

Electron-transfer Catalyzed Cycloaddition Reactions of Unactivated Olefins in
a Weakly-Coordinating Anion Electrolyte

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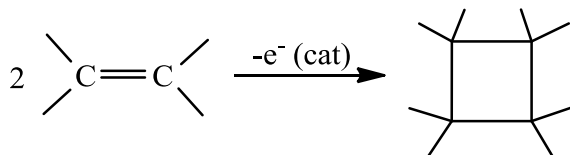
Abstract

A series of five unactivated cyclic olefins ranging from cyclooctene (COE, both *cis* and *trans*) to cyclopentene have been shown to undergo efficient electron-transfer (ET) catalyzed cycloaddition reactions in dichloromethane containing $[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ as supporting electrolyte. The reactions were initiated by *in-situ* anodic generation of catalytic amounts of either $[\text{N}(2,4\text{-C}_6\text{H}_3\text{Br}_2)_3]^+$ (**1**⁺, “magic green”) or $[\text{ReCp}(\text{CO})_3]^+$ (**2**⁺, Cp = $(\eta^5\text{-C}_5\text{H}_5)$). The olefin radical chain reaction induced by ET mediation was complete in 1-10 minutes, some 100 to 1000 times faster than the optimum photochemically-induced preparations of cyclobutane compounds from cyclic olefins. Both *cis*-COE and *trans*-COE gave good yields of a stereoisomeric mixture of the [2 + 2] cyclobutane adduct, $\text{C}_{16}\text{H}_{28}$, **4**. The *trans*-COE isomer was oxidized directly at an electrode, without aid of an ET mediator. Cycloheptene and cyclohexene underwent similar [2 + 2] coupling to give cyclobutane products. Cyclohexene also gave a [2 + 2 + 2] cyclized trimer, as did cyclopentene. Use of the weakly coordinating $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, rather than a traditional small anion such as $[\text{PF}_6]^-$ or $[\text{ClO}_4]^-$, was required to carry out the cyclization reactions. The mechanism appears to involve a key propagation step in which an olefin radical cation reacts with a neutral olefin to give a cyclobutyl radical cation, which then, accepts an electron, most likely from another olefin, to form the final neutral compound. Although the $E_{1/2}$ potentials of the ET mediators are 660-900 mV lower than the estimated oxidation potentials of the olefins, the endergonic nature of the ET initiation step works to the advantage of the chain process by favoring a radical-substrate propagation step.

Introduction

A number of examples are known in which an olefin radical cation initiates olefin [2 + 2] coupling reactions to give cyclobutane products. This process may be triggered by either one-electron oxidation (Scheme 1)¹ or by photochemical excitation of the olefin.² Originally reported by Ledwith³, this reaction was developed primarily by Bauld and co-workers,^{1,4,5} who extended it to include radical-induced Diels-Alder reactions.^{1,5} Compared to strictly thermal reactions of the neutral olefins and diolefins, the rates of both [2 + 2] and [2 + 4] coupling reactions are enormously accelerated by radical cation initiation.^{6,7} For reasons to be discussed below, application of this reaction has been largely restricted to “activated” olefins having comparatively low oxidation potentials. The present paper follows our previous communication,⁸ and offers a full report on extension of the radical-cation catalyzed [2 + 2] cycloaddition reaction to unactivated olefins having relatively high oxidation potentials.⁸

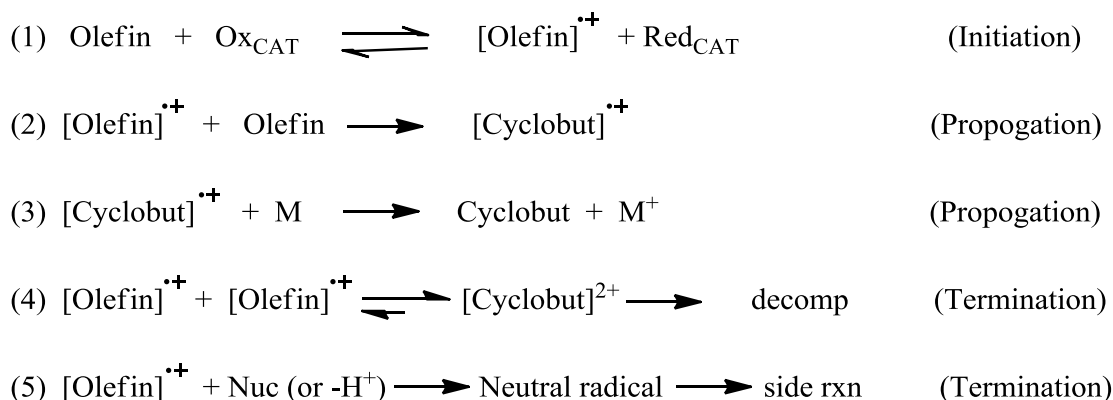
Scheme 1. Electron-transfer catalyzed [2 + 2] cycloaddition reaction of an olefin



The cyclization reaction, which is often described as following the general mechanism of Scheme 2, has several interesting features. Although the initiation step can, in principle, be triggered by direct anodic oxidation of the olefin, it is usually initiated by an oxidizing agent, O_{XCAT} (Eq 1), having a less positive potential than the olefin itself. The resulting olefin radical cation, $[Olefin]^{\cdot+}$, then reacts either with a neutral olefin (Eq 2) or with another olefin radical cation (Eq 4). Although the radical-radical (R-R) coupling reaction of Eq 4 is found under some conditions,⁹ it is not likely to lead to a stable cyclized product owing to the highly unstable nature of a doubly-oxidized cyclobutane ring. The better route to the cyclized product is the radical-substrate (R-S) reaction of Eq 2, which can be favored by generating the olefin radical cation in the presence of an excess of the neutral olefin (*vide infra*). The resulting cyclobutyl radical cation, $[Cyclobut]^{\cdot+}$, has some kinetic stability owing to its retention of partial C-C unsaturation. Proposed early on by Bauld^{6,10} and by others^{3,11}, the relevance of the cyclobutyl

radical cation intermediate has been strengthened recently by DFT calculations¹² and by its experimental detection using electrospray ionization mass spectrometry.^{12,13}

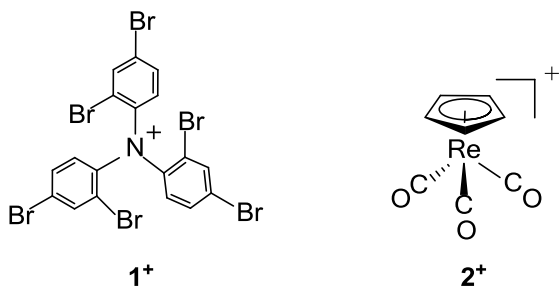
Scheme 2. Mechanism for an electron-transfer catalyzed olefin radical cation-olefin substrate chain reaction. Equations (1)-(3) describe the initiation and propagation steps, and equations (4) and (5) describe possible termination processes. Ox_{CAT} and Red_{CAT} are the oxidized and reduced forms, respectively, of the electron-transfer mediator. M is an unspecified reducing agent (see text).



The fact that the overall reaction begins and ends with neutral compounds, but proceeds through cationic intermediates, solicits the question: what is the reducing agent (labeled M in Eq 3) that provides the electron to neutralize the intermediate? The two most likely candidates are the starting olefin and Red_{CAT} (the reduced form of the original oxidizing agent). In these cases, a unit of either [Olefin]^{•+} or Ox_{CAT} is generated, thereby propagating the reaction and allowing an overall “zero electron” electron transfer (ET)-catalyzed chain process.

Thermodynamic aspects of the reactions in Eqs 1 and 3 involve the redox potentials of three ET participants, specifically those of [Olefin]^{0/+}, Red_{CAT}/Ox_{CAT}, and [Cyclobut]^{0/+}. The key factor in the initiation step, namely the comparative E_{1/2} potentials of the olefin and the redox agent, has been discussed in a number of papers.^{1,9,14-18} It has been specifically stated that these reactions will not proceed at discernible rates unless the potential of the catalyst is within about 500 mV of that of the olefin.¹⁶⁻¹⁸ In fact, a catalyst seems to be most effective if its oxidation potential is a few hundred millivolts less than that of the olefin. This allows sufficient production

of the olefin radical cation (Eq 1) to trigger its radical-substrate reaction with neutral olefin (Eq 2), but not such a high concentration that the radical-radical termination step of Eq 4 becomes important. The most widely employed redox agents have been those based on bromoaryl amines, specifically the radical cation of either tris(4-bromophenyl)amine ($E_{1/2} = 0.70$ vs ferrocene, FcH; the radical cation is “magic blue”) or tris(2,4-dibromophenyl)amine (**1**, $E_{1/2} = 1.14$ V vs FcH; **1**⁺ is “magic green”) ¹⁹.



