although extrapolations are clearly possible to other solvents.[47] Furthermore, the kinetic data apply only to the liquid–liquid system examined by Starks.[29] It has been shown that similarities exist for solid–liquid and liquid–liquid systems when a quaternary salt is used as the catalyst,[48] but it is not clear that our own work bears extension in accord with these observations.

Summary

It is shown that homogeneous sodium cation binding (K_s in methanol) is linearly proportional to the number of binding sites available in the PEG cation binder. It is further apparent that these substances can catalyze liquid–liquid phase-transfer reactions as well as aliphatic crown ethers can. From the kinetics and other comparisons, it seems that each oligoethylene glycol chain complexes and transports one cation in the phase-transfer process. Thus, increasing the number of PEG molecules without increasing the number of donor atoms increases the rate of the phase-transfer catalytic process.

Experimental Section

Binding Constants. The poly(ethylene glycols) and poly(ethylene glycol) methyl ethers of average molecular weight 300–14 000 were obtained from the Aldrich Chemical Co. The binding constants for these ligands with sodium ion (chloride counterion) were determined in absolute methanol solution at 25.0 ± 0.1 °C. The measurements were made with an Orion Model 701A Ionalyzer millivolt meter by using a Corning 476210 sodium ion electrode and an Ag/AgCl reference electrode. The apparatus was contained in a dry box, and the solution temperature was maintained by using di-*n*-butyl phthalate as a heat-transfer solvent.

Experiments consisted of measuring the emf of the cell for the solutions of sodium ions with and without the ligand. The typical concentration of sodium (NaCl) was approximately 2 mM, and that of the ligands was 3–5 mM. Binding constants were calculated by the method of Frensdorff.[23]

Since the binding constants varied linearly with the average molecular weight of the poly(ethylene glycol), a series of measurements were done in which complexation of sodium was studied with solutions containing a constant weight (0.5 g in 50 mL) of all the poly(ethylene glycols) in the molecular weight range 300–14 000. The emf readings showed that the extent of sodium ion complexation in all these solutions was nearly the same, with a slight peak at the poly(ethylene glycol) with an average molecular weight of 1000.

Kinetics of Phase-Transfer Processes. The reactions were conducted as described by Starks[29] except that one-tenth the scale was employed. A 100-mL round-bottomed flask was charged with *n*-octyl chloride (0.067 mol, 10 g), *n*-decane (2.5 mL), H_2O (2.5 mL), and the particular catalyst (1.5 mol %, 0.001 mol). This mixture was heated to ~50 °C and stirred magnetically at maximum speed. Sodium cyanide (0.204 mol, 10 g) was then added, and this mixture was quickly heated to the reflux temperature (~105 °C). Aliquots were removed from the reaction flask at various time intervals beginning with $t = 0$. The aliquots were diluted with an equal volume of H_2O. The samples were analyzed by injecting 1 μL of the organic layer into a Varian Associates Model 920 analytical gas chromatograph equipped with a thermal conductivity detector and a 5 ft × 0.25 in. 1.5% OV-101 on a 100–120-mesh NAW Chromosorb G column at a flow rate of ca. 60 mL/min of He with a column temperature of 70 °C. Chromatogram peak heights were then measured and compared relative to internal standard *n*-decane. The percent unreacted octyl chloride was calculated utilizing eq 2 and 3.

$$\frac{(\text{octyl chloride})_{t=0}(n\text{-decane})_{t=t}}{(n\text{-decane})_{t=0}} = (\text{octyl chloride})_{\text{initial}} \quad (2)$$

$$\frac{(\text{octyl chloride})_{t=t_{\text{obsd}}}}{(\text{octyl chloride})_{\text{initial}}} \times 100 = \%\ \text{unreacted octyl chloride} \quad (3)$$

Rate constants were obtained by averaging the percent halide remaining at each time interval, determining its natural logarithm, and then determining the slope (by least-squares analysis) of ln % vs. time. The pseudo-first-order rate constants are given in reciprocal seconds and are the average of at least three runs in each case.

Chemicals and Reagents. All solvents were of the highest grade commercially available and were used without further purification. Polyethylene glycols, monomethyl ethers, and crowns were purchased from the Aldrich Chemical Co. 21-Crown-7 and 24-crown-8 were prepared by a modification of our previously reported procedure,[49] and all crowns were distilled prior to use.

Acknowledgment. We warmly thank the NIH for grants (GM-29150 and GM-29706) which supported this work.

Registry No. 1, 25322-68-3; 2, 9004-74-4; 3, 24991-55-7; 4 (*n* = 1), 33100-27-5; 4 (*n* = 2), 17455-13-9; 4 (*n* = 3), 33089-36-0; 4 (*n* = 4), 33089-37-1; sodium cation, 17341-25-2; 1-chlorooctane, 111-85-3.

