This result stands in sharp contrast to the rapid skeletal rearrangement of the closed-shell 2-phenylnorbornyl cation[7,8] and provides experimental support for calculations that implicate significant delocalization of the unpaired electron throughout the π system of conjugated olefinic radical cations. That is, chemical reactivity of unstrained, delocalized radical cations may more closely resemble that of neutral free radicals

   (7) Kleinfelter, D. C.; Schleyer, P. v. R. *J. Org. Chem.* **1961**, *26*, 3740.
   (8) Coxon, J. M.; Robinson, W. T.; Steel, P. J. *Aust. J. Chem.* **1979**, *32*, 167.
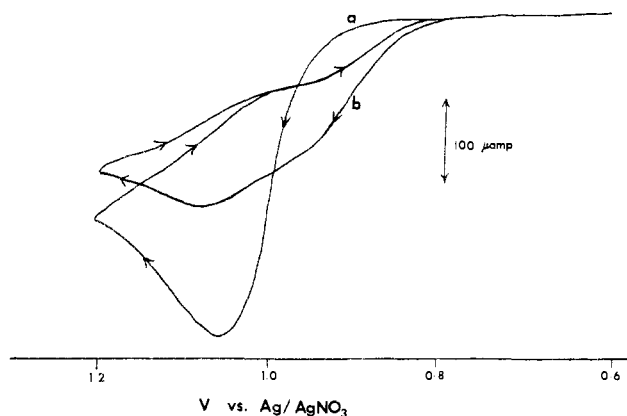
Figure 5. Cyclic voltammogram for the electrooxidation of **1**. As in Figure 1, except (a) first scan, (b) after 30 cyclic voltammetric cycles.
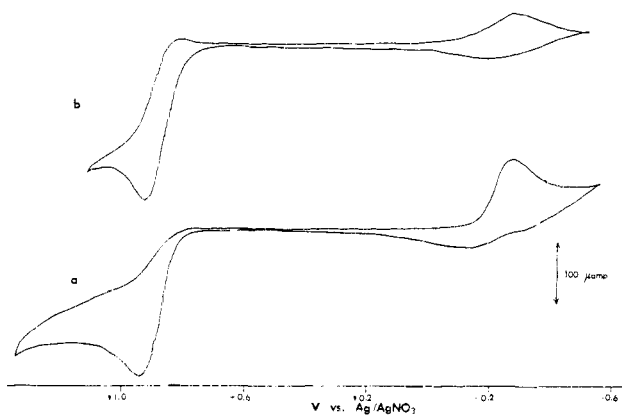

Figure 6. Cyclic voltammogram for the electrooxidation of **2**: (a) mixture obtained after electrolysis of **1**; (b) authentic sample of **2**.

than that of closed shell cations.

Such a generalization is consistent with previous reports of solution-phase radical cation rearrangements where, almost without exception, the release of strain in three- or four-membered rings is involved.[2-4] Although conformational equilibration of radical ions has been extensively described,[9] this phenomenon occurs relatively slowly on a cyclic voltammetric time scale and, furthermore, is limited to stable (i.e., electrochemically reversible or nearly reversible) systems in which intermolecular reaction is much less rapid than is observed for sterically accessible hydrocarbon radical cations like **1**. In some,[10] though not all,[11] radical ions in which conformational equilibration can be detected, localization of the odd electron is observed.

Diene Synthesis. The isolation of synthetically useful yields of diene (oxidative coupling product) upon electrooxidation of **1** in acetonitrile is also interesting.[12] Although preparative electrolyses of styrenes have been described before,[13-16] all have been conducted in methanol where varying distributions of stereo- and regioisomers of the possible dimethoxylated dimers are obtained.

(9) See, for example, a series of papers on hydrazine radical cation conformational equilibria: (a) Nelsen, S. F.; Echegoyen, L.; Evans, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 3530. (b) Nelsen, S. F.; Echegoyen, L.; Clennan, E. L.; Evans, D. H.; Corrigan, D. A. *Ibid.* **1977**, *99*, 2392. (c) Nelsen, S. F.; Haselbach, E.; Gschwind, R.; Klemm, U.; Lanyova, S. *Ibid.* **1978**, *100*, 4367. (d) Nelsen, S. F.; Clennan, E. L.; Evans, D. H. *Ibid.* **1978**, *100*, 4012.