Owing to the requirement imposed by Eq 1, ET-induced coupling reactions of olefins have been constrained to those activated towards oxidation (i.e., having lower $E_{1/2}$ potentials) by either delocalization (e.g., stilbenes) or by substitution with electron-releasing (e.g., methoxy) groups. ^{1,5,20} Unactivated olefins are considerably more difficult to oxidize, having potentials that significantly exceed the literature “limit” ¹⁶⁻¹⁸ of a 500 mV differential with the $E_{1/2}$ potential of magic green. We were surprised, therefore, when we observed that *cis*-cyclooctene (*cis*-COE), *cis*-**3**, with a nominal oxidation potential of 1.85 V (*vide infra*) underwent cyclobutanation in the presence of catalytic amounts of *in-situ* generated [ReCp(CO)₃]⁺ (**2**⁺ Cp = η⁵-C₅H₅), which has a potential of only 1.16 V vs FcH in CH₂Cl₂. ²¹ Furthermore, as will be shown below, other cyclic olefins undergo efficient [2+2] cyclization reactions, even when their estimated oxidation potentials are as much as 900 mV positive of that of the ET catalyst.

In our earlier communication, ²⁰ we raised the possibility of an inner-sphere ET mechanism for the initiation reaction of olefin with **2**⁺, perhaps involving a transition state or intermediate structure with a coordinated olefin, such as 19 e⁻ [Re(η⁵-C₅H₅)(CO)₃(η²-olefin)]⁺ or ring-slipped 17 e⁻ [Re(η³-C₅H₅)(CO)₃(η²-olefin)]⁺. To test this possibility, we have now compared the rate of the [ReCp(CO)₃]⁺-induced cyclooctene cyclization with that induced by magic green. The latter has virtually the same $E_{1/2}$ (oxidizing power) as [ReCp(CO)₃]⁺, but lacks the ability to coordinate the olefin. As will be shown below, there are no significant differences in the rates of

cyclization using the two different catalysts. Based on this finding, we assume a simple outer-sphere ET reaction between olefin and $O_{X_{CAT}}$ in the initiation step.

The present work was carried out using the weakly coordinating anion (WCA) tetrakis(perfluoroaryl)borate (TFAB)²², in contrast to earlier reports, which employed one or another of the more traditional anions such as $[PF_6]^-$, $[BF_4]^-$, triflate, or $[SbCl_6]^-$. As will be shown, a WCA appears to be a necessary component in carrying out the ET-induced conversion of unactivated cyclic olefins to cyclobutane products.

Experimental

All electrochemical procedures were carried out under dry nitrogen, using either Schlenck techniques or a Vacuum Atmospheres drybox typically maintained at 1-3 ppm oxygen.

Solvents were dried and distilled using practices similar to those previously reported.²¹ Commercial sources were used for tris(2,4-dibromophenyl)amine (Aldich), $ReCp(CO)_3$ (Strem), and each of the cyclic olefins, except for *trans*-cyclooctene. The latter was prepared as analytically pure and free of its *cis* isomer by a modification of the literature method,²³ details being given in supplementary material (IR spectra of *cis* and *trans* cyclooctene isomers in Figure SM1). $[NBu_4][PF_6]$ (Tokyo Chemical Industry) was thrice recrystallized from absolute ethanol and vacuum dried for at least 24 h at 100° C. $[NBu_4][B(C_6F_5)_4]$ was prepared as described earlier²⁴ and also vacuum dried at 100° C.

Preparation of $[N(2,4-C_6H_3Br_2)_3][B(C_6F_5)_4]$, $[1][TFAB]$: $[1][SbCl_6]$ ^{25(a)} (15g, 14.2 mmol) and $K[TFAB]$ (Boulder Scientific Co.) (11.3 g, 15.7 mmol) were dissolved in 700 mL of dry dichloroethane and stirred at room temperature for 30 min. The reaction was cooled at -20°C for 45 minutes and then filtered. The solvent was removed under reduced pressure and the resulting green solid was dissolved in 700 mL of dry dichloromethane. The solution was filtered again to remove residual $K[SbCl_6]$. The filtrate was concentrated to 100 mL and then added to 700 mL of dry hexane, leaving a green amorphous solid. The liquid was decanted off, another 100 mL of dichloromethane was added, and the resulting solution was again added to 700 mL of hexanes (the redissolving process gave a purer final product). After cooling the solution to -20°C for 30 min, followed by filtration and overnight vacuum drying of the deep green precipitate, 19.9 g (85%) of the desired product was obtained [elemental analysis: C: Calcd = 36.22%, found 35.79

%; H: Calcd = 0.65 %, found 0.79 %; N: Calcd = 1.01 %, found 1.13 %]. A carborane salt of magic green has been previously reported.^{25(b)}

Electrochemistry was carried out within a drybox using EG&G Princeton Applied Research potentiostats controlled by either M270 or PowerSuite software. Data were exported and managed using Microsoft Excel. A traditional three-electrode cell setup was employed, with the reference electrode separated by a fine frit from the working electrode solution. For bulk electrolyses, a glass fine frit also was used to separate the working and auxiliary compartments. The working electrodes used for voltammetry were glassy carbon electrode (GCE) disks of 1-2 mm diameter purchased from Bioanalytical Systems and polished before each use using diamond polishing compound, followed by rinsing with nanopure water and vacuum drying. The working electrode for bulk electrolyses was a platinum gauze basket that was stored in nitric acid, washed with copious amounts of nanopure water, and dried in an oven at 120° C for at least 24 h before use. The volumes of the working compartment solutions were between 3 mL and 15 mL. The auxiliary electrode was a platinum wire. A Ag/AgCl wire, used as the experimental reference electrode, was prepared by electroplating AgCl onto a silver wire anodized in a 1 M solution of hydrochloric acid. However, all potentials in this paper are referred to the ferrocene/ferrocenium potential²⁶, obtained using the *in-situ* method^{26(b)} to track the experimental potential vs ferrocene.

Bulk anodic electrolysis and product workup: The olefin and the catalyst were added to the anodic compartment of the electrochemical cell and the electrolysis was carried out at a potential 100-200 mV more positive than the $E_{1/2}$ of the catalyst. The progress of the reaction was regularly checked by transferring a small amount of the working compartment solution (90 μ L) *via* syringe to 1 mL of dichloromethane for GC/MS analysis. After complete loss of cyclic olefin, the solution was worked up for product recovery. Example procedures are as follows: (a) with $\text{ReCp}(\text{CO})_3$ as precatalyst. A 10 mL solution containing 54 mg (500 μ mol) of *cis*-cyclooctene and 6.7 mg (20 μ mol) of **2** in 10 mL $\text{CH}_2\text{Cl}_2/0.05\text{M} [\text{NBu}_4][\text{TFAB}]$ was electrolyzed for 12 min at $E_{\text{appl}} = 1.3$ V. The working compartment solution was removed and 30 mL of hexanes added to it to precipitate the supporting electrolyte. After filtration and vacuum evaporation of the solution, the residue was dissolved in hexanes and put through a small column of activated alumina using pentane as an eluent. After vacuum drying, a 43 mg oil of the cyclobutane adduct was obtained; (b) with $[\text{N}(2,4\text{-C}_6\text{H}_3\text{Br}_2)_3]$ as precatalyst: the preceding

electrolysis procedure was followed on 2 mmol of *cis*-cyclooctene and 7.2 mg (0.01 mmol) of **1**. The crude oil was eluted through a silica gel column with pentane and then distilled under reduced pressure using a Kugelrohr apparatus, giving 192 mg (87%) of a colorless oil.

Gas chromatographic (GC) data were obtained using a Varian CP-3800 GC with a CP-8510 reverse-phase column, a CP-8410 autosampler, and a flame ionization detector. Temperature programming at 30°C/min was employed after initiation at 50°C for 2 min. GC-MS data were obtained using a Varian Saturn 2100T GC-MS in conjunction with a Varian 3900 GC having a CP8944 reverse phase column. It was operated in either an electron impact (EI) ionization or positive chemical (methanol) ionization (PCI) mode. In this case the temperature was programmed at 20°C/min after initiation at 50°C for 2 min. Mass spectra of the hydrocarbon products displayed a high degree of fragmentation, as is expected for saturated hydrocarbons. However, methanol-based chemical ionization generally allowed observation of what were interpreted to be M and M+1 peaks.

NMR data were obtained using a Bruker AXR 500 MHz instrument. Elemental analyses were obtained either from Robertson Microlit Laboratories (Madison, NJ) or using an Elementar Model Vario Micro Tube instrument operated by the Rory Waterman group at the University of Vermont.

Results

I. Oxidation Potentials of Cyclic Olefins

Although anodic potentials have been reported for a few unactivated cyclic olefins, the literature potentials vary considerably (Table 1). These variations are understandable owing to both the differences in the electrolyte media employed and to the complications inherent to these anodic reactions, which involve highly irreversible processes that are frequently prone to electrode passivation and electrode history problems. With the exception of *trans*-COE, we were unable to directly measure the oxidation potentials of these olefins under our experimental conditions owing to the fact that their anodic processes are positive of the window that can be reached with the TFAB electrolyte system. Therefore, we employed an extension of the method of Robinson and Osteryoung²⁷ to estimate olefin $E_{1/2}$ values under our conditions. These authors

measured the oxidation potentials of a series of hydrocarbons in a molten salt medium, finding a fit of the first ionization potentials with either $E_{1/2}$ or E_p values for the hydrocarbon oxidation.

Table 1. Electrochemical oxidation potentials (vs FcH) and ionization potentials (IP) of selected cyclic hydrocarbons. Estimated $E_{1/2}$ is for $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{H}_5)_4]$ solution vs FcH.