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Formal Synthesis of Pentaprismane

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A new synthetic route to pentaprismane (1) has been developed. The key intermediate, *endo*-carbomethoxypentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-7-one (**5a**), was prepared in six steps from 4,4-dimethoxycyclohexa-2,5-dien-1-one (**10b**) in an overall yield of 23%. Photochemical closure of the Diels–Alder adduct **8b**, obtained from cyclobutadiene and **10b**, gave 10,10-dimethoxypentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-7-one (**7b**). Methylenation of **7b** followed by hydroboration and oxidation afforded 9-hydroxy-10-oxahexacyclo[6.4.0.0^{2,7}.0^{3,6}.0^{4,12}.0^{5,9}]dodecan-11-one (**18a**), which was esterified to give **5a**.

The recent synthesis of pentaprismane (1)[1,2] follows more than a decade of research by numerous chemists employing diverse strategies to obtain this elusive hydrocarbon.[3] The attraction lies not only in the aesthetic

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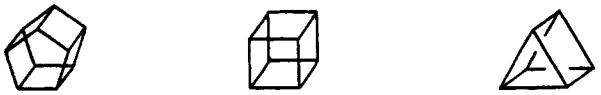
simplicity of the polycycle but also in its high strain energy which has been estimated as 135.7 kcal/mol.[4] Studies of the more strained analogues of pentaprismane, tetraprismane (cubane, **2**),[5,6] and triprismane (prismane, **3**)[7,8] have



1 **2** **3**

revealed several interesting skeletal rearrangements.[9] Thus, a prime motive for the preparation of pentaprismane is the study of its reactivity relative to the other members of its class.

Our work toward the pentaprismane skeleton has been directed along two general routes: the transannular reductive coupling of the *seco*-pentaprismanedione **4**[10] and

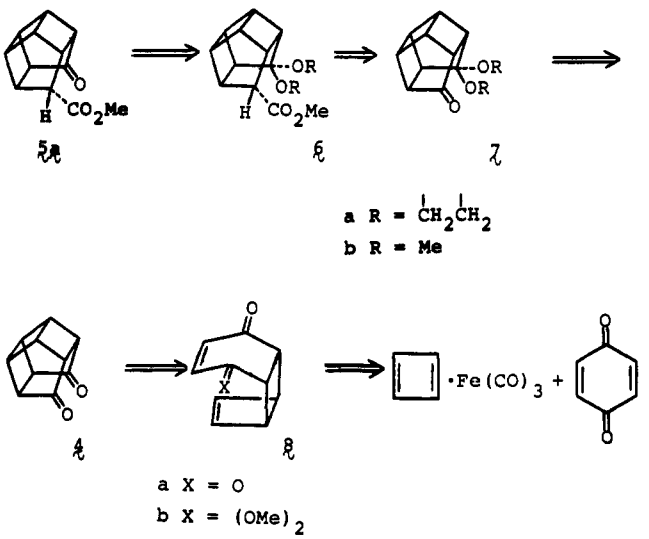
4 **5**

a R = OMe
b R = H

the preparation of a dicarbonyl compound **5**[11] suitable for an acyloin condensation and a subsequent Favorskii ring contraction. The ineffectiveness of the former strategy was exposed throughout many trials under diverse reaction conditions. The inability to obtain the pentaprismane skeleton by such couplings was attributed to the distance between the coupling centers.[10] The latter approach was developed in an effort to surmount this difficulty, by bringing the coupling centers closer together. Indeed, this strategy was employed by Eaton[2] in his recent reported synthesis of **1**. Eaton prepared pentaprismane from the tricyclic Diels–Alder adduct of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopenta-1,3-diene and benzoquinone in 17 steps via the key intermediate, ketoester **5a**. In the present work, an alternate synthesis of **5a** is described which offers a new variant for the preparation of pentaprismane compounds.

Retrosynthetically, **5a** can arise from the hydrolysis of the ketal **6**, whereas **6** is derived from a one-carbon homologation of the ketone **7a**. The ketone **7a** should be

Scheme I



5a **6** **7**

a R = CH_2CH_2
b R = Me

4 **8**

a X = O
b X = $(OMe)_2$

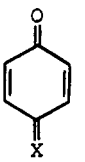
readily obtained from the dione **4**. Pettit and co-workers[3c] have prepared **4** by the photochemical closure of *endo*-tricyclo[4.4.0.$0^{2,5}$]deca-3,8-diene-7,10-dione (**8a**), obtained as a Diels–Alder adduct by the oxidative liberation of cyclobutadiene from its iron complex in the presence of benzoquinone (see Scheme I).

