J. Org. Chem. **1987**, *52*, 1337–1339

General Procedure for the Preparation of 4-Alkyl- or 4-Aryl-Substituted Derivatives of 6-(Acetoxymethyl)isochroman-3-one (10a–j). A solution of the appropriate cyano compound (**9a–j**; 0.005 mol) in acetic acid (10 mL), water (1 mL), and H_2SO_4 (0.25 mL) was refluxed for 1 h. The reaction mixture was then cooled, diluted with water (100 mL), and extracted with methylene chloride (2 × 100 mL). The combined methylene chloride extracts were successively washed with water (2 × 100 mL), saturated $NaHCO_3$ (2 × 75 mL), and brine (2 × 75 mL) and then dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give the corresponding lactone product (**10a–j**). All the lactone products (**10a–j**) were purified by flash column chromatography (EtOAc:hexane = 1:9) to give pure **10a–j**. The yields are given in Table II.

6-(Acetoxymethyl)isochroman-3-one (10a): colorless thick liquid; ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 3 H), 3.73 (s, 2 H), 5.12 (s, 2 H), 5.32 (s, 2 H), 7.25–7.30 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 170.40, 170.04, 136.74, 131.27, 131.19, 127.07, 126.61, 124.67, 69.53, 65.31, 30.84, 20.62; IR ($CHCl_3$) 1740 cm^{-1} (>C=O); MS, m/z 220 (M^+), 188, 186; m/z (M^+) for $C_{12}H_{12}O_4$, calcd 220.0735, found 220.0736.

4-Methyl-6-(acetoxymethyl)isochroman-3-one (10b): white crystals (from ethyl acetate); mp 76 °C; ^{1}H NMR ($CDCl_3$) δ 1.65 (d, J = 7 Hz, 3 H), 2.11 (s, 3 H), 3.64 (q, J = 7.5 Hz, 1 H), 5.12 (s, 2 H), 5.28 (s, 1 H), 5.31 (s, 1 H), 7.23–7.32 (m, 3 H); IR ($CHCl_3$) 1740, 1460, 1380 cm^{-1}; MS, m/z 234 (M^+), 190 ($M - CO_2$). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.64; H, 6.02. Found: C, 66.71; H, 6.06.

4-Ethyl-6-(acetoxymethyl)isochroman-3-one (10c): colorless thick liquid; ^{1}H NMR ($CDCl_3$) δ 1.09 (t, J = 7.5 Hz, 3 H), 1.75–2.0 (m, 2 H), 2.12 (s, 3 H), 3.56 (t, J = 7 Hz, 1 H), 5.13 (s, 2 H), 5.05 (d, J = 10 Hz, 1 H), 5.37 (d, J = 10 Hz, 1 H), 7.21–7.30 (m, 3 H); IR ($CHCl_3$) 1740, 1460, 1380, 1230 cm^{-1}; MS, m/z 248 (M^+), 204 ($M - CO_2$); m/z (M^+) for $C_{14}H_{16}O_4$, calcd 248.1044, found 248.1051.

4-*n*-Propyl-6-(acetoxymethyl)isochroman-3-one (10d): colorless thick liquid; ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3 H, J = 8 Hz), 1.2–1.9 (m, 4 H), 2.1 (s, 3 H), 3.6 (br t, 1 H), 5.3 (s, 2 H), 5.4 (s, 2 H), 7.25–7.4 (m, 3 H); IR ($CHCl_3$) 1740, 1465, 1380 cm^{-1}; MS, m/z 362 (M^+), 320, 318.

4-Phenyl-6-(acetoxymethyl)isochroman-3-one (10e): colorless thick liquid; ^{1}H NMR ($CDCl_3$) δ 2.11 (s, 3 H), 5.04 (s, 1 H), 5.12 (s, 2 H), 5.25 (s, 2 H), 7.15–7.38 (m, 8 H); IR ($CHCl_3$) 1740, 1600, 1460, 1380, 1240 cm^{-1}; MS, m/z (M^+) for $C_{18}H_{16}O_4$, calcd 296.1044, found 296.1042.