Hydrocarbon	Reported Oxdn Potl (V vs FcH)	Conditions	Ref	IP (eV) ^a	Estimated $E_{1/2}$ (V)
cyclopentene	N.A.		----	9.15	2.06
cyclohexene	1.7 ^{b,c} , 1.9 ^d , 2.0 ^e	$\text{CH}_2\text{Cl}_2/[\text{NEt}_4][\text{BF}_4]$ ^b $\text{CH}_3\text{CN}/\text{Li}[\text{ClO}_4]$ ^c $\text{CH}_3\text{CN}/[\text{NEt}_4][\text{ClO}_4]$ ^d	b-e	9.11	2.04
cycloheptene	N.A.		----	9.00	1.96
<i>cis</i> -cyclooctene	1.5 ^c	$\text{CH}_3\text{CN}/\text{Li}[\text{ClO}_4]$ ^c	e	8.82	1.85
<i>trans</i> -cyclooctene	N.A.		----	8.53	1.65

N.A.: not available.

^a Lias, S.G.; Liebman, J.F., Ion Energetics Data in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, Linstrom, P.J. and Mallard, W.G. (Eds), National Institute of Standards and Technology, Gaithersburg, Maryland, <http://webbook.nist.gov>. ^b Clarke, D.B.; Fleischmann, M.F.; Pletcher, D. *J. Electroanal. Chem.* **1973**, 42, 133; $[\text{NEt}_4][\text{BF}_4]$ ^c Shono, T.; Ikeda, A.; Hayashi, J.; Hakozaki, S. *J. Am. Chem. Soc.* **1975**, 97, 4261 converted to FcH by subtraction of 0.40 V. ^d Arnold, D.R.; Snow, M.S. *Can. J. Chem.* **1988**, 66, 3012, converted to FcH by subtraction of 0.40 V. ^e Ogibin, Yu.N.; Nikishin, G.I. *Russ. Chem. Reviews* **2001**, 70, 543.

Adapting this approach to our conditions, we first measured the $E_{1/2}$ vs ferrocene of the naphthalene^{0/+} couple (1.39 V) in $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ and used this value along with the known naphthalene ionization potential of 8.13 eV to generate Eq 6, which, along with the published olefin IP values, served to give the estimated $E_{1/2}$ potentials collected in Table 1 (see $E_{1/2}$ vs IP plot in Figure SM2). The fact that the $E_{1/2}$ potentials are between 460 mV and 900

$$(6) \quad E_{1/2} (\text{V}) = 0.66 \text{ IP} - 3.98$$

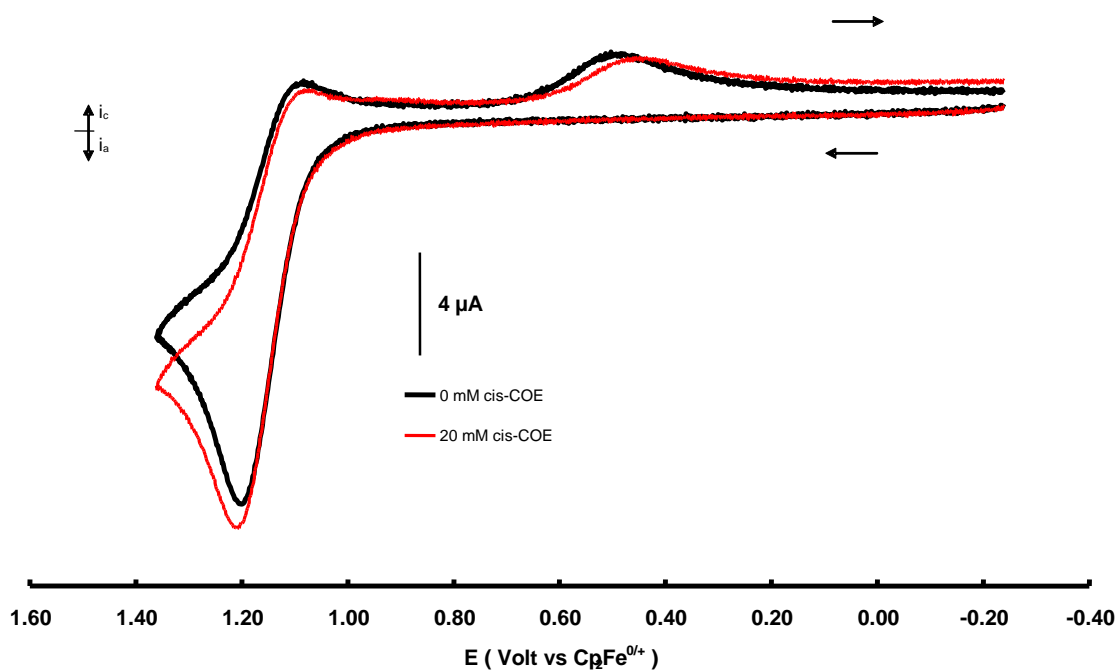
mV above those of the ET catalysts $[\text{ReCp}(\text{CO})_3]^+$ (2^+ , 1.16 V) and magic green (1^+ , 1.14 V) should be kept in mind as our discussion proceeds.

II. Application to *cis*-Cyclooctene, *cis*-**3**

II.A. Cyclic Voltammetry

Our discovery of cycloaddition reactions of unactivated cyclic olefins had its origin in experiments intended to probe the possibility of ET-induced substitution of a carbonyl ligand by cyclooctene, **3**, in the 17-electron radical cation $[\text{ReCp}(\text{CO})_3]^+$.²⁸ Although the very minor changes observed in the CVs of $\text{ReCp}(\text{CO})_3$ upon addition of excess *cis*-**3** (Fig 1) indicated the lack of ligand substitution²⁹, a one-hour bulk electrolysis at $E_{\text{appl}} = 1.3 \text{ V}$ was nevertheless

Figure 1. Cyclic voltammogram of 1 mM $\text{ReCp}(\text{CO})_3$, **2**, in $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ with (red line) and without (black line) 20 eq of added *cis*-cyclooctene (COE). Conditions: scan rate 0.2 V s^{-1} , 2 mm GCE, ambient temperatures.



carried out. Surprisingly, in spite of the fact that there was little loss of $\text{ReCp}(\text{CO})_3$, GC (Figure 2) showed complete loss of **3** and four products shown by GC/MS to have a molecular weight of 220 (MS in Figure SM3), corresponding to the cyclobutane derivative $\text{C}_{16}\text{H}_{28}$, **4**.

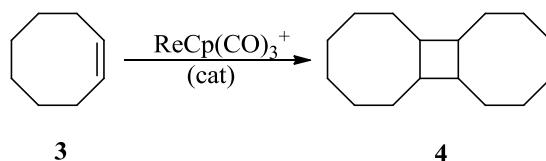
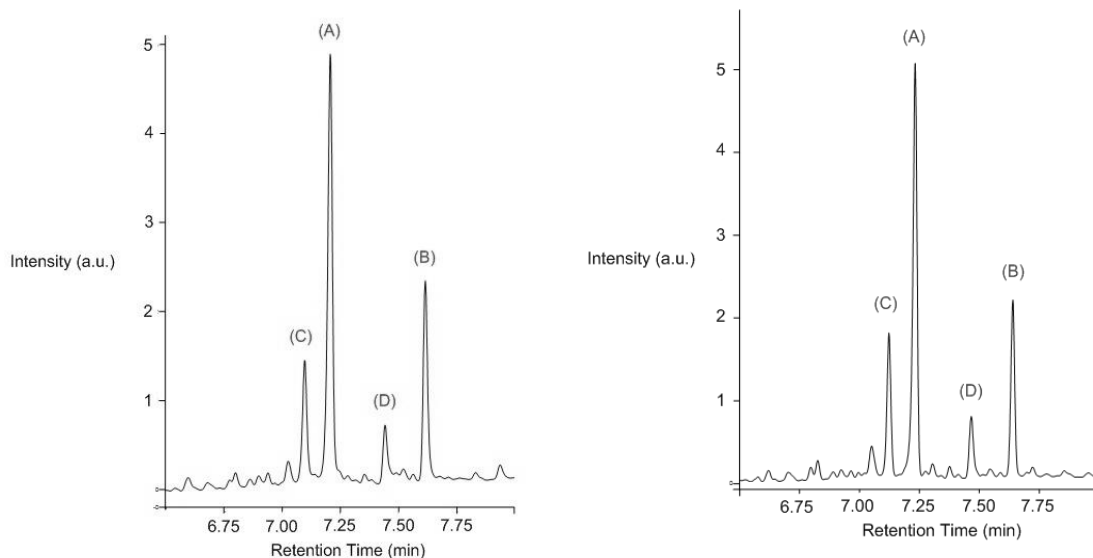