(10) Nelsen, S. F.; Hintz, P. J.; Buschek, J. M.; Weisman, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 4930.

(11) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1977**, *99*, 2392. Nelsen, S. F.; Kessel, C. R.; Brace, H. N. *Ibid.* **1979**, *101*, 1874.

(12) Diene products have been reported in the electrooxidation of diamino-substituted olefins: Fritsch, J. M.; Weingarten, H. *J. Am. Chem. Soc.* **1968**, *90*, 793.
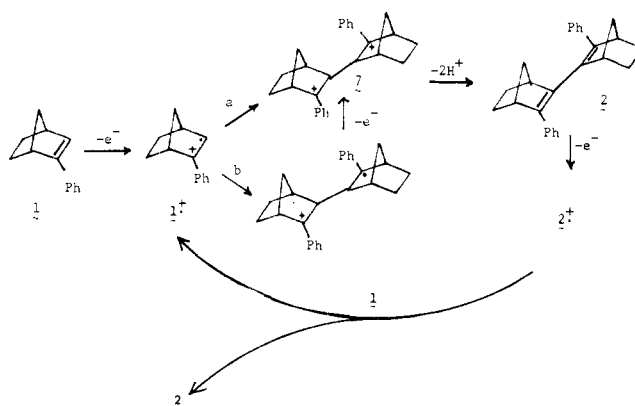
(13) Kojima, M.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1981**, 1707.

(14) Inoue, T.; Tsutsumi, S. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 661.

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Scheme I. Proposed Mechanism for Curve Crossing

Since the acetamides **3** and **4** are obtained in minor amounts, it is clear that the electrodimerization, either through collapse of two electrogenerated cation radicals (path a, Scheme I[17]) or through the attack of the electrogenerated cation radical on olefinic starting material (path b, Scheme I), is much faster than capture of the cation radical by acetonitrile, a weakly nucleophilic solvent.

The contrasting behavior observed in methanol indicates that the capture of the initially formed cation radical by methanol is more rapid than either of the pathways leading to dimerization. The reduced yield of monomethoxylated product in the presence of pyridine is consistent with acid-catalyzed methanolysis of **1** as a prime route to the methanol adduct and with the occurrence of deprotonation as a important step at some stage of the electrooxidation. Capture of the initially formed radical cation by methanol or by oxygen is also consistent with the inhibition of curve crossing in the cyclic voltammetry of **1** (see below).

Curve Crossing. A further interesting feature of the electrochemistry of **1** relates to the unusual crossing of the cyclic voltammetric traces for its oxidation and scan reversal. Although curve crossing has occasionally been observed in polarography and in cyclic voltammetry,[18-21] its occurrence is sufficiently rare so as to lend significant interest to processes in which it occurs. Those cases in which crossing has been reported previously have all involved catalytic reductions, and our observations represent the first case of which we are aware in which such effects have been described for a catalytic oxidation.

We interpret the curve crossing as diagnostic of a series of chemical reactions occurring within the electrochemical time scale of the cyclic voltammetric scan. The continued current growth at potentials less positive than the original oxidation peak potential requires that a chemical reaction ensue after the oxidation, giving a product that is more easily oxidized than the starting material. The formation of such a product (a simple ECE reaction) cannot be responsible for the curve crossing, however, since scan reversal should give rise to the normal trace characteristic of the product. Only if there exists further electrochemical equilibration should curve crossing be observed.

A reasonable scenario that can explain both the observed products and the cyclic voltammetric curve crossing is presented in Scheme I. Here electrooxidation leads to a radical cation, concentration-dependent dimerization of which gives a dication **7**. Proton loss from this charge-intensive species would produce the observed dimer **2** at a potential anodic of its own oxidative peak potential. Accordingly, **2** would be oxidized as rapidly as it is formed. The isolation of **2** in substantial yields in the

(17) Dimerization of an electrogenerated cation radical has been suggested in the anodic dimerization of vinyl ethers: Belleau, B.; Au-Young, Y. K. *Can. J. Chem.* **1969**, *47*, 2117.

(18) Saveant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323.

