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Mechanistic insight into the photoinduced rearrangement of the tricyclo[4.1.0.0^{2,7}]heptyl skeleton

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Cyclic voltammetry (Figure 1) was used to further probe the electrocatalytic system. Without dioxygen, all solutions have voltammograms typical of a one-electron reversible Mn(III/II) couple (Figure 1, curve 1, $E^\circ = -0.27$ V). With dioxygen, the Mn(TPP)Cl reduction and oxidation peak currents⁹ are increased (Figure 1, curve 2), consistent with partial oxygen binding and a net two-electron reversible reduction to a Mn(III) superoxo complex.⁴ Voltammetry of a similar solution containing porphyrin and benzoic anhydride (Figure 1, curve 3) gives, upon dioxygen addition, greatly enhanced reduction currents (Figure 1, curves 4 and 5)¹⁰ that, after normalization with respect to (scan rate)^{1/2}, have characteristic catalytic wave shapes and scan-rate dependencies. In Scheme I, the postulated high-valent manganese oxo-porphyrin should¹¹ be easily reduced (Scheme I, dashed arrow) at the potentials of the catalytic waves. In an electrolysis with olefin present, such a reduction occurs in competition with epoxidation, perhaps accounting for the less than 100% faradaic efficiencies. This kinetic competition should be amenable to further study by electrochemical methods.

This paper shows that electrochemistry provides a powerful new format within which to study model cytochrome P-450 systems. Judicious choice of electrode material and applied potential allows one to discriminate against undesired reaction pathways and background processes. We anticipate that the available electrochemical methodology will permit detailed study of the kinetics and mechanism of this and similar systems.

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Registry No. Mn(TPP)Cl, 32195-55-4; cyclooctene, 931-88-4; *trans*-2-octene, 13389-42-9; cytochrome P-450, 9035-51-2.

(9) We have observed that the increases in current are less when larger quantities of chloride or axial base are used, owing to competition with O₂ binding (unpublished results, see also ref 6n).

(10) The transient oxidation wave at $E_p = -0.11$ V in Figure 1, curves 4 and 5, is associated with benzoate produced from the anhydride cleavage as will be detailed later. Benzoate may act as an axial base (L in Scheme I), displacing 1-Melmd at different stages of the cycle.

(11) (a) Bortolini, O.; Meunier, B. *J. Chem. Soc., Chem. Commun.* **1983**, 1364-1366. (b) Carnier, N.; Harriman, A.; Porter, G. *J. Chem. Soc., Dalton Trans.* **1982**, 931-938.

Mechanistic Insight into the Photoinduced Rearrangement of the Tricyclo[4.1.0.0^{2,7}]heptyl Skeleton

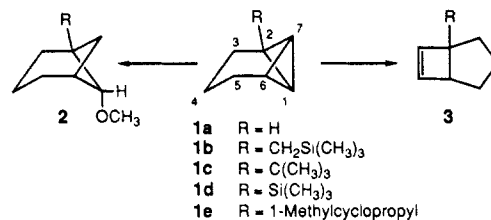
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Electrochemically¹ and photochemically² induced single electron transfers from the HOMOs of highly strained polycyclic molecules have recently attracted considerable attention.¹⁻³ Although extensive effort has been focused on the photoinduced generation of one-electron carbon-carbon bonds within the framework of these polycyclic molecules, relatively little is understood concerning those

factors which determine whether the intermediate cation radicals undergo valence isomerization,³ nucleophilic solvent addition,^{2a,b} or molecular rearrangement.^{2c,d,4} This problem is illustrated by the conversion of **1a** [R = H, $E_{1/2} = 1.50$ V]⁵ into **2a** and of **1b**



[R = CH₂Si(CH₃)₃, $E_{1/2} = 1.37$ V] into **3b** under identical photochemical conditions.⁶ We now wish to report studies of a series of 2-substituted tricyclo[4.1.0.0^{2,7}]heptanes which provide additional mechanistic insights into the behavior of the intermediate cation radicals.

The first question to be answered was whether the rearrangement of the cation radical generated from **1b** was the result of the steric effect or of the electronic effect of the trimethylsilylmethyl substituent at C2. This was evaluated initially by placing a *tert*-butyl moiety at C2 of **1** [**1c**, R = C(CH₃)₃, $E_{1/2} = 1.38$ V].^{7,8} Under our standard photosensitized reaction conditions,⁶ **1c** gave **2c** as the only isolable product (78% yield). In order to demonstrate that there was no major unique factor associated with the presence of a silicon moiety in the molecule, a trimethylsilyl group was placed at C2 of **1** [**1d**, R = Si(CH₃)₃, $E_{1/2} = 1.38$ V]. Again, under our standard photosensitized reaction conditions, only **2d** was formed (86% yield). In addition, neither **1c** or **1d** gave rearrangement products related to **3** on prolonged photosensitized irradiation in tetrahydrofuran. These two studies suggest that it was neither the steric bulk nor the presence of the silyl group which promoted the rearrangement of **1b** to **3b** but rather the propensity of the trimethylsilylmethyl group to stabilize an adjacent incipient carbocationic center.⁹ If the effect was primarily electronic, a group intermediate between the *tert*-butyl group and the trimethylsilylmethyl group in carbocation stabilizing power should give a mixture of **2** and **3**.