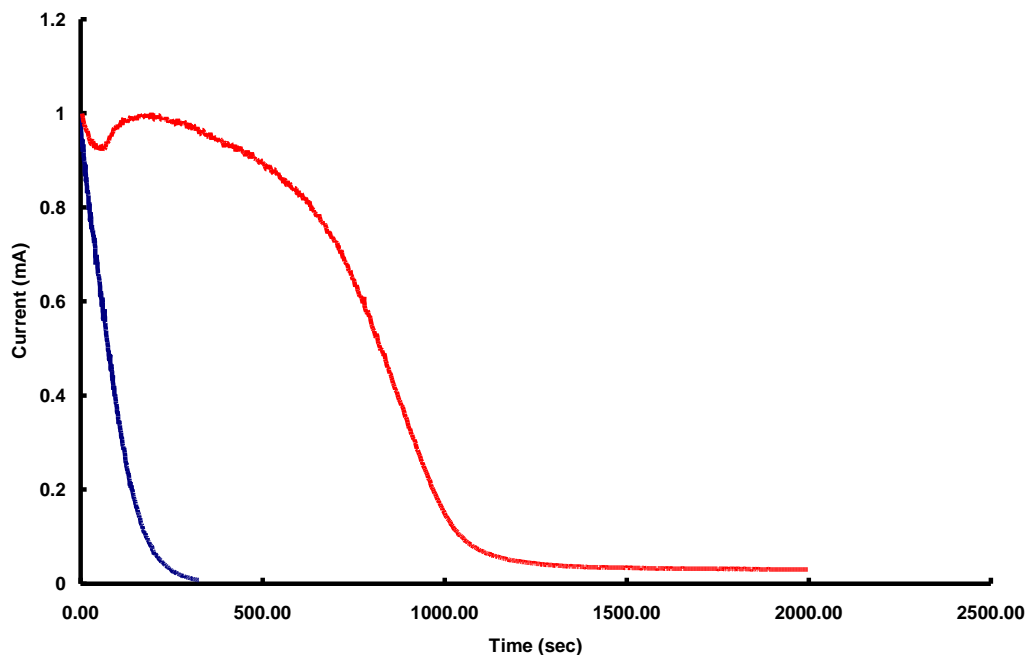
Figure 2. Gas chromatograms (GCs) showing four major $C_{16}H_{24}$ products formed by ET-catalyzed cycloaddition reactions of *cis*-cyclooctene: left: $N(C_6H_3Br_2)_3$, **1**, as pre-catalyst; right, $ReCp(CO)_3$, **2**, as pre-catalyst.



II.B. Bulk Anodic Electrolysis

Figure 3 shows a typical current *vs* time curve resulting from a bulk electrolysis of solutions containing either only 1 mM $ReCp(CO)_3$ (dark blue line) or 1 mM $ReCp(CO)_3$ and 20 mM *cis*-**3** (red line). In the absence of olefin, the oxidation of $ReCp(CO)_3$ proceeds to completion, passing 1 F per equivalent of **2**. Higher coulomb counts and more extended electrolysis times are obtained when *cis*-**3** is also present. As discussed below, the additional anodic currents do not arise from the [2 + 2] cycloaddition reaction, which is a zero-current process, but from chain-terminating side reactions of the radical cation [*cis*-**3**]⁺ (see Eqs 5 and 6) produced by the oxidation of *cis*-**3** by **2**⁺. These coulomb counts are typically between 0.1 and 0.2 F per *cis*-**3**,³⁰ suggesting a 5-10% generation of side products if they are formed in two-electron processes.

Figure 3. Current vs time curves for bulk electrolysis at Pt electrode at 293 K in CH₂Cl₂/0.05 M [NBu₄][B(C₆F₅)₄], E_{appl} = 1.3 V. Black curve: 1 mM ReCp(CO)₃, **2**. Red curve: 1 mM **2** and 20mM *cis*-cyclooctene mM.

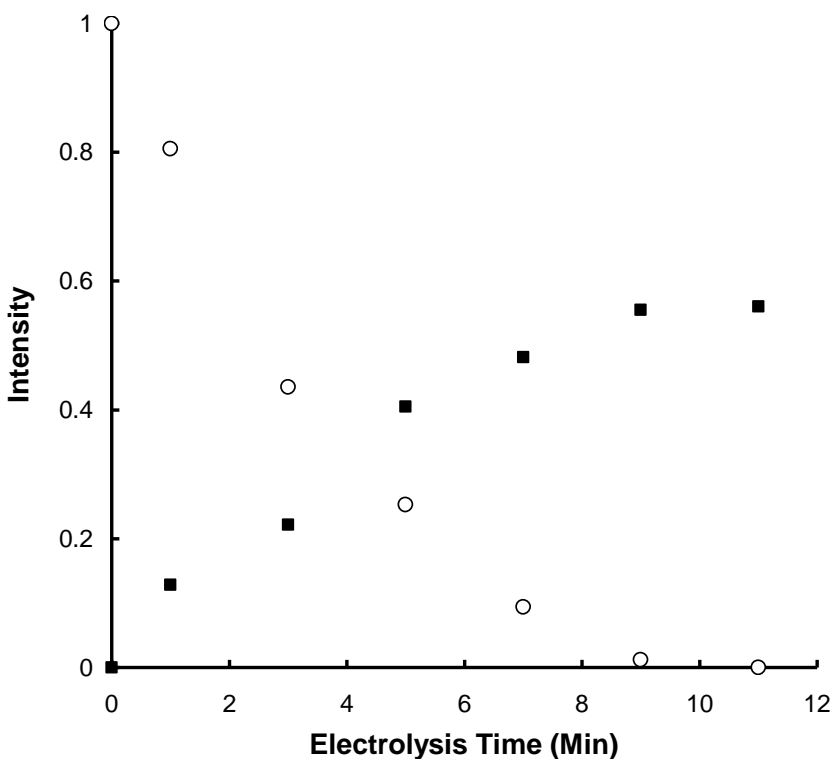


This analysis was confirmed by post-electrolysis CV scans, which always showed irreversible cathodic waves ($E_{pc} \approx -0.67$ V and -0.91 V) having peak currents consistent with this level of radical cation decomposition.³¹ Virtually identical results were obtained when **1** was used in place of **2** as the precursor to the ET catalyst (Figure SM4).

II.B.1. Qualitative Product Analysis

Owing to the fact that neither the *cis*-**3** starting material nor the major cyclized product is electroactive in the available potential window, monitoring of the cyclization reaction was followed by GC and GC/MS analyses of samples extracted from the electrolysis solution as a function of time.³² Typical GC results have been shown in Figure 2. At retention times between 7 and 8 minutes, four major products are detected having a mass of 220, C₁₆H₂₈ (**4**). The ratio of the four isomers is essentially independent of the ET catalyst (**2**⁺ on top, **1**⁺ on bottom). The loss of *cis*-**3** was also followed by monitoring its GC response as a function of time. Figure 4 shows that the concentration of *cis*-**3** (open circles) falls off and the summed response for the four cyclobutyl stereoisomers comes in cleanly over a 10 minute period. The fact that the reaction is

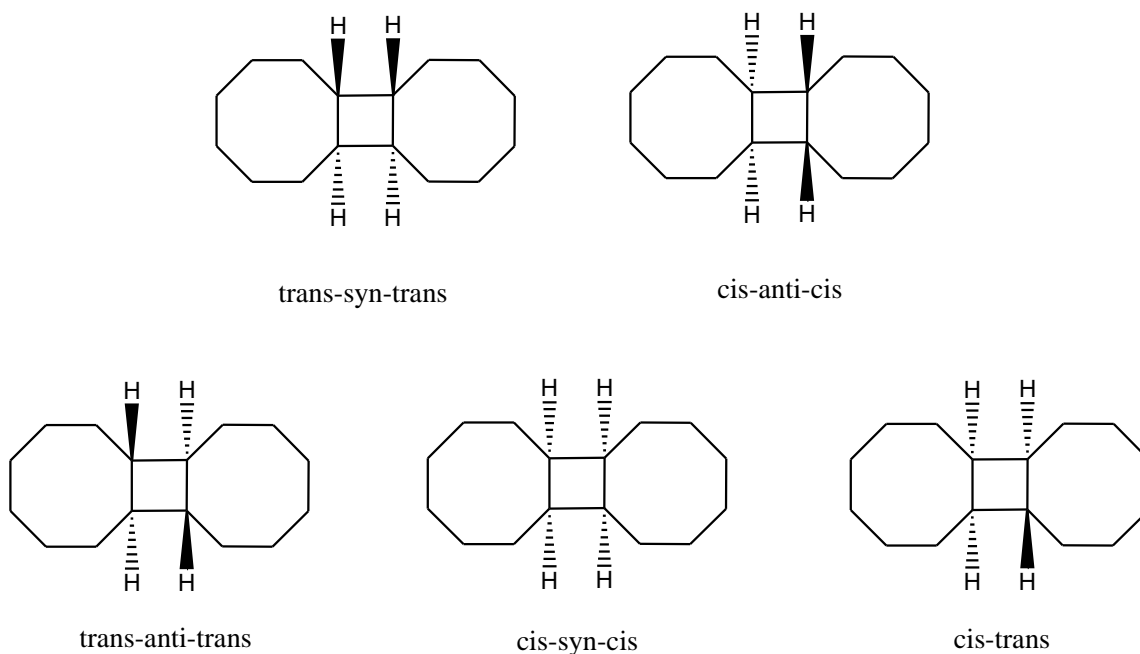
Figure 4. Plot of GC intensities for reactants and products as a function of bulk electrolysis times. Legend: circles are for reactant, *cis*-cyclooctene; solid squares are for the sum of the intensities for the four major products, which are isomers of C₁₆H₂₈.



complete in this time period stands in remarkable contrast to previous synthetic approaches to the cyclobutane of **3**, which require many days of copper-catalyzed photochemical excitation.³³

Although stereoisomeric identifications of all four principal cyclobutyl products were not possible, an attempt was made to identify the major product (A in Figure 2) by NMR spectroscopy. The product isolation procedure is given in the Experimental section. The five possible stereoisomers of **4** are shown in Figure 5. Based on ¹H, ¹³C, and 2D NMR (HMQC, HMBC, ¹H-¹H HOMOCOSY and TOCSY), the major isomer was assigned as having the *cis-anti-cis* structure.²⁰

Figure 5. Structures of the five possible stereoisomers of the cyclobutane derivative $C_{16}H_{28}$. The *cis-anti-cis* structure was identified as the principal cycloaddition product from oxidation of *cis*-cyclooctene.