4-(3-Methoxyphenyl)-6-(acetoxymethyl)isochroman-3-one (10f): colorless thick liquid; ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 3 H), 3.78 (s, 3 H), 5.01 (s, 1 H), 5.12 (s, 2 H), 5.23 (split s, 2 H), 6.76–6.89 (m, 3 H), 7.27–7.40 (m, 4 H); IR ($CHCl_3$) 1740, 1595, 1510, 1380, 1250, 1140 cm^{-1}; MS, m/z 326 (M^+); m/z (M^+) for $C_{19}H_{18}O_5$, calcd 326.1149, found 326.1160.

4-(3,4-Dimethoxyphenyl)-6-(acetoxymethyl)isochroman-3-one (10g): colorless thick liquid; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3 H), 3.78 (s, 3 H), 3.86 (s, 3 H), 4.95 (s, 1 H), 5.13 (s, 2 H), 5.27 (s, 2 H), 6.37 (s, 2 H), 7.16–7.43 (m, 4 H); IR ($CHCl_3$) 1740, 1595, 1510, 1380, 1250, 1140 cm^{-1}; MS, m/z 356 (M^+); m/z (M^+), calcd 356.1254, found 356.1263.

4-(3,4,5-Trimethoxyphenyl)-6-(acetoxymethyl)isochroman-3-one (10h): colorless thick oil; ^{1}H NMR ($CDCl_3$) δ 2.11 (s, 3 H), 3.84 (s, 6 H), 3.87 (s, 3 H), 4.97 (s, 1 H), 5.12 (s, 2 H), 5.25 (s, 2 H), 6.84 (s, 2 H), 7.28–7.46 (m, 3 H); IR ($CHCl_3$) 1740, 1595, 1460, 1380, 1230, 1180 cm^{-1}; MS, m/z for $C_{21}H_{22}O_7$, calcd 386.1359, found 386.1368.

4-(4-Fluorophenyl)-6-(acetoxymethyl)isochroman-3-one (10i): colorless thick liquid; ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3 H), 4.97 (s, 1 H), 5.09 (s, 2 H), 5.24 (s, 2 H), 7.07–7.28 (m, 4 H), 7.32–7.40 (m, 3 H); IR ($CHCl_3$) 1740, 1610, 1510, 1460, 1380, 1240, 1165 cm^{-1}; MS, m/z 314 (M^+), 270 ($M - CO_2$).

4-(3-Fluorophenyl)-6-(acetoxymethyl)isochroman-3-one (10j): colorless thick liquid; ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3 H), 4.99 (s, 1 H), 5.09 (s, 2 H), 5.23 (s, 2 H), 7.00–7.36 (m, 7 H); IR ($CHCl_3$) 1740, 1615, 1595, 1490, 1380, 1290, 1175 cm^{-1}; MS, m/z 314 (M^+), 270 ($M - CO_2$); m/z (M^+) for $C_{18}H_{15}O_4F$, calcd 314.0954, found 314.0944.

Acknowledgment. This work was sponsored in part by Grant N-118 from the Welch Foundation, Houston, TX. S.P.K. thanks the Robert Welch Foundation for the award of a postdoctoral fellowship. We thank Dr. J. Maguire for performing microanalysis. We are also grateful to the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE 8211164), for recording high-resolution mass spectra.

Registry No. **3**, 106520-26-7; **5a**, 106520-27-8; **5b**, 106520-28-9; **5c**, 106520-29-0; **5d**, 106520-30-3; **5e**, 106520-31-4; **5f**, 106520-32-5; **5g**, 106520-33-6; **5h**, 106542-90-9; **5i**, 106520-34-7; **5j**, 106520-35-8; **5k**, 106520-36-9; **6**, 106520-37-0; **9a**, 106520-38-1; **9b**, 106520-39-2; **9c**, 106520-40-5; **9d**, 106520-41-6; **9e**, 106520-42-7; **9f**, 106520-43-8; **9g**, 106520-44-9; **9h**, 106520-45-0; **9i**, 106520-46-1; **9j**, 106520-47-2; **10a**, 106520-48-3; **10b**, 106520-49-4; **10c**, 106520-50-7; **10d**, 106520-51-8; **10e**, 106520-52-9; **10f**, 106520-53-0; **10g**, 106520-54-1; **10h**, 106520-55-2; **10i**, 106520-56-3; **10j**, 106520-57-4; 3-fluorophenylacetonitrile, 501-00-8; 2-bromo-*p*-xylene, 553-94-6; α,α'-dibromo-2-bromo-*p*-xylene, 19900-52-8; 2-furfurylacetonitrile, 2745-25-7; acetonitrile, 75-05-8; propionitrile, 107-12-0; butyronitrile, 109-74-0; valeronitrile, 110-59-8; phenylacetonitrile, 140-29-4; 3-methoxyphenylacetonitrile, 19924-43-7; 3,4-dimethoxyphenylacetonitrile, 93-17-4; 3,4,5-trimethoxyphenylacetonitrile, 13338-63-1; 4-fluorophenylacetonitrile, 459-22-3; acetic acid, 64-19-7.