In order to test this theory, we prepared **1e**⁷ (R = 1-methylcyclopropyl, $E_{1/2} = 1.26$ V) and subjected it to our reaction conditions. Irradiation of a tetrahydrofuran solution of **1e** and 1-CN in Pyrex gave a 79% yield of **3e** as the only volatile product.¹⁰ In contrast, irradiation of a methanolic solution containing **2** ×

(4) Padwa, A.; Chou, C. S.; Rieker, W. F. *J. Org. Chem.* **1980**, *45*, 4555.

(5) The nonreversible oxidation potentials listed were determined by single-sweep cyclic voltammetry at a platinum electrode and referenced to a saturated calomel electrode.¹ The solvent used for these measurements was acetonitrile and the electrolyte was tetra-*n*-butylammonium perchlorate (0.1 M).

(6) The photochemical reactions were carried out in methanol containing 1-cyanonaphthalene (1-CN) as photosensitizer.² In general, a Rayonet reactor containing 16 300-nm lamps was used as the light source and the reactions were carried out in a Pyrex reaction vessel. Normally, 0.1% potassium hydroxide was added to the reaction mixture in order to prevent the acid-catalyzed rearrangement of **1**.

(7) The synthesis of **1** involved the addition of dibromo- or dichlorocarbene to the appropriate 3-substituted cyclohexene to yield the intermediate 2-substituted 7,7-dihalobicyclo[4.1.0]heptane. Treatment of this intermediate with methyllithium or *n*-butyllithium produced **1** via insertion of the initially generated cyclopropylidene. Experimental details will be provided in a full paper on this subject.

(8) Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds. In all cases, IR, ¹H NMR, and ¹³C NMR data were consistent with the assigned structures.

(9) Traylor, T. J.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715. Bassindale, A. R.; Eaborn, C.; Walton, D. R. M.; Young, D. J. *J. Organomet. Chem.* **1967**, *20*, 49. See also: Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.

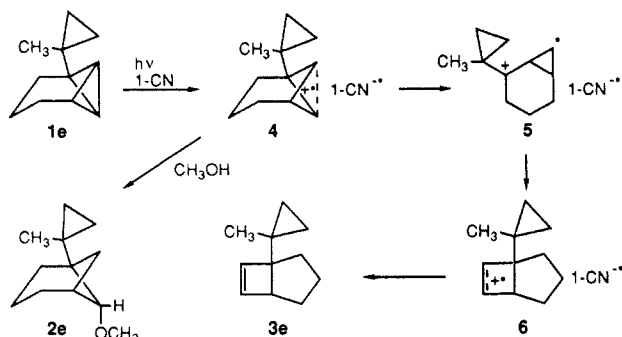
(10) Compound **3e** showed the following properties: bp 45-70 °C (10 mm); IR (neat) 3120, 3060, 2940, 1380, 730 cm⁻¹; ¹H NMR (C₆D₆) δ 5.90 (2 H, br s), 2.08 (1 H, br d), 2.0-1.2 (7 H, m), 1.15 (3 H, s), 0.50 (4 H, m); ¹³C NMR (C₆D₆) δ 138.76 (d), 135.73 (d), 62.84 (s), 49.03 (d), 29.88 (t), 27.01 (t), 24.49 (t), 21.62 (q), 19.36 (s), 11.50 (t); mass spectrum, *m/e* 148.1250 (calcd for C₁₁H₁₆ 148.1252). Anal. Calcd for C₁₁H₁₆: C, 89.12; H, 10.88. Found: C, 89.14; H, 11.06.

(1) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308. Gassman, P. G.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392. Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5793. Richtsmeier, S. C.; Gassman, P. G.; Dixon, D. A. *J. Org. Chem.* **1985**, *50*, 311.

(2) (a) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. (b) Gassman, P. G.; Olson, K. D. *Ibid.* **1982**, *104*, 3740. (c) Roth, H. D.; Schilling, M. L. M.; Gassman, P. G.; Smith, J. L.; *Ibid.* **1984**, *106*, 2711. (d) Gassman, P. G.; Hay, B. A. *Ibid.* **1985**, *107*, 4075.

(3) For additional examples and leading references, see: Jones, G. II; Chiang, S.-H.; Becker, W. G.; Welch, J. A. *J. Phys. Chem.* **1982**, *86*, 2805. Jones, G. II; Chiang, S.-H. *Tetrahedron* **1981**, *37*, 3397. Abelt, C. J.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4148 and references contained therein.