II.B.2. Quantitative Product Analysis.

Under a diversity of experimental conditions, some of which will be detailed below, the composite yield of $C_{16}H_{28}$ isomers was determined to be 55-75 %, before optimization (see below), based on several different analytical methods: (i) weight of isolated oil (ii) 1H NMR integration and (iii) GC response of reactant *vs* products (Figure 4). The efficacy of (i) was based on the fact that the isolated oil had the correct elemental assay [C, 87.07 % (87.27 % calc); H, 12.80 % (12.73 % calc.)]. Regarding (ii), resonances in the aliphatic CH region (δ 0.7 – 1.8 ppm) were integrated for CD_2Cl_2 solutions of the isolated oil and compared with that of a known amount of ferrocene serving as an internal standard (details available³⁴). Methods (i) and (ii) have the shortcoming of specificity to hydrocarbons in general, rather than to **4** in particular. That was addressed by analysis (iii), in which the GC responses of the four major product peaks seen in Figure 2 were compared with that of COE in the pre-electrolysis solution. The sum of the GC intensities of the product peaks was about 60% of that measured for the starting material (see Figure 4), which we take as a lower limit³⁵ for the yield of **4** in the reaction. Whereas any of methods used for product analysis has limitations owing, in part, to the chemical makeup of the

product, taken together they give a consistent picture of a relatively pure mixture of C₁₆H₂₈ isomers formed in moderate to good yield from *cis*-**3**.

II.C. Effect of Supporting Electrolyte Anion.

The effect of changes in supporting electrolyte anion on the process was tested by substituting either [PF₆]⁻ or [ClO₄]⁻ for TFAB. The aminium radical **1**⁺ was used as the ET mediator. Although bulk electrolysis for 12 minutes in a 20:1 ratio of *cis*-**3**:**1** resulted in complete consumption of the olefin when carried out in CH₂Cl₂/0.1 M [NBu₄][PF₆], no cycloaddition products were formed. Rather, GC/MS showed eight product peaks with retention times between 6.5 and 7.2 min (Figure SM5), none of which had a spectrum with an M+1 = 221 value that would be consistent with a cyclobutyl product, or a 223 peak that would be consistent with a linear dimer. One product appeared to have a parent peak at 238, suggesting the presence of fluorine, but ¹⁹F NMR failed to show anything besides [PF₆]⁻. Other products had some activity at 218 or 219, which may be due to fragments of heavier masses (possibly oligomers), in keeping with the difficulty of obtaining molecular ion peaks for hydrocarbons and halogenated hydrocarbons under these analytical conditions.³⁶ Although we have not identified the COE oxidation products in the traditional [PF₆]⁻ - containing electrolyte solution, it is clear that the olefin-to-cyclobutane reaction is not favored, if it occurs at all. A similar result was obtained when [NBu₄][ClO₄] was used as the supporting electrolyte. It is likely that the increased nucleophilicities of the [PF₆]⁻ and [ClO₄]⁻ anions, compared to [B(C₆F₅)₄]⁻, result in attack on either [*cis*-**3**]⁺ or another electrophile (possibly [Cyclobut]⁺) generated in the reaction. There is now a growing number of examples of organic anodic reactions following different pathways depending on whether traditional anions or WCAs are used in the supporting electrolyte.^{8,37}

II.D. Cyclization Induced by the Chemical Oxidant **1**⁺ or in “Catalyst Free” Media.

The cyclization reaction can also be induced by means of a chemical oxidant free of electrochemical control. Thus, some conversion to **4** was observed when *cis*-**3** was treated with catalytic amounts of **1**[TFAB] in CH₂Cl₂. This approach proved to be less effective, however, than when **1**⁺ was generated *in-situ* by electrochemistry. When using only the chemical oxidant, the reaction had to be regularly “restarted” by adding more **1**⁺ and never went to completion.

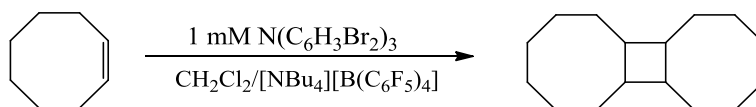
A curious result was found during electrochemical “control” experiments in which *no* ET precursor (either **1** or **2**) was added to the electrolysis solution. When a potential of 1.1 V to 1.3 V was applied to a 20 mM solution of *cis*-**3** in CH₂Cl₂/0.05 M [NBu₄][B(C₆F₅)₄], there was, as expected, no loss of *cis*-**3** over 12-20 min, this being the time period for completion of the cyclobutanation reaction when an ET catalyst was present. However, in experiments that were repeated several times,³⁸ after a long induction period of 1-2 hours at E_{appl} = 1.1 V, there was a sudden and rapid conversion of *cis*-**3** to **4**, with product workups giving yields similar to those quoted above for ET-catalyzed conversions. CV scans taken near the end of the induction period showed a reversible wave at about 1.2 V, leading us to believe that some compound formed from slow oxidation of solvent, electrolyte, or impurities eventually triggered the oxidation of *cis*-**3**. Owing to the relative electrochemical inefficiency of such a “catalyst free” reaction, no further inquiries were deemed warranted.

II.E. Optimization of *cis*-Cyclooctene Cyclobutanation

A series of experiments was carried out in which the concentration of *cis*-**3** was increased while that of the ET mediator was kept constant, for the purpose of maximizing the synthetic utility of the method while minimizing the amount of catalyst employed. As shown in Table 2, a good yield of the desired cycloadduct was obtained even when a 200:1 molar ratio of **3**:**1** was used in the electrolysis. The increase in cyclization product with increase in olefin concentration most likely arises from favoring of the radical-substrate reaction pathway at high concentrations of neutral olefin in the bulk of solution. Using the 200:1 ratio of *cis*-**3**:**1** in an electrochemical cell holding just 15 mL of solvent (entry 4 of Table 2) allowed facile preparation of 192 mg of the cyclobutane product **4** (see Experimental section for details).

The experiment employing 2,6-ditertbutylpyridine as a proton scavenger additive (entry 5) was carried out to see if there was evidence of a proton catalyzed mechanism for the olefin coupling reaction. The very slight decrease in % yield indicates that proton-driven cyclization is not important in this system.

Table 2. Isolated yields of cycloadduct **4** under different conditions.



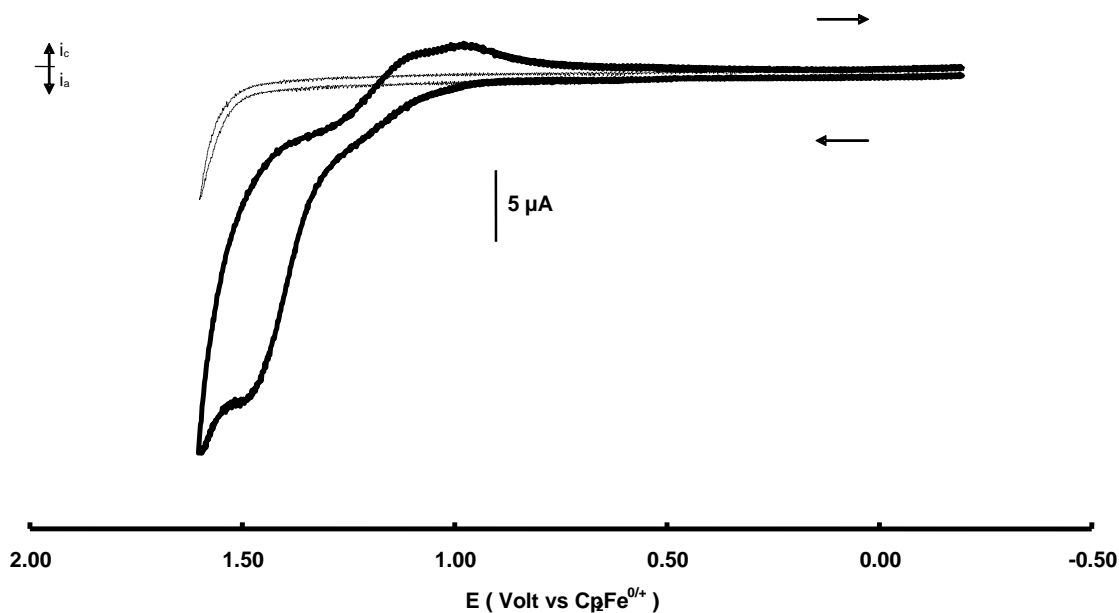
Entry	<i>Cis</i> -cyclooctene conc (mM)	Additive ^a	% Yield of cycloadduct 4
1	20	None	73
2	40	None	74
3	110	None	90
4	200	None	87
5	200	6mM 2,6-Diterbutylpyridine	66