An Electrochemical "Switch" for Starting and Stopping the Energy-Releasing Conversion of Quadricyclanes to Norbornadienes

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Since its independent discovery by Hogeveen and Volger[1] and by Gassman et al.[2] in the mid sixties,[3] the catalytic conversion of quadricyclanes to norbornadienes[4] has attracted considerable attention because of its potential as a crucial component of a solar energy storage cell.[5–7] Both

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(1) Hogeveen, H.; Volger, H. C. *J. Am. Chem. Soc.* **1967**, *89*, 2486.

(2) Gassman, P. G.; Aue, D. H.; Patton, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 7271.

(3) The initial example of this type of isomerization was probably observed by Cristol and co-workers. However, the implications of their observations were not appreciated. Cristol, S. J.; Snell, R. L. *J. Am. Chem. Soc.* **1958**, *80*, 1950.

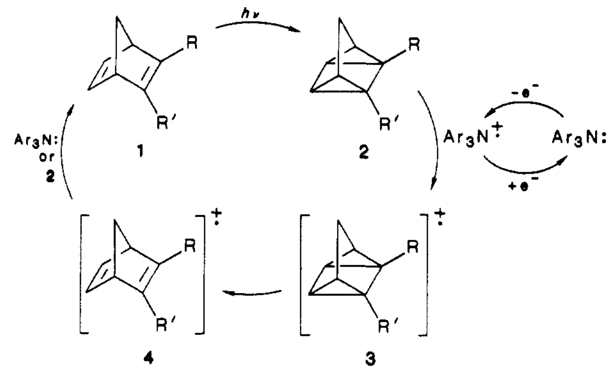
(4) Because of its common usage, the skeleton of **1** is referred to as the norbornadiene skeleton rather than as a bicyclo[2.2.1]hepta-2,5-diene, while **2** is classified as a quadricyclane instead of as a tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane derivative.

(5) For leading references, see: (a) Cristol, S. J.; Snell, R. L. *J. Am. Chem. Soc.* **1958**, *80*, 1950. (b) Dauben, W. G.; Cargill, R. L. *Tetrahedron* **1961**, *15*, 197. (c) Hammond, G. S.; Turro, N. J.; Fischer, A. *J. Am. Chem. Soc.* **1961**, *83*, 4674. (d) Schwendiman, D. P.; Kutal, C. *Inorg. Chem.* **1977**, *16*, 719 (e) Schwendiman, D. P.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 5677. (f) Grutsch, P. A.; Kutal, C. *Ibid.* **1979**, *101*, 4228. (g) Hautala, R. R.; Little, J.; Sweet, E. M.; Jones, G., II. *Sol. Energy* **1977**, *19*, 503. (h) Scharf, H. D.; Fleischbauer, J.; Leismann, H.; Ressler, I.; Schieker, W.; Weitz, R. *Angew. Chem.* **1979**, *91*, 696. (i) Mirbach, M. J.; Mirbach, M. F.; Vartan-Boghossian, R.; Saus, A. *Nouv. J. Chim.* **1981**, *5*, 113. (j) Maruyama, K.; Terada, K.; Yamamoto, Y. *J. Org. Chem.* **1981**, *46*, 5294. (k) Grutsch, P. A.; Kutal, C. *J. Chem. Soc., Chem. Commun.* **1982**, 893. (l) Toda, T.; Hasegawa, E.; Mukai, H.; Tsuruta, T.; Tagiwara, T.; Yoshida, T. *Chem. Lett.* **1982**, 1551. (m) Jones, G., II.; Xuan, P. T.; Schwarz, W. *Tetrahedron Lett.* **1982**, *23*, 5505. (n) Hautala, R. R.; King, R. B.; Kutal, C. *Solar Energy: Chemical Conversion and Storage*; Humana Press: Clifton, NJ, 1979; pp 333–369. (o) Jones G., II.; Ramachandran, B. R. *J. Org. Chem.* **1976**, *41*, 798. (p) Hogeveen, H.; Nusse, B. J. *Tetrahedron Lett.* **1973**, 3667; **1974**, 159. (q) King, R. B.; Ikai, S. *Inorg. Chem.* **1979**, *18*, 949. King, R. B.; Sweet, E. M. *J. Org. Chem.* **1979**, *44*, 385. King, R. B.; Hanes, R. M. *Ibid.* **1979**, *44*, 1092. (r) Maruyama, K.; Tamiaki, H. *Chem. Lett.* **1982**, 1699. (s) Fife, D. J.; Morse, K. W.; Moore, W. M. *J. Am. Chem. Soc.* **1983**, *105*, 7404. (t) Maruyama, K.; Tamiaki, H.; Kawabata, S. *Chem. Lett.* **1984**, 743.