Initial attempts to prepare **7a** gave inconsistent results. The diene **8a** was found to be unstable and light sensitive, and the dione **4** had a propensity for hydration. For minimization of these difficulties, the three-reaction sequence from benzoquinone to **7a** was conducted with purification only after ketalization. Yields for this transformation ranged from 5% to 10%, and often mixtures of **7a** and the diketal **9** were obtained. Although **9** could be

9

converted to **7a** in good yield, this route was abandoned, and the search for a more dependable sequence began.

A monoprotected benzoquinone was employed in the Diels–Alder reaction with cyclobutadiene to avoid the problems associated with the diketone **4a**. Reaction of 4-cyano-4-(trimethylsiloxy)cyclohexa-2,5-dien-1-one (**10a**)[12]



10

a X = $OSiMe_3$,CN
b X = $(OMe)_2$
c X = NSO_2Ph

or *N*-phenylsulfonyl-*p*-benzoquinone monoimine (**10c**)[13] with cyclobutadiene afforded only polymeric products and tars, regardless of the solvent or the oxidant of the cy-

(1) Hexacyclo[5.3.0.$0^{2,6}$.$0^{3,10}$.$0^{4,9}$.$0^{5,8}$]decane.
(2) Eaton, P. E.; Or, Y. S.; Branca, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 2134.
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(4) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.
(5) Pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane.
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(7) Tetracyclo[2.2.0.$0^{2,6}$.$0^{3,5}$]hexane.
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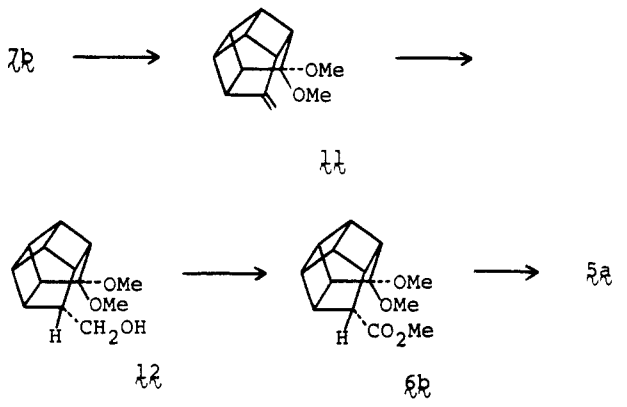
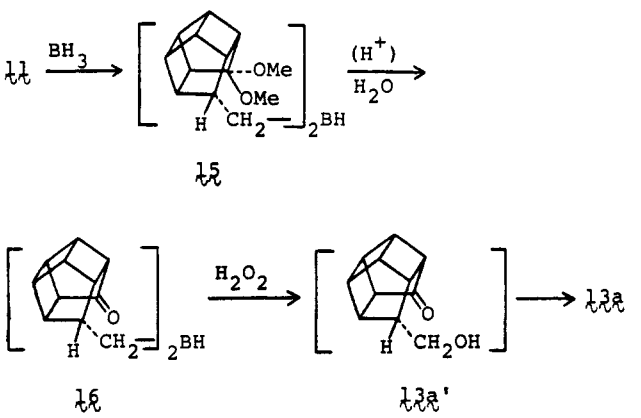
(13) Adams, R.; Edwards, J. D., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 2605.

Scheme II



Scheme III

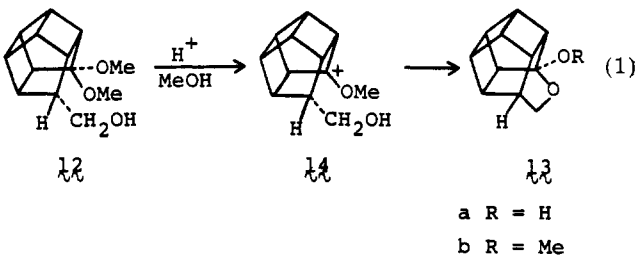


clobutadiene complex employed.[14] The desired adduct **8b** was obtained when the cycloaddition was carried out in a nonaqueous, basic medium with 4,4-dimethoxycyclohexadienone (**10b**)[15] as the dienophile.