^a All solutions contained 1 mM N(C₆H₃Br₂)₃

III. Application to *trans*-Cyclooctene, *trans*-**3**

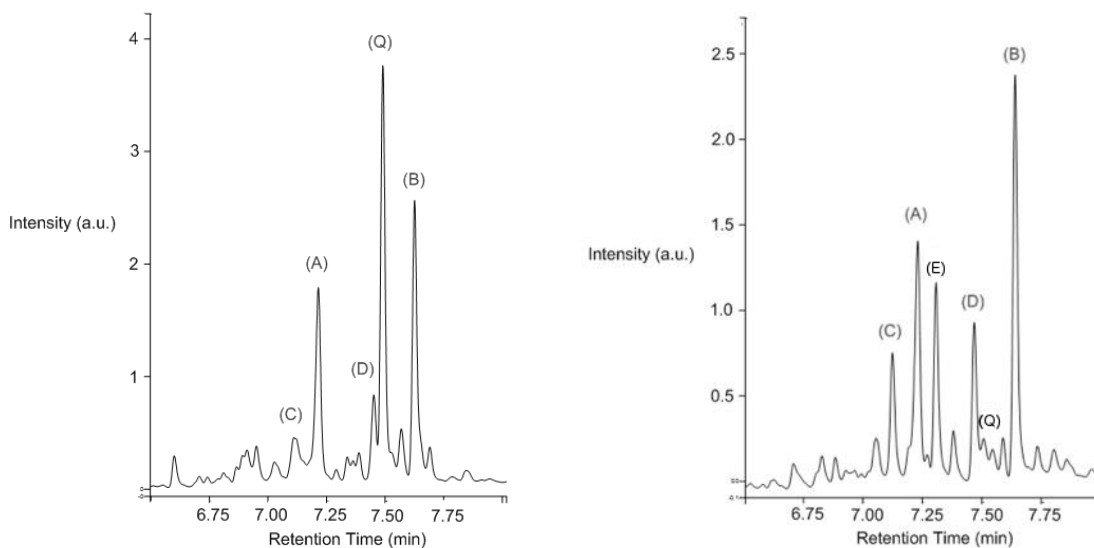
Owing to the fact that removal of an electron from *trans*-**3** is more facile by about 200 mV than from its *cis* isomer, the oxidation of *trans*-**3** may be observed direct by anodic voltammetry in CH₂Cl₂/[NBu₄][B(C₆F₅)₄]. The recorded CV scans were not highly reproducible, varying from one experiment (and even one scan) to another, despite frequent re-polishing of the electrode. The CV scan shown in Figure 6 is typical of the most common result. The oxidation of *trans*-**3** is irreversible, the wave is poorly shaped, and small product peaks are observed. The fact that the anodic peak potential ($E_{\text{pa}} = 1.46 \text{ V}$ at $v = 0.2 \text{ V s}^{-1}$) is almost 200 mV negative of the estimated $E_{1/2}$ of this system (1.65 V, Table 1) may be due to the effect of a fast follow-up reaction on the putative radical cation [*trans*-**3**]^{•+}. The direct anodic oxidation of this COE isomer was carried out by bulk electrolysis at a platinum electrode. After application of the under-potential value of 1.3 V for only *one minute*, GC/MS sampling showed complete consumption of the starting material and its conversion to several C₁₆H₂₈ isomers. Furthermore, as shown in Figure 7, when samples were extracted from the working compartment over a period of several minutes, the relative amounts of the isomers were seen to change with time. After 9 minutes, GC/MS analysis

Figure 6. Cyclic voltammogram of 5 mM solution of *trans*-cyclooctene in CH₂Cl₂/0.05 M [NBu₄][B(C₆F₅)₄]. Conditions: 2 mm GCE, ambient temperature, 0.2 V s⁻¹. Background scan (dashed line) is also shown.



gave five the expected five isomers of C₁₆H₂₈, labeled A through E in the right part of Figure 7. Four of these (A through D) were those observed in oxidation of the *cis* isomer of **3**. A detailed understanding of these isomeric changes would require specific identification of the five different isomers of **4**, which went beyond the goals of the present study. A curiosity in these experiments was the observation of an additional product, labeled Q in the left side of Figure 7, which had essentially disappeared after 9 minutes. This sample also had a significant MS *m/z* = 221 peak. However, GC peaks Q and E cannot both be assigned as isomers of the final cyclobutane product, as this would raise the number of detected C₁₆H₂₈ isomers to six. It is likely that Q is an intermediate in the process, although a candidate such as the radical cyclobutyl radical cation does not seem likely under these conditions.

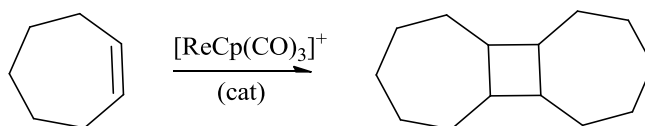
Figure 7. Gas chromatographic responses for cycloaddition products of *trans*-cyclooctene electrocatalyzed by $[\text{ReCp}(\text{CO})_3]^+$, **2**⁺. Left: result after electrolysis time of 1 minute; right: result after electrolysis time of 9 minutes.



IV. Applications to Other Cyclic Olefins

Experiments very similar to the anodic ET catalyzed reaction of *cis*-**3** were carried out on three other unactivated cyclic hydrocarbons: cycloheptene, cyclohexene, and cyclopentene. Cyclized products were observed in each case.

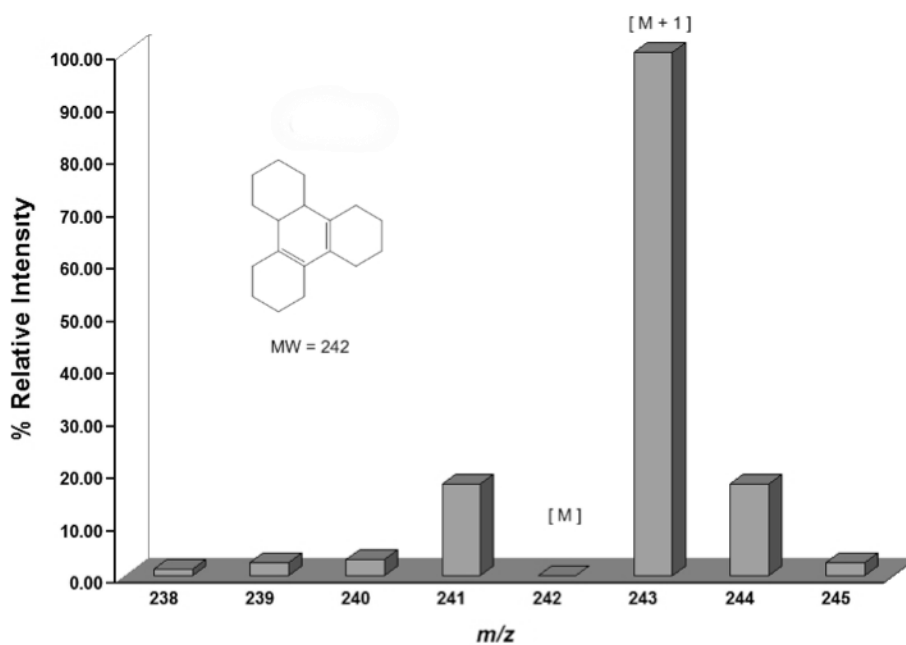
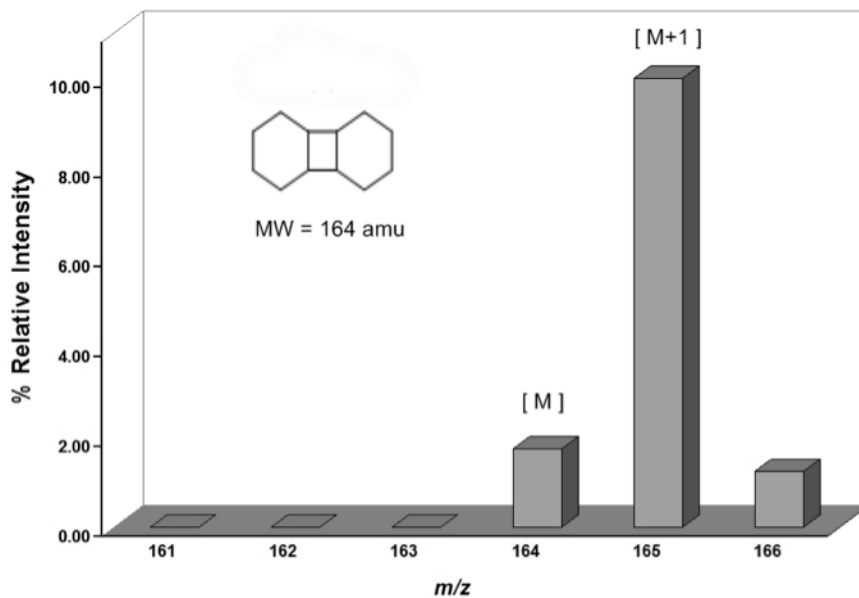
IV.1. Cycloheptene 20:1 Cycloheptene-to-Re catalyst (**2**) mixtures gave electrolysis results that were closely analogous to those observed for *cis*-**3**: cycloheptene was consumed within 11 minutes with a coulomb count of 0.2 F or less, side products were formed ($E_{\text{pc}} = -0.69$ V and -0.93 V), and the major product was the [2+2] cycloaddition product $\text{C}_{14}\text{H}_{24}$. In this case, besides



the major isomer, seven other products (including four MW = 192 isomers) were observed by GC/MS (Figure SM6). A 50% (by weight) isolated yield of $\text{C}_{14}\text{H}_{24}$ isomers was obtained.