(19) Amatore, C.; Pinson, J.; Saveant, J. M.; Thiebault, A. *J. Electroanal. Chem.* **1979**, *107*, 59.
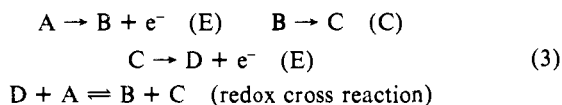
(20) Amatore, C.; Pinson, J.; Saveant, J. M.; Thiebault, A. *J. Electroanal. Chem.* **1979**, *107*, 75.

(21) Bard, A. J. *J. Electrochem. Soc.* **1977**, *124*, 189.

preparative electrolysis requires either that the radical cation of **2** be stable until workup or that it function efficiently as a redox catalyst to some other oxidizable couple present. The quasi-reversibility observed in the cyclic voltammogram of an authentic sample of **2** (in the absence of **1**) negates the first of these possibilities. The most easily oxidizable partner for the necessary redox cross reaction, especially at low conversions of starting material, is **1**. Thus, electron exchange between $2^{+\cdot}$ and **1** will generate $1^{+\cdot}$ in catalytic fashion, continuing an autocatalytic cycle that will generate more **2**, etc.

The catalytic oxidation of **1** by electrogenerated $2^{+\cdot}$ will be disfavored because the peak potential for the oxidation of **1** is about 200 mV more positive than that of **2**. Nonetheless, since neither peak potential is reversible, the potential difference lacks thermodynamic significance, and because a more rapid reaction route (dimerization) exists for $1^{+\cdot}$ than for $2^{+\cdot}$, redox equilibration can still occur. This process will take place with an efficiency that depends on the scan rate chosen for the cyclic voltammetry since the rate-determining chemical reaction must be of comparable order to the scan rates employed. As the redox cross reaction occurs, an anodic current will flow, and the trace will cross the base line at potentials positive of the oxidation potential of the product but less positive than that of the olefinic starting material.

This sequence involves therefore an electrooxidation (E), a rapid chemical dimerization followed by deprotonation (C) before the product oxidation (E) occurs and can therefore be termed an ECE reaction, a variant on the classical Nicholson–Shain[22] classification of coupled charge-transfer chemical reactions. The theory of relevant chronoamperometric details of ECE reactions complicated by redox cross reactions (eq 3) have been treated in detail.[23,24]

$$A \rightarrow B + e^- \quad (E) \qquad B \rightarrow C \quad (C)$$
$$C \rightarrow D + e^- \quad (E) \tag{3}$$
$$D + A \rightleftharpoons B + C \quad \text{(redox cross reaction)}$$

In particular, Feldberg has shown, for reversible reductions, that this mechanism should lead to curve crossing.[25] Simple extension of his reasoning to our catalytic oxidation (A = **1**, B = $1^{+\cdot}$, C = **2**, D = $2^{+\cdot}$) justifies a prediction of time- and concentration-dependent curve crossing in our catalytic oxidation scheme.

Conclusions. A further elaboration of the reasons for the resistance to rearrangement of radical cations (compared with structurally analogous carbocations) is under active investigation in our laboratory. We believe that our observation of curve crossing may be more general than has been so far recognized and that it may be a valuable diagnostic tool for the description of ion radical reactivity, particularly in the prediction of reaction pathways of photogenerated ion radical pairs.

Experimental Section

General Methods. Cyclic voltammetry and preparative electrochemistry were conducted with a Princeton Applied Research (PAR) Model 173 potentiostat equipped with a universal programmer. Current–voltage curves were recorded on a Houston Instruments x–y recorder, and current flow was monitored on a PAR Model 179 digital coulometer. For cyclic voltammograms obtained at rapid scan rates, a storage oscilloscope was employed.

The cell was a standard three-electrode cell with an adaptor for adding solids attached to the side. The cell was equipped with a platinum working electrode (0.05 cm²), a platinum coil counterelectrode, and a silver/silver nitrate reference electrode. For preparative electrolyses, a divided cell was employed with a platinum mesh working electrode, a platinum coil counterelectrode (with a surface area more than twice that of the mesh), and a silver wire quasi-reference electrode. The anodic and cathodic compartments were separated by glass frits and an intervening solution of electrolyte.