Established procedures for obtaining cyclobutadiene adducts under basic conditions require the use of pyridine as the solvent and lead tetraacetate as the oxidizing agent, with a cyclobutadiene complex/dieneophile molar ratio of 2.0.[16] Small-scale preparations under these conditions posed no great problems. However, due to the sensitivity of **8a** to hydrolysis, an aqueous workup could not be used. This caused large-scale preparations, requiring the removal of large volumes of pyridine, to be quite tedious. It was found that reduction of the pyridine/lead tetraacetate molar ratio to 1.5 and substitution of benzene for the remaining solvent was quite effective for this transformation.[17] Although this necessitated an increase in the cyclobutadiene complex/dienophile molar ratio from 2.0 to 2.75 to ensure complete consumption of the dienophile, it was accompanied by an increase in yield of cycloadduct **8b** from 62% to 92%. Photochemical closure of **8b** proceeded smmoothly to give the polycyclic ketal ketone **7b** in 45–65% yield.

The projected transformation of **7b** to the keto ester **5a** is illustrated in Scheme II. Wittig olefination of **7b** to give the unsaturated ketal **11**, followed by hydroboration, should afford the hydroxymethyl compound **12**. The endo stereochemistry, essential for the eventual dicarbonyl coupling, is fixed by the delivery of hydrogen by borane to the more substituted carbon of the olefin from its sterically accessible exo face. The endo face of olefin **11** is shielded from attack by the carbon framework and the ketal functionality. Oxidation and esterification of **12** would give the ester **6b** which should be easily converted to **5a** upon hydrolysis.

Treatment of **7b** with 2 equiv of methylenetriphenylphosphine, forming the ylide in benzene with sodium *tert*-amylate,[18] gave **11** in 85% yield. Allowing **7b** to react with an ether solution of the ylide, generated by *n*-butyllithium,[19] or with a dimethyl sulfoxide solution of the ylide, generated by sodium dimyslate,[20] failed to produce any characterizable compounds. Hydroboration[21] of **11** usually afforded the desired alcohol **12** as the major product in 80–90% yield, but always with varying amounts of a byproduct. In one trial, this "byproduct" was the sole product and was identified as the hemiketal **13a**, the formal hydrolysis product of **12**. The hemiketal **13a** does not arise from simple acid hydrolysis of **12** since this process has been shown to give the methyl ketal **13b**. The formation of **13b** from hydrolysis of **12** is attributed not only to an entropic preference of intramolecular attack over intermolecular attack of the methoxy-stabilized carbonium ion **14** (see eq 1) but also to the relief of considerable steric



(1)

a R = H

b R = Me

strain. The change in enthalpy for the transformation of **12** to **13b** and methanol has been estimated by molecular mechanics[22] as −0.49 kcal/mol, whereas the change in strain energy for this system is −2.90 kcal/mol.

Thus, **13a** must result from the hydrolysis of the intermediate **15** prior to peroxide oxidation (see Scheme III). This is feasible due to the absence of an internal nucleophile, as the nascent hydroxyl functionality is masked as an alkylborane. Hydrolysis of **15** proceeds to give the keto borane **16**. Oxidation of **16** yields the transient keto alcohol **13a′** which tautomerizes to its more stable hemiketal form **13a**.[23]

The acid promoting this deketalization is suspected to be boric acid, resulting from the quenching of borane with water. Control experiments, however, pointed to a more complex phenomena. It was expected that longer time periods between the aqueous quench and the basic peroxide oxidation would lead to a greater predominance of **13a** in the product mixture. This was not observed, and the percentage of **13a** in the product mixture has yet to be correlated with experimental conditions. But, addition

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(17) House, H. O. "Modern Synthetic Reactions", 2nd ed., The Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1942; pp 363–364. The elimination of pyridine from the reaction mixture was not a feasible alternative since it is known to enhance the oxidative power of lead tetraacetate. This is thought to be due to the formation of a lead–pyridine bond which facilitates the loss of an acetate ion, thus decreasing the electron density around the lead atom.
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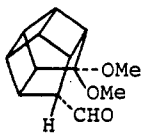
(23) The existence of an equilibrium between **13a** and **13a′** cannot be detected by ^{1}H NMR, IR, or ^{13}C NMR spectroscopy.

of dilute mineral acid after the aqueous borane quench, followed by neutralization and the normal oxidation procedure, did give **13a** as the exclusive product in 76% yield.

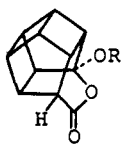
All attempts to oxidize the alcohol **12** under acidic conditions (i.e., Jones oxidation,[24] PCC,[25] and a phase-transfer method using chromic acid[26]) led either to the isolation of **13b** or to a diverse array of products. The isolation of **13b** came as little surprise considering the acid lability of **12**. Examination of the other products by ^1H NMR revealed that the carbon framework had been degraded, as signals corresponding to aliphatic protons or protons attached to unstrained carbon atoms were present. The Collins oxidation[27] of **12** gave the corresponding aldehyde **17** in good yield. Unfortunately, **17** resisted oxi-



17

dation or decomposed when treated with basic silver oxide,[28] silver oxide in THF,[29] or purple benzene.[30] It is probable that the oxidation of **17** is sluggish due to steric congestion about the carbonyl center. This could allow degradative oxidations to become competitive, given a sufficiently strong oxidant. Attempted hydrolysis of **17** to the keto aldehyde **5b** or its hemiketal led only to bad mixtures by TLC analysis.