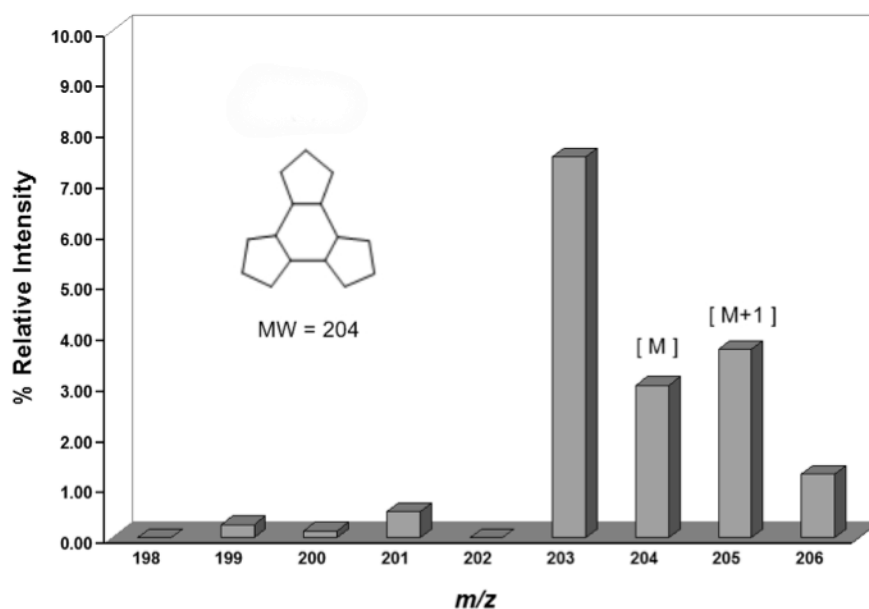
IV.2. Cyclohexene Electrolysis of cyclohexene was carried out for one hour using either **1** or **2** as precatalyst, passing 0.2 to 0.3 F and giving cathodically active side products with $E_{pc} = -0.65$ V and -0.9 . Two major and two minor products were observed in the GC/MS analysis (Figure SM7). The more rapidly separating major product (4.88 min retention time) had the dominant $M + 1$ peak expected for the [2+ 2] cycloaddition product $C_{12}H_{20}$, with the second major product (7.75 min) having its most intense MS peak at $m/e = 243$ (Figure 8). This peak is only consistent with *cyclotrimerization* of cyclohexene. Assigning the 243 feature as an $M + 1$ peak suggests that the major product is $C_{18}H_{26}$, which would require partial dehydrogenation of the intermediates along the pathway from monomer to “trimer”. While it seems clear that both di-cyclization and tri-cyclization are possible in this system, the degree of unsaturation in the tricyclized product is still in question.

Figure 8. Mass spectral responses in the parent region for the two major cycloaddition products of cyclohexene. Top: assigned to cyclodimerization derivative; bottom: assigned to cyclotrimerization product. The degree of unsaturation and the location of any C=C bonds in the cyclic trimer are not known.

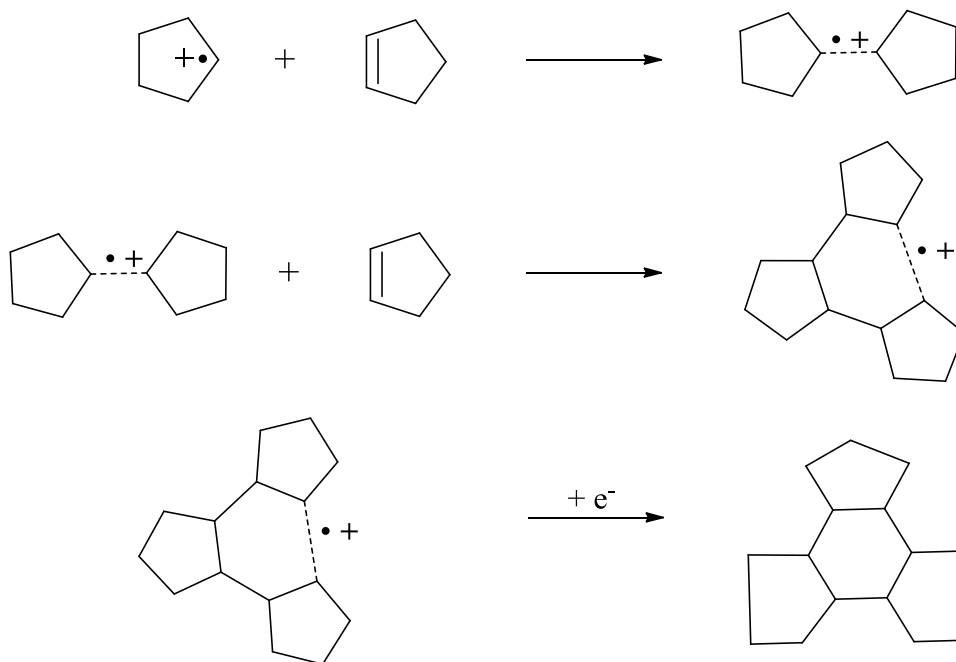


IV.3. Cyclopentene One-hour electrolyses using **2** as precatalyst passed 0.1 to 0.2 F per olefin and again resulted in a cathodically-active side product ($E_{pc} = -0.85$ V, 200 mV s^{-1} scan rate). Surprisingly, there was no evidence for formation of a cyclobutane product. Rather, a single product (Figure SM8), isolated in 75% yield (by weight), had a mass spectrum consistent with a cyclotrimer (Figure 9). We favor the saturated structure of $C_{15}H_{24}$ (MW 204) for the product, based on assignment of the $m/e = 205$ peak as $M + 1$, which would require the base peak at 203 to be of $M-1$ origin. Although the MS data are not definitive for the number of hydrogens possessed by the major product, it is clearly a $[2 + 2 + 2]$ cycloaddition product, perhaps formed according to Scheme 3.

Figure 9. Mass spectral response in the parent region for the cyclotrimerization product of cyclopentene. Assignment of $m/z = 204$ as the molecular ion peak suggests the cyclohexane trimer shown.



Scheme 3. Possible mechanism of cyclotrimerization of cyclopentene after formation of cyclopentene radical cation.