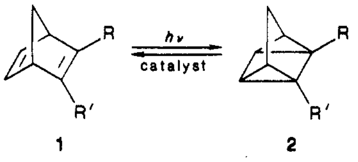
(6) Estimates of the energy difference between **1** (R = R′ = H) and **2** (R = R′ = H) range from ca. 23 to 27 kcal/mol. Wiberg, K. B.; Connor, H. A. *J. Am. Chem. Soc.* **1976**, *98*, 5411.

0022-3263/87/1952-1337$01.50/0

Scheme I



the photochemical conversion of norbornadienes 1 to quadricyclanes 2^{5a-n} and the metal-complex-catalyzed conversion of quadricyclanes to norbornadienes[1,2,5o-t] have been extensively studied.[6] While many of the problems associated with the photochemical conversion of 1 into 2 have been circumvented, attempts to develop a simple system for the controlled release of energy from 2 have been less rewarding.[7] We now report the development of a simple electrochemical "switch" that allows the conversion of 2 to 1 to be turned on or off at will. This switch is based on the principle of a single-electron transfer (SET) promoted isomerization of 2 to 1.[9,10]



In an initial approach to the development of an electrochemical method for the conversion of 2 to 1, we investigated the direct generation of the cation radical, 3, through oxidation of 2 at a platinum anode. However, as anticipated on the basis of our earlier work on the electrochemical oxidation of strained hydrocarbons,[11] this approach was unsuccessful due to the rapid fouling of the electrode surface by polymerized substrate.[12,13] This indicated the need for a "carrier oxidant" if this approach was to be successful.

As shown in Scheme I, an efficient, readily controlled method for electrochemically switching the quadricyclane to norbornadiene conversion on and off was made possible through the use of a triarylamine–triarylaminium cation radical pair. In each case the triarylamine had to be carefully matched (on a potentiometric basis) with the appropriate quadricyclane. For example, in the case of the parent system (R = R′ = H), which has an $E_{1/2}^{ox} = 0.91$ V,[11] tris(*p*-bromophenyl)amine has an oxidation potential that is too high ($E^{\circ\prime} = 1.02$ V). The use of this triarylamine resulted in some direct oxidation of 2 to 3 at the electrode surface with resultant slow deactivation of the electrode. In contrast, tri-*p*-tolylamine ($E^{\circ\prime} = 0.66$ V)[14] was oxidized more readily than 2, which permitted an effective cycle without electrode contamination. Since the transfer of an electron from 2 to the tris(*p*-tolyl)aminium cation radical is endoergic, any equilibrium would not be in favor of the formation of 3 and tri-*p*-tolylamine. However, the reaction occurs because we are not dealing with a true equilibrium since 3 is converted into 4 in a rapid exoergic reaction.