At this point, attention was directed to the oxidation of the hemiketal **13a**. Specifically, the possibility of oxidizing **13a** to the hydroxy lactone **18a** with ruthenium tetraoxide

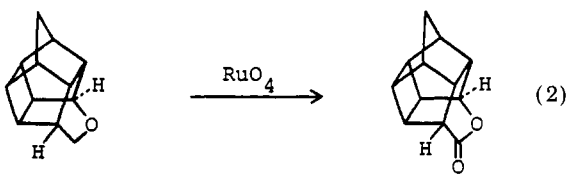


18

a R = H

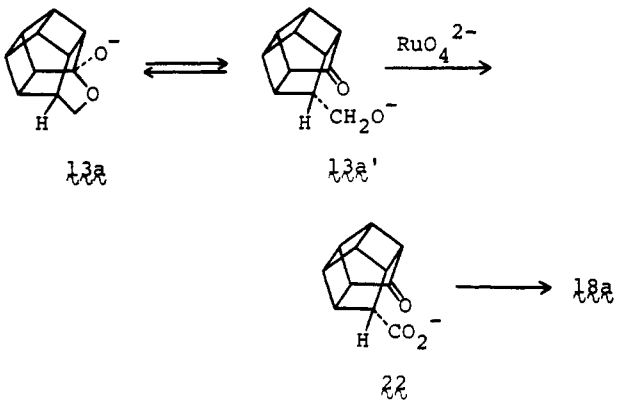
b R = Me

was explored. Ruthenium tetraoxide is known to be a powerful oxidant,[31] capable of converting ethers to lactones. In fact, in this laboratory, the oxidation of the polycyclic ether **19** to its lactone **20** has been accomplished in 80% yield by utilizing this oxidant (see eq 2). The



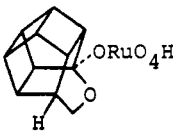
19 **20** (2)

Scheme IV



13a **13a'** **18a** **22**

reaction of **13a** in a two-phase system of carbon tetrachloride and aqueous sodium metaperiodate with a catalytic amount of ruthenium dioxide[31c] failed to give **18a**. This unreactivity was attributed to the formation of the ruthenate ester **21**. Since **21** is a tertiary ruthenate ester,



21

there is no pathway for the reductive elimination of a ruthenium species, thus effectively blocking this catalytic oxidation. Under identical reaction conditions, the methoxy lactone **18b** was obtained by oxidation of **13b** in 85% yield.

The oxidation of **13a** was achieved in 80% yield by the addition of 4 equiv of potassium hydroxide to the reaction mixture. The function of the base is to establish an equilibrium between the anion of **13a** and the anion of its open form, the alkoxy ketone **13a'** (see Scheme IV). The primary alkoxide **13a'** is then oxidized to the carboxylate **22** which upon acidification yields **18a**. Under these conditions, the active oxidant is ruthenate ion (RuO_4^{2-}), which is formed by the two-electron reduction of ruthenium tetraoxide by hydroxide ion.[32] Although ruthenate ion is less reactive than ruthenium tetraoxide, it has proven very useful in the oxidation of alcohols in basic media.[32] The oxidation of **13a** to **18a** can also be carried out stochiometrically in aqueous sodium ruthenate.

The keto ester **5a** was easily obtained in 61% yield by treatment of **18a** with potassium fluoride and methyl iodide in DMF.[33] Eaton[2] has also accomplished this conversion using diazomethane. The overall yield of **5a** based on 4,4-dimethoxycyclohexadienone (**10b**) is 23%.

The true versatility of this synthetic route lies in the easy access of substituted pentaprismanes, which may be useful in reactivity studies. By modification of the monoprotected benzoquinone derivatives used in the cycloaddition with cyclobutadiene, various 3-, 5-, 8-, or 10-multisubstituted pentaprismanes can be obtained. Furthermore, by synthesis of (cyclobutadiene)iron tricacarbonyl derivatives, substituents can also be placed at the 1-, 2-, 6-, and 7-positions.