Before electrochemistry was done, all solvent–electrolyte mixtures were scanned by cyclic voltammetry to ensure the absence of air, water, and other electroactive impurities. All electrolyses were conducted under an atmosphere of dry nitrogen or argon. All cyclic voltammograms described here were obtained in freshly distilled acetonitrile containing 0.1 M LiClO_4, unless otherwise noted.

Proton and carbon nuclear magnetic resonance (NMR) spectra were obtained at ambient probe temperature on a Varian EM 390 90-MHz spectrometer with chemical shifts reported in parts per million downfield from tetramethylsilane as an internal standard. Infrared spectra (IR) were recorded on a Beckman Acculab 7 spectrophotometer. Gas chromatography–mass spectroscopy (GC–MS) analysis was performed on a Finnigan Model 4023 automated GC–MS with a INCOS data system. High-resolution mass spectra were obtained with a CEC 21-110 instrument. Preparative liquid chromatography was performed with a Waters R401 liquid chromatography system on a Preppak silica column. Melting points were obtained on a Fisher-Johns melting point block and are uncorrected.

Preparative Electrolysis of 1 in Acetonitrile. To 40 mL of acetonitrile, freshly distilled from calcium hydride and made 0.2 M in recrystallized LiClO_4, was added 262 mg (1.55 mmol) of 2-phenylnorbornene (**1**).[26] The resulting solution was electrolyzed at +1.1 V (vs. Ag/AgNO_3) until 0.98 faraday/mol had been removed. The solution was concentrated by partial removal of the solvent under rotary evaporation and was treated with 20 mL of distilled water. The aqueous solution was extracted with ether, and the organic layer was dried over anhydrous MgSO_4. Preparative thin-layer chromatography (neutral silica gel eluted with 50/50 hexane/ether) led to three fractions: **2**, 142 mg, 56%; **3**, 14 mg, 4%; **4**, 36 mg, 10%. The fractions containing **3** and **4** were mixtures of isomers that could not be separated by normal or reverse-phase liquid chromatography. No starting material remained.

2: mp 153–157 °C; ¹H NMR (CDCl₃) δ 6.6–7.4 (m, 5 H), 2.3–3.4 (m, 2 H), 1.4–2.0 (m, 6 H); ¹³C NMR (CDCl₃) δ 26.47, 31.97, 36.94, 45.70, 48.25, 122.20, 125.51, 126.29, 127.20, 128.12, 142.88; IR (CHCl₃) 2960, 1600 (w), 1495, 1450, 1210 cm⁻¹. High-resolution mass spectrum calcd. for $\text{C}_{26}\text{H}_{26}$: 338.2034. Found: 338.2030.

3: ¹H NMR (CDCl₃) δ 7.23 (s, 5 H), 5.20 (br s, 1 H), 4.13 (m, 1 H), 2.36 (br s, 1 H), 1.61 (s, 3 H), 1.33–2.27 (m, 8 H); IR (CHCl₃) 3418. 3310, 1660 cm⁻¹. High-resolution mass spectrum calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}$: 229.1466. Found: 229.1470.

4: ¹H NMR (CDCl₃) δ 7.31 (m, 5 H), 4.64 (s, 1 H), 1.93 (s, 3 H), 0.91–2.54 (m, 9 H); IR (CHCl₃) 1670 cm⁻¹. High-resolution mass spectrum calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}$: 227.1310. Found: 227.1310.

Electrolysis of 1 in Acetonitrile/Methanol. To a preelectrolyzed solution of $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ (4:1) made 0.1 M in freshly recrystallized LiClO_4 and held under an atmosphere of argon was added 150 mg of **1**. Electrolysis and workup were conducted as described above. Three products were detected upon GC–MS analysis (150-ft capillary column, 200 °C): two monomethoxylated products (m/e 200 and 202 (p), respectively) and a dimethoxylated product (m/e 232 (p)). The yield of each of the three products was below 20%, and no further attempts at characterization were pursued.

If this same electrolysis were conducted in the presence of 1% pyridine, the m/e 202 peak could not be detected in the GC–MS spectrum of the worked-up electrolysis mixture.

5: 1,4-Diphenylbutadiene (Aldrich) was recrystallized twice from methanol before its cyclic voltammetric behavior was examined.

6: 1-Phenylnortricyclene (**6**), prepared by the procedure of Schleyer et al.,[27] was redistilled twice before its cyclic voltammetric behavior was determined.

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