In a typical experiment, 2 (R = R′ = H; 0.01 mol) and tri-*p*-tolylamine (3.4×10^{-4} mol) were dissolved in 30 mL of methylene chloride containing 0.20 M tetra-*n*-hexylammonium perchlorate in a three-compartment electrolysis cell.[15] Oxidation of the triarylamine was performed at 0.3 V vs. a saturated NaCl–SCE reference electrode. The current remained reasonably constant at ca. 1 mA. The progress of the conversion was followed by both coulometry and GLC analysis. After 3.9 C had passed, 2 had been completely consumed. With tri-*p*-tolylamine, the conversion of 2 to 1 slowed quickly if the applied current was removed. However, when tris(*p*-bromophenyl)amine was used as the carrier, the conversion of 2 to 1 continued after the current was shut off. The reaction could be stopped instantly through the application of a cathodic potential and restarted through the use of an anodic potential. Thus, the conversion of 2 to 1 could be turned on and off at will. The fact that the conversion of 2 to 1 in the presence of tri-*p*-tolylamine eventually stopped after the applied anodic potential was removed indicated that an intermediate cation-radical was being inactivated in a slow side reaction. This suggests either that our conversion of 2 to 1 is less than quantitative or that the carrier oxidant is consumed.

For a series of experiments, the yield of 1 was 100 ± 3% as determined by GLC analysis vs. an internal standard. On the basis of coulometry, the catalytic turnover was 247. This represents the average number of norbornadiene molecules produced from the corresponding quadricyclane per triarylaminium ion generated by anodic oxidation. Furthermore, based on the 10-V compliance potential measured for our cell, the conversion of 1 mol of 2 to 1 consumed 0.93 kcal of electrical energy. This represents an energy gain of better than 25 to 1. We anticipate that the efficiency of electrochemical energy release cells of this type may be able to be improved substantially.

In order to establish the generality of our method and to illustrate its use with a quadricyclane–norbornadiene pair where the photoreaction could be accomplished with readily accessible wavelength radiation, we prepared **1a** (1: R = C_6H_5, R′ = CH_3CO) through the Diels–Alder addition of 4-phenyl-3-butyn-2-one[16] to cyclopentadiene (82% yield). The ultraviolet spectrum of **1a** showed a broad

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(7) In spite of intensive study,[5o-t] most of the systems that have been developed for the conversion of 2 into 1 are not cleanly reversible. In most cases, including the original example,[1] the metal-promoted reversion of 2 into 1 is an extremely complex reaction in which adducts of 2 (or 1) and the catalyst may be involved.[8] These adducts serve to destroy part of the starting material and, when carried into solution, destroy 2 as rapidly as it is formed from 1. For a *possible* exception to this general statement, see ref 5t.

(8) Gassman, P. G.; Nikora, J. A. *J. Organomet. Chem.* **1975**, *92*, 81.

(9) For leading references to this SET-promoted reaction, see: Murov, S.; Hammond, G. S. *J. Phys. Chem.* **1968**, *72*, 3797. Jones, G., II.; Chiang, S.-H.; Becker, W. G.; Greenberg, D. P. *J. Chem. Soc., Chem. Commun.* **1980**, 681. Jones, G., II.; Becker, W. G. *Chem. Phys. Lett.* **1982**, *85*, 271. Roth, H. D.; Schilling, M. L. M.; Jones, G., II. *J. Am. Chem. Soc.* **1981**, *103*, 1246. Jones, G., II.; Chiang, S.-H.; Becker, W. G.; Welch, J. A. *J. Phys. Chem.* **1982**, *86*, 2805. Schwarz, W.; Dangel, K.-M.; Jones, G., II.; Bargon, J. *J. Am. Chem. Soc.* **1982**, *104*, 5686.

(10) Hoffman, R. W.; Barth, W. *J. Chem. Soc., Chem. Commun.* **1983**, 345. For an example of an acid-catalyzed isomerization, see: Hirao, K.; Ando, A.; Hamada, T.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1984**, 300. *Neither of these systems is suitable for recycling.*

(11) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308. As noted in this reference, the quoted $E_{1/2}^{ox}$ values are not for reversible reactions. Thus, there will be a small variance in the observed values as a function of scan rate when the oxidation potentials are measured by cyclic voltammetry.

(12) This phenomenon has also been noted by other workers: Borsub, N.; Kutal, C. *J. Am. Chem. Soc.* **1984**, *106*, 4826. Yasufuku, K.; Takahashi, K.; Kutal, C. *Tetrahedron Lett.* **1984**, *25*, 4893.

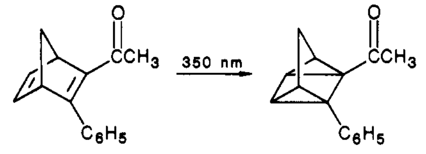
(13) The electrode was rapidly fouled (<30 s). No norbornadiene was formed.

(14) Measured in methylene chloride.