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Experimental Section

General Methods. Solvents were dried and/or distilled under a nitrogen atmosphere prior to use when this was deemed necessary: from sodium–benzophenone ketyl for ethyl ether and tetrahydrofuran (THF); from CaH_2 for benzene; with 3A molecular sieves for *N,N*-dimethylformamide; from barium oxide for pyridine. Reagents were purified by standard procedures when appropriate.[34]

Preparative thin-layer chromatography was performed on 1- or 2-mm thick, 12-cm diameter, circular silica gel plates, which were rotated by using a Harrison Research Model 7824 Chromatotron. Most reactions were followed by analytical thin-layer chromatography with precoated Analtech Uniplates (0.25 μm thick). Compounds were visualized by aqueous sulfuric acid spray, ethanolic phosphomolybdic acid spray or iodine vapor. Column chromatography was done by using 70–230 mesh silica gel. Medium-pressure liquid chromatography (MPLC) was done by using an apparatus constructed of Ace or Altex columns packed with Whatman LPS-1 (13–24 μm) silica gel, a FMI lab pump and pulse dampener, and a Waters differential refractometer.

Melting points were determined on a Büchi melting point apparatus and are uncorrected.

^1H NMR were recorded on a Varian T-60 (60 MHz), a Varian EM-390 (90 MHz), a UCB-180 (180 MHz, FT), or a UCB-250 (250 MHz, FT) spectrometer. ^{13}C NMR were recorded on a Nicolet TT-23 (25.14 MHz) or a UCB-250 (63 MHz) spectrometer. Chemical shifts are reported in units of δ from internal tetramethylsilane. ^1H NMR data are tabulated in the following order: multiplicity (s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet), number of protons, coupling constants in hertz. IR spectra were recorded on a Perkin-Elmer Model 281 or Model 710A spectrometer. Mass spectral data were collected on an AEI MS-12 (low resolution) or a Du Pont CEC 21-110B (high resolution) instrument. Elemental analyses were performed by the Microanalytical Laboratory operated by the College of Chemistry, University of California, Berkeley.

10,10-Dimethoxy-*endo*-tricyclo[4.4.0.0^{2,5}]deca-4,8-dien-7-one (8b). To a mechanically stirred solution of 24.2 g (25 mL, 0.2 mol) of pyridine in benzene (115 mL) under a nitrogen atmosphere was added 90.7 g (0.2 mol) of lead tetraacetate. The reaction mixture, dark orange from the formation of the lead tetraacetate–pyridine complex, was allowed to stir at room temperature for 0.5 h. A solution of 3.1 g (20 mmol) of 4,4-dimethoxycyclohexa-2,5-dienone (**10b**) in benzene (10 mL) was added to the reaction mixture, followed by the dropwise addition, during 3.5 h, of a solution of 10.52 g (55 mmol) of tricarbonyl(η^4-1,3-cyclobutadiene)iron[35] in benzene (60 mL), and the reaction mixture was allowed to stir at room temperature until carbon monoxide evolution had ceased (~2 h). The mixture was filtered through a bed of activity I neutral alumina and concentrated to give an orange oil. The oil was purified by medium-pressure liquid chromatography (2:1 hexane/ether) to afford 3.76 g (18 mmol, 92%) of a yellow oil which solidified upon refrigeration. This material was sufficiently pure to be utilized in the subsequent irradiation. The analytically pure, white, crystalline solid was obtained upon trituration with hexane: mp 63.0–63.5 °C; IR ($CHCl_3$) 3045, 1715, 1675, 1365, 1215, 1135, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.07 (s, 3), 3.13 (br m, 2), 3.17 (s, 3), 3.40 (br m, 2), 5.73 (m, 1), 5.80 (br dd, 1, J = 11.0, 1.5 Hz), 5.90 (m, 1), 6.36 (br dd, 1, J = 11.0, 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 37.7, 41.5, 44.1, 45.4, 48.2, 48.9, 95.4, 134.4, 137.4, 139.2, 147.5, 198.7. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.70; H, 6.73.

10,10-Dimethoxypentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-7-one (7b). A solution of 1.24 g (6.0 mmol) of **8b** in ether (650 mL) was degassed with nitrogen for 15 min and then irradiated with a 450-W medium-pressure Hanovia lamp through a uranium filter for 2.0 h. The solution was concentrated to give a light yellow oil. The oil was purified by medium-pressure liquid chromatography (1:1 ether/hexane) to afford 0.65 g (3.2 mmol, 53%) of a white solid. The material was recrystallized from ether to give an analytical sample: mp 112.5–114.0 °C; IR ($CHCl_3$) 3000, 1735, 1325, 1145, 1105, 1060, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.83 (m, 2), 3.07 (s, 3), 3.18 (s, 3), 3.30 (m, 6); ^{13}C NMR ($CDCl_3$) δ 35.8 (2), 41.3 (2), 43.6 (2), 45.3 (2), 49.2, 52.0, 110.7, 217.6. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.83; H, 6.76.