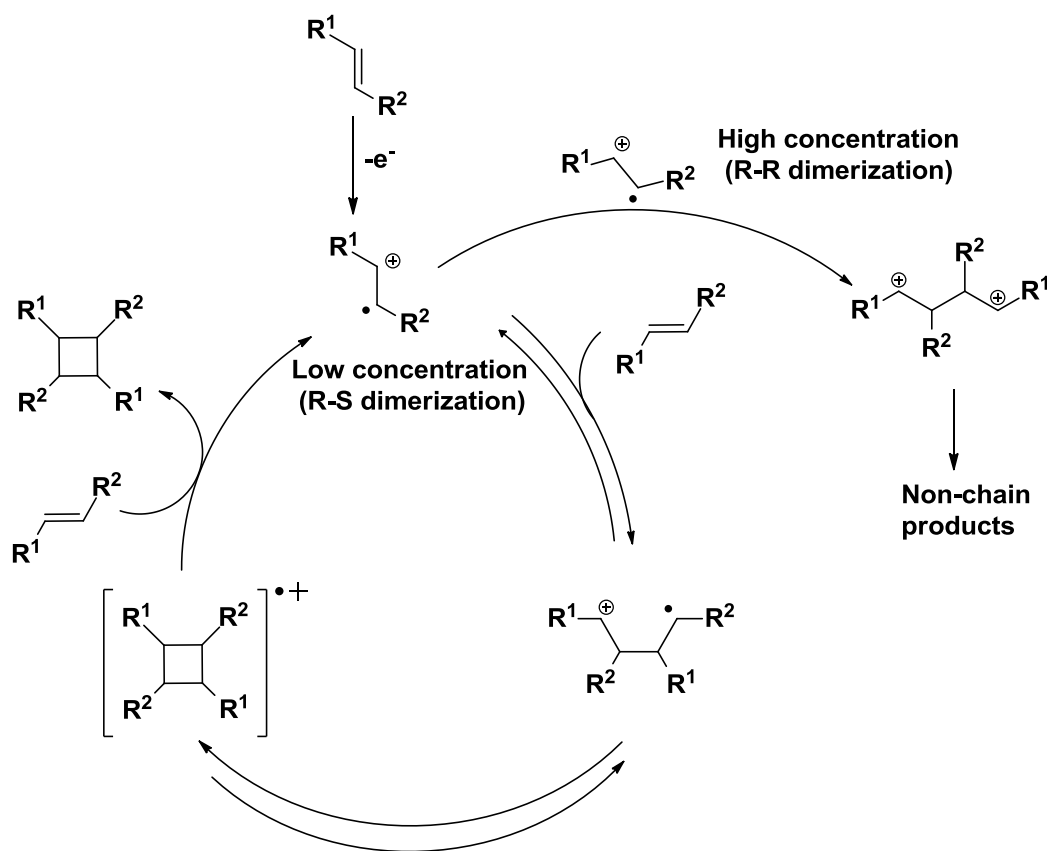


Several attempts were made to extend the cycloaddition reactions to difficult-to-oxidize functionalized olefins. These included 3-bromocyclohexene, 3-methylcyclooctene, 2-cyclohexen-1-one, 3-acetoxycyclooctene, 3-*t*-butyldimethylsilyloxycyclooctene and 1,4-cyclooctadiene monoxide. Even though, all cases, numbers of products were formed using either **1** or **2** as the ET precursor, no evidence of cyclized products was obtained. Higher coulomb counts, generally about 0.5 F per olefin, were also obtained. Although other functional groups might prove to be more supportive of the radical chain mechanism, the ones investigated to date appear to have the effect of favoring side reactions which quench the chain process.

Discussion

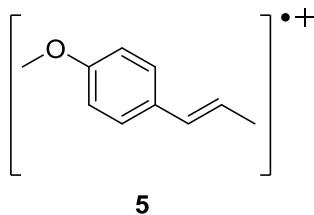
What appears to be the simplest mechanism that accounts for the observed results is shown in Scheme 4. The key issue appears to be competition between two competing dimerization

Scheme 4. Mechanism for ET-induced reactions of olefins. Reaction of the radical cation (R) with a neutral olefin substrate (R-S coupling) can initiate the “zero electron” radical chain mechanism, whereas reaction of R with another radical cation (R-R coupling) produces an unstable dimer dication. R-S coupling dominates when the concentration of the radical cation is low compared to that of the neutral olefin substrate.



pathways: either a radical-substrate (R-S) process giving a dimer radical cation, or a radical-radical (R-R) process giving a dimer dication. The R-S coupling reaction affords a relatively stable cyclized radical cation intermediate capable of oxidizing another mole of olefin and thereby propagating the chain reaction. The very reactive dimer dication produced by R-R coupling would be expected to rapidly terminate the chain process by undergoing irreversible

follow-up reactions. Generating the radical cation in the presence of a large excess of neutral olefin will favor R-S coupling. Except for the direct oxidation of *trans*-**3**, which is discussed below, this condition is easily met in all of the ET catalyzed reactions reported in this paper, owing to the fact that the $E_{1/2}$ values for catalysts **1** and **2** are so negative compared to the oxidation potentials of the olefins. The term “underpotential” is appropriate to describe reactions of this type, being carried out under conditions in which the driving force for the olefin oxidation (by either the oxidizing agent or the electrode) is weak. In fact, there is such a large potential difference between the ET agent and the present family of olefins that it is reasonable to ask why the chain reactions occur at all. In some of the earlier cycloaddition literature, a “cutoff” of no more than 500 mV was suggested for the maximum separation between the $E_{1/2}$ potentials of the ET catalyst and the olefin (or, in the case of Diels-Alder reactions, the diolefin).¹⁶⁻¹⁸ In the current case, based on the estimated $E_{1/2}$ potentials in Table 1, the potential differences are at least 660 mV, suggesting an equilibrium constant for the initiation step (Eq 1) of 10^{-11} or less. If the olefin radical cation were kinetically stable, an equilibrium concentration of only about 10^{-5} mM [Olefin]^{•+} would be present at a chemical or electrochemical driving force of 1.3 V. However, the very fast dimerization of the olefin radical cation (Eq 2) shifts the equilibrium and speeds the chain reaction. The rates of R-S and R-R coupling reactions can be very fast.³⁹ For example, Demaille and Bard used scanning electrochemical microscopy to determine the radical-radical dimerization rate of the *trans*-anethole radical cation (**5**) to be $4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$.⁹ We can think of no reason to expect the R-S coupling reactions of cyclic olefins to proceed at dramatically lower rates. The cyclobutyl cation radical produced in this reaction (Eq 2) would then react with more



starting olefin or Red_{CAT}, either in the reaction layer (*ca* 10-100 μm from the electrode) or in the bulk of solution, to produce the neutral cyclized product.

In light of this interpretation, it is interesting to consider the fact that *trans*-**3** undergoes a rapid chain cyclization even when it is *directly oxidized* by the electrode. In this case, higher

fractions of the radical cation [*trans*-**3**]^{•+} are formed in the reaction layer. However, the chain reaction can still proceed owing to the fact that the E_{1/2} value of *trans*-**3** (estimated as being 1.65 V) is actually quite a bit positive of the E_{appl} value of 1.45 V. The anodic peak potential has been brought in to less positive potentials owing to the rapid follow-up reaction of the radical cation which, in fact, propagates the chain reaction.⁴⁰

Thus, at least in the case of *cis*-**3** vs *trans*-**3**, whether the olefin oxidation is initiated by a homogeneous ET catalyst or by an electrode, the cyclobutanation reaction proceeds rapidly and in modest to good yield.

Summary

The conversion of unactivated cyclic olefins to cyclobutane derivatives has been difficult to carry out by previously described synthetic methods, the best of which employed Cu(I) catalysts and photochemical excitation for a week or more on the neat liquids.³³ In dramatic contrast, solutions of these olefins in CH₂Cl₂/[NBu₄][B(C₆F₅)₄] may be converted to the desired cyclized products in 10 minutes or less when treated with a catalytic amount of a one-electron transfer agent sufficient to oxidize at least a small amount of the olefin to its radical cation. Two ET agents, generated *in situ*, with E_{1/2} potentials of 1.15 ± 0.01 V vs FcH, namely [N(2,4-C₆H₃Br₂)⁺ (**1**⁺) and [ReCp(CO)₃]⁺ (**2**⁺), initiated efficient radical chain reactions of C₈ to C₅ cyclic olefins, even though the oxidative E_{1/2} potentials of the olefins are estimated as 1.85 V to 2.06 V vs FcH. The ET reaction, estimated to be endergonic by at least 15 kcal/mol, triggers a chain process owing to rapid reaction of the olefin radical cation with unreacted neutral olefin. An intriguing aspect of these reactions is that they are efficient when carried out in the presence of the weakly coordinating anion [B(C₆F₅)₄]⁻, but that cyclized products are not formed when the supporting electrolyte anion is one of the traditional electrolyte anions ([PF₆]⁻ and [ClO₄]⁻ were tested). Whereas the specific role played by [PF₆]⁻ or [ClO₄]⁻ in suppressing the chain reaction is not known, it is reasonable to assume that they react nucleophilically with a radical cation, either [Olefin]^{•+} or [Cyclobutyl]^{•+}, thereby terminating the chain reaction.

The [2 + 2] cyclizations of cyclooctenes produce mixtures of four or five isomers, irrespective of whether one starts with the *cis* or *trans* isomer of cyclooctene. Although the structures of the

different isomers have, apart from one case, not been determined, a relatively simple method for isolation and characterization of the isomeric mixtures is now available. A [2 + 2] cyclization reaction to give a cyclobutane derivative is also seen as the major ET-induced reaction of cycloheptene. Cyclohexene gives both the [2 + 2] cyclic dimer and a [2 + 2 + 2] cyclic trimer of unspecified unsaturation. Cyclopentene gives a single [2 + 2 + 2] cyclic trimer. Efforts to extend the cycloaddition reactions to cyclic olefins having functional groups were unsuccessful.

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Supporting Information Available. 12 pages. Preparation of *trans*-cyclooctene and eight figures showing relevant cyclic voltammograms, gas chromatographic responses, and chemical ionization mass spectra of products in parent *m/z* region.

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30. The coulomb counts subtract the one F per ET catalyst that is passed after the olefin is exhausted and the catalyst resides in its oxidized state.
31. If one assumes two-electron cathodic waves and a diffusion coefficient similar to that of ferrocene, one estimates 3-5% yields for these electroactive side products.
32. Syringe-extracted electrolysis samples were diluted in pure dichloromethane to give appropriate concentrations for analysis. Control experiments (e.g., methanol quenching) showed that the concentrations of products and reactants did not change with time after transfer from the electrolysis solution.
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“equal per carbon” response relationship reported for FI-analyzed hydrocarbons (Tong, H.Y.; Karasek, F.W. *Anal. Chem.* **1984**, *56*, 2124; Dietz, W.A. *J. Gas Chromatogr.* **1967**, *5*, 68; Perkins, G.; Laramy, R.E.; Lively, L.D. *Anal. Chem.* **1963**, *35*, 360), we assumed that the GC responses for the C₁₆ product peaks were double that of the C₈ reactant peak. If the FI adjustment term is less than a factor of two, the actual yield would be larger than 60% based on this method.

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