(15) Control experiments showed that no change occurred in the system on prolonged standing in the absence of current.

(16) Prepared according to the procedure of Nightingale, D.; Wadsworth, F. *J. Am. Chem. Soc.* **1945**, *67*, 416.

absorption at λ_{max} 294 nm. Irradiation with 350-nm light gave a quantitative yield of **2a**. The $E_{1/2}^{ox}$ for **2a** was 0.90 V vs. SCE. Thus, while the substituents dramatically changed the photoefficiency with which **1a** could be converted into **2a** with 350-nm light as compared to the parent hydrocarbons, the substituents had a balanced electronic effect on the HOMO of **2a** in comparison to quadricyclane itself ($E_{1/2}^{ox}$ = 0.91 V vs. SCE). Utilization of the electrochemical "switching" process with tri-*p*-tolylamine as the cation-radical precursor gave **1a** from **2a** in analogy to the process outlined above.



In summary, we have developed an electrically driven "on–off switch" for the release of thermal energy in the conversion of **2** to **1**. This switch is highly efficient. However, we stress that while the chemical efficiency approaches 100%, *it is not 100%* since the conversion of **2** into **1** eventually ceases after the applied current is turned off (indicating the presence of a very minor side reaction). Clearly, considerable developmental work would be required before this concept could be utilized in a practical solar energy storage cell.[17]

Experimental Section[18]

Quadricyclane (Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane, 1). Compound **1** (R = R′ = H) was prepared according to the literature procedure.[19]

2-Acetyl-3-phenylbicyclo[2.2.1]hepta-2,5-diene (1a). A solution of 4.82 g (35 mmol) of 4-phenyl-3-butyn-2-one, ca. 50 mg of *p*-methoxyphenol (to inhibit polymer formation), and 3.3 g (25 mmol) of distilled dicyclopentadiene was placed in a round-bottomed flask equipped with a reflux condenser, and the reaction mixture was heated to 160 °C under a nitrogen atmosphere for 10 h. The resulting amber oil was distilled to give 6.0 g (82% yield) of **1a**: bp 93–95 °C (0.05 mm); ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 5 H), 6.90 (br s, 2 H), 4.03 (m, 1 H), 3.72 (m, 1 H), 2.30–2.00 (m, 2 H), 1.94 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 196.6, 166.4, 149.6, 143.9, 141.4, 137.3, 128.6, 128.4, 127.3, 70.4, 59.4, 52.3, 29.1; IR (neat) 3060, 2980, 2938, 2865, 1655, 1595, 1560, 1495, 1448, 1363, 1334, 1300, 1240, 810, 760, 723, 700 cm^{-1}; UV $\lambda_{max}^{acetonitrile}$ = 294 nm (ε 4000); exact mass, *m/e* 210.1036 (calcd for $C_{15}H_{14}O$, 210.1045).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.34; H, 6.75.

1-Acetyl-5-phenyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (2a). A solution of 3.0 g (14 mmol) of **1a** in 35 mL of hexane in a Pyrex tube was purged with nitrogen and irradiated for 12 h at ambient temperature in a Rayonet reactor equipped with 16 350-nm lamps. Removal of the solvent gave a quantitative yield of **2a**, which varied from having no detectable impurities (including **1a**) to material that was contaminated with up to 5% of **1a** as the only detectable impurity. Similar results were obtained when chloroform was used as solvent and in the absence of solvent. For irradiation in the absence of solvent, neat **1a** was sealed in a Pyrex tube under vacuum. Compound **2a** had the following physical properties: ^{1}H NMR ($CDCl_3$) δ 7.24 (s, 5 H), 2.74–2.09 (m, 6 H), 1.72 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 203.8, 137.2, 129.2, 128.0, 126.6, 42.1, 39.2, 33.4, 32.3 (2C), 31.7, 27.4, 20.7; IR (neat) 3060, 2930, 2860, 1674, 1610, 1510, 1454, 1386, 1310, 1300, 1235, 1170, 1160, 1075, 1020, 955, 910, 830, 750, 700 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.31; H, 6.78.