10,10-Dimethoxy-7-methylidenepentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (11). To a stirred suspension of 1.82 g (5.1 mmol) of methyltriphenylphosphonium bromide in benzene (20 mL) under a nitrogen atmosphere was added 3.6 mL of a 1.40 M solution of sodium *tert*-amylate in toluene (5.1 mmol). The resulting bright yellow solution was allowed to stir at room temperature for 10 min, and 0.60 g (2.9 mmol) of **7b** was added. The reaction mixture was heated under reflux for 10 h. The reaction mixture was diluted with water (15 mL) and extracted with ether (2 × 25 mL). The combined ethereal extracts were washed with saturated sodium chloride solution (20 mL), dried ($MgSO_4$), and concentrated to give a viscous tan oil. The oil was chromatographed on 50 g of silica gel (1:1 ether/hexane) to give 0.51 g (2.5 mmol, 85%) of a clear oil: IR (neat) 2980, 2840, 1665, 1320, 1140, 1105, 1055, 1015, 885 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.07 (s, 3), 3.13 (m, 8), 3.17 (s, 3), 4.66 (s, 2); ^{13}C NMR ($CDCl_3$) δ 39.2 (2), 40.9 (2), 43.7 (2), 44.1 (2), 48.0, 51.5, 102.3, 112.3, 156.1. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.26; H, 7.87.

9-Hydroxy-10-oxahexacyclo[6.4.0.0^{2,7}.0^{3,6}.0^{4,12}.0^{5,9}]dodecane (13a). To a stirred solution of 0.26 g (1.3 mmol) of **11** in THF (5 mL) at 0 °C under a nitrogen atmosphere was added, dropwise via syringe during 5 min, 1.3 mL of a 1 M solution of borane in THF (1.3 mmol). The reaction mixture was allowed to warm to room temperature and stir for 0.5 h. The excess hydride was destroyed by the addition of water (0.5 mL). After hydrogen evolution had ceased, 0.4 mL of a 3 M solution of sulfuric acid (1.2 mmol) was added, and stirring was continued for 0.5 h. At this time, 0.9 mL of a 3 M solution of sodium hydroxide was added to the mixture followed by the dropwise addition, during 5 min, of 0.9 mL of a 30% solution of hydrogen peroxide. The reaction mixture was heated under reflux for 1.5 h. The reaction mixture was diluted with water (10 mL) and extracted with ether (2 × 15 mL). The combined ethereal extracts were dried ($MgSO_4$) and concentrated to give a gummy solid. The solid was purified by medium-pressure liquid chromatography (1:1 ether/hexane) to afford 0.17 g (1.0 mmol, 76%) of a white solid. An analytical sample was obtained by recrystallization from ether: mp 200–203 °C dec; IR ($CHCl_3$) 3580, 3340 (br), 2980, 1325, 1300, 1170, 1130, 1060, 955 cm^{-1}; ^1H NMR (CCl_4) δ 1.83 (br s, 1), 2.77 (m, 2) 3.07 (m, 6), 3.86 (br s, 1), 4.18 (d, 2, J = 2.25 Hz); ^{13}C NMR ($CDCl_3$) δ 39.3, 41.1 (2), 42.4 (2), 43.5 (2), 46.3 (2), 67.7, 107.4; mass spectrum (70 eV), m/e 176 (parent). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.10; H, 6.87.

9-Hydroxy-10-oxahexacyclo[6.4.0.0^{2,7}.0^{3,6}.0^{4,12}.0^{5,9}]dodecan-11-one (18a). To a stirred suspension of 0.10 g (0.6 mmol) of **13a** and 0.02 g (0.13 mmol) of ruthenium dioxide in CCl_4 (8 mL) and 0.7 mL of a 3 M solution of sodium hydroxide (2.1 mmol) was added a solution of 0.38 g (1.8 mmol) of sodium metaperiodate in water (8 mL). The reaction mixture was allowed to stir until the yellow color of ruthenium tetraoxide persisted (~3 h). The excess oxidant was quenched by the addition of 2-propanol (1 mL). The reaction mixture was filtered to remove the precipitated ruthenium dioxide, acidified to pH 3 with a 6 M solution of hydrochloric acid, and extracted with chloroform (5 × 20 mL). The combined chloroform extracts were dried ($MgSO_4$) and concentrated to give 0.08 (0.4 mmol, 80%) of an off-white solid. The material was recrystallized from ether to afford an analytical sample: mp 217–219 °C dec; IR (KBr) 3375, 3000, 1705, 1408, 1330, 1303, 1243, 980, 760 cm^{-1}; ^1H NMR (CD_3COCD_3) δ 2.65 (m, 1), 2.84 (m, 2), 3.19 (m, 6), 6.07 (br s, 1); ^{13}C NMR (CD_3COCD_3) δ 38.7 (2), 41.4 (4), 44.5 (2), 47.6, 113.1, 172.2. Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.62; H, 5.49.