Conversion of Quadricyclane (2) to Norbornadiene (1) Using an Electrochemical Switch. In a typical experiment, 1.00 mL (0.92 g, 10 mmol) of **2** (R = R′ = H) and tri-*p*-tolylamine[20] (0.10 g, 0.34 mmol) were dissolved in 30 mL of methylene chloride containing 0.20 M tetra-*n*-hexylammonium perchlorate in the working compartment of a divided preparative electrolysis cell. The solution was purged with nitrogen at ambient temperature, and an anodic current of about 1 mA was passed through the solution while controlling the working electrode potential at +0.30 V vs. a saturated-NaCl–SCE electrode. The formation of **1** (R = R′ = H) was monitored by GLC. After the passage of 3.9 C, the conversion of **2** to **1** was complete. The electrochemical catalytic turnover number (mol of product/faraday) was 247. Similar results were obtained by using tetraethylammonium tetrafluoroborate as electrolyte.

Conversion of 2a to 1a Using an Electrochemical Switch. In the working compartment of a divided preparative electrolysis cell were placed 0.50 g (2.4 mmol) of **2a** and 0.034 g (0.12 mmol) of tri-*p*-tolylamine in 30 mL of methylene chloride containing 0.05 M tetraethylammonium tetrafluoroborate. The nitrogen-purged solution was subjected to controlled-potential oxidation at 0.50 V vs. a saturated-NaCl–SCE until 1.3 C of current had passed. Workup of the reaction mixture showed that **2a** had been completely converted into **1a**.

In a repeat of the same experiment, the progress of the reaction was monitored by IR spectroscopy utilizing the carbonyl frequencies at 1665 cm^{-1} and 1641 cm^{-1} of **2a** and **1a**, respectively.[21] These studies indicated a catalytic turnover number of 290 for the conversion of **2a** to **1a**.

Acknowledgment. We are indebted to the National Science Foundation for a grant that supported this investigation.

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[17] We are continuing to investigate applications of this concept. For an initial disclosure, see: Gassman, P. G.; Hershberger, J. W. U.S. Pat. 4 582 578, April 18, 1986.

[18] ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian EM-360 and Bruker WH-90 spectrometers, respectively. IR spectra were obtained with a Beckman IR 4240 spectrophotometer. A Perkin-Elmer Lambda 3B was used for UV measurements. Elemental analyses were done by Galbraith Analytical Laboratories, Inc. Cyclic voltammetry was performed on a Princeton Applied Research Model 174A polarographic analyzer. A typical solution consisted of 10^{-3} M substrate dissolved in acetonitrile which contained 0.1 M tetraethylammonium tetrafluoroborate at ambient temperature with a scan rate of 100 mV/s. A platinum bead working electrode and a saturated-NaCl-SCE reference electrode were employed. Preparative electrolyses were performed in a three-compartment cell equipped with a platinum gauze working electrode.

[19] Smith, C. D. *Org. Synth.* **1971**, *51*, 133.

[20] Walter, R. I. *J. Am. Chem. Soc.* **1955**, *77*, 5999.

[21] The values used here are those observed in methylene chloride containing electrolyte. They are considerably shifted from those observed for the neat liquid.

Radical Spirocyclization: Synthesis of an Appropriately Oxygenated Spiro Compound Related to the Antitumor Antibiotic Fredericamycin A

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As judged by the number of very recent publications on the subject,[1] there is appreciable interest in the synthesis

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[1] (a) Rama Rao, A. V.; Reddeppa Reddy, D.; Deshpande, V. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1119. (b) Parker, K. A.; Koziski, K. A.; Breault, G. *Tetrahedron Lett.* **1985**, *26*, 2181. (c) Eck, G.; Julia, M.; Pfeiffer, B.; Rolando, C. *Ibid.* **1985**, *26*, 4723. (d) Eck, G.; Julia, M.; Pfeiffer, B.; Rolando, C. *Ibid.* **1985**, *26*, 4725. (e) Kende, A. S.; Ebetino, F. H.; Ohta, T. *Ibid.* **1985**, *26*, 3063. (f) Braun, M.; Veith, R. *Ibid.* **1986**, *27*, 179. (g) Bach, R. D.; Klix, R. C. *Ibid.* **1986**, *27*, 1983. (h) Bach, R. D.; Klix, R. C. *J. Org. Chem.* **1986**, *51*, 749. (i) Parker, K.; Breault, G. A. *Tetrahedron Lett.* **1986**, *27*, 3835. (j) Bennett, S. M.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 878. (k) The first total synthesis has recently been completed: Kelly, T. R., personal communication.