***endo*-10-Carbomethoxypentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-7-one (5a).** A solution of 0.24 g (2.5 mmol) of potassium fluoride dihydrate and 0.23 g (0.1 mL, 1.6 mmol) of methyl iodide in *N,N*-dimethylformamide (4 mL) was allowed to stir at room temperature for 0.5 h. At this time, 0.09 g (0.5 mmol) of **18a** was added, and stirring was continued for 5 h. The reaction mixture was diluted with water (40 mL) and extracted with ether (5 × 20 mL). The combined ethereal extracts were dried ($MgSO_4$) and

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concentrated to give an oily yellow solid. The solid was chromatographed on 25 g of activity I neutral alumina (3:2 ether/hexane) to afford 0.06 g (0.3 mmol, 61%) of a white solid: mp 92–93 °C (lit.[2] mp 93–95 °C); IR ($CHCl_3$) 3000, 1740, 1435, 1285, 1265, 1210, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.53 (t, 1, J = 3.3 Hz), 2.83 (m, 2), 3.17 (m, 2), 3.30 (m, 2), 3.48 (s, 3), 3.50 (m, 2); ^{13}C NMR ($CDCl_3$) δ 35.6 (2), 42.7 (2), 44.6 (2), 46.2 (2), 51.4, 52.1, 170.7, 219.1. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.84; H, 5.99.

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Electrochemical Reductive Carboxylation: Reduction of Unsaturated Compounds in the Presence of Methyl Chloroformate

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Mono- and dicarboxylated derivatives have been obtained by electroreduction of various unsaturated compounds in acetonitrile at a mercury-pool cathode in the presence of methyl chloroformate. Unsaturated compounds included activated olefins, ketones, aromatic Schiff bases, nitro compounds, and nitrogen heterocycles. The distribution of the products and their yields depend on the nature of the supporting electrolyte (Et_4NClO_4 or $LiClO_4$). Reduction mechanisms accounting for the nature of the reduction products are proposed on the basis of voltammetric and coulometric data. In some cases it is possible to obtain the kinetic parameters.

The electrochemical reductive carboxylation with CO_2 in aprotic solvents has been described for a number of substrates: polycyclic aromatic hydrocarbons,[1] olefins,[2-10] acetylenes,[3] ketones,[3,11] alkyl halides,[8] azomethine compounds,[12-14] and N-heterocyclic compounds.[15-18]

The standard potential for the reduction of CO_2 in dry DMF is −2.21 V vs. SCE,[19] and its value should not be very different in acetonitrile. This negative value explains that few carboxylations have been carried out by reduction of CO_2 to its radical anion $CO_2^{-}\cdot$, which would further react with the substrate. Besides the formation of oxalic acid by reaction of $CO_2^{-}\cdot$ with CO_2,[20] only ethylene[9] and butadiene[10] have been carboxylated in this way. In all the other experiments, the substrate is reduced to a radical anion that reacts with CO_2 to give a carboxylated radical. This radical is reduced in turn to a dianion that undergoes a second carboxylation or a protonation by the residual water (Scheme I). Most often these carboxylic acids are then transformed into esters.

Scheme I

$$A + e \rightleftharpoons A^{-}\cdot \xrightarrow{CO_2} ACOO^{-}\cdot$$

$$ACOO^{-}\cdot + e \rightarrow ACOO^{2-} \xrightarrow{CO_2} A(COO^{-})_2$$

$$ACOO^{2-} \xrightarrow{H^+} HACOO^{-}$$

We report herein the direct formation of esters through the reduction of unsaturated compounds in acetonitrile in the presence of methyl chloroformate.

As concerns the mechanism of this reaction, several possibilities must be taken into account as in the case of the reduction of unsaturated derivatives in the presence of halogenated derivatives as electrophiles:[21-24]

(i) A reaction between the substrate and $ClCOOCH_3$ may occur to give a cation.[25] This positively charged species will be more easily reduced than the substrate—for example, an immonium cation is more easily reduced than an imine—and a new more positive reduction wave will appear on the cyclic voltammogram.[24]

(ii) In other cases an ECEC mechanism as in Scheme I may take place, and the different possible reactions are summarized in Scheme II. The substrate is first reduced to a radical anion, which can either react with $ClCOOCH_3$

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