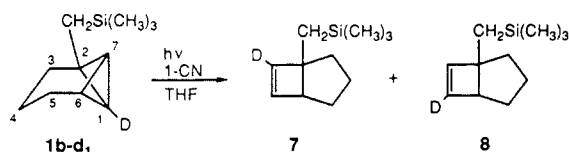
10^{-3} M **1e** and 2×10^{-3} M 1-CN gave 5% of **3e** and 22% of **2e**.¹¹ The relatively low yields obtained in this reaction could be traced to the destruction of both **2e** and **3e** under our reaction conditions in methanol. Addition of 1,4-cyclohexadiene as a free radical scavenger coupled with stopping the reaction at 15% conversion gave a 24% yield of **3e** and a 53% yield of **2e** based on unrecovered starting material.¹² This demonstrated that with a substituent



which was intermediate in carbocation stabilizing ability, both products could be formed and that diverse reaction paths were followed from a single starting material.

Earlier, we suggested that the conversion of **1b** into **3b** proceeded by a stepwise process involving initial electron transfer from the C1-C7 bond of **1** to give a cation radical-anion radical pair analogous to that represented by **4**.^{2d} Conversion of **4** into **5** followed by rearrangement to **6** and back electron transfer¹³ to yield **3** would explain the formation of the rearranged product. The formation of only **3e** in tetrahydrofuran, benzene, or acetonitrile¹⁴ coupled with the relatively low yield of **3e** and the formation of **2e** as the major product in the nucleophilic solvent methanol suggests to us that **4** is an intermediate in the formation of both **2e** and **3e**. The presence of methanol as a nucleophile resulted in the interception of **4** prior to rearrangement.¹⁵

The last question to be addressed was whether **4** might rearrange directly to **6** via migration of C5 from C6 to either C1 or C7 of **4**. This possibility was eliminated through a study of the photoinduced rearrangement of **1b-d₁**,¹⁶ which gave **7** and **8** in the ratio of 1.24:1.¹⁷ No **3b** deuterated at the bridge-head position was found, which ruled out the migration of C5 from C6 to either C1 or C7.



(11) Compound **2e** showed the following properties: IR (neat) 3070, 2940, 2820, 1450, 1200, 1000 cm^{-1} ; ^1H NMR (C_6D_6) δ 3.12 (1 H, d, $J = 5.18$ Hz), 3.02 (3 H, s), 2.28–2.19 (2 H, m), 1.85–1.78 (1 H, m), 1.70–1.50 (4 H, m), 1.24 (1 H, d, $J = 9.62$ Hz), 1.00 (3 H, s), 0.80 (1 H, d of d, $J = 9.56$, $J = 6.21$ Hz), 0.55 (1 H, m), 0.36 (1 H, m), 0.20–0.08 (2 H, m); ^{13}C NMR (C_6D_6) δ 79.26 (d), 55.34 (q), 50.20 (s), 33.39 (d), 26.41 (t), 22.65 (t), 21.89 (t), 21.40 (s), 21.16 (q), 16.55 (t), 10.63 (t), 10.13 (t); mass spectrum, m/e found 182.1669 (calcd for $\text{C}_{12}\text{H}_{20}\text{O}$ 182.1670). Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{O}$: C, 79.94; H, 11.18. Found: C, 79.93; H, 11.18.

(12) These relative yields were in agreement with the limiting quantum yields of 0.01 and 0.02 for the formation of **3e** and **2e**, respectively. In THF, with a 10^{-3} M 1-CN concentration and 1.7×10^{-2} M concentration of **1e**, the quantum yield for fluorescence quenching of 1-CN was 0.21.

(13) It should be noted that back electron transfer to **5** from the 1-CN anion radical, followed by rearrangement of the zwitterion, would also produce **3**.

(14) The yields of **3e** from **1e** in benzene and acetonitrile were 66% and 28%, respectively. In acetonitrile, a large amount of oligomeric material was formed.

(15) On the basis of presently available data, we cannot establish whether a highly delocalized cation radical, where the cation radical character is shared between the C1-C7 bond and the C1-C2 bond, is involved. However, we are reluctant to propose the intermediacy of such a "nonclassical" cation radical.

(16) Treatment of **1b** with *n*-butyllithium followed by quenching with deuterium oxide gave **1b-d₁** which was 93% deuterated at C1 as determined by NMR and mass spectrometry.

(17) The ratio of **7** to **8** and the structural assignments were based on NMR analysis. This included extensive NOE studies.

In summary, we have elucidated some of the factors which control the behavior of photogenerated cation radicals. Our findings support the concept that one-electron carbon-carbon bonds are subject to molecular rearrangement if suitably strong carbocation-stabilizing groups are properly situated. We are continuing our efforts in this study of photogenerated cation radicals.

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(Trifluoromethyl)cyclopentadienide: A Powerful Electron-Withdrawing Ligand for Transition-Metal Complexes

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Recently, we have devoted considerable effort to the evaluation of the effects of substituents on the cyclopentadienyl moiety on the electronic character of complexed transition metals.¹ We have demonstrated through the use of X-ray photoelectron spectroscopy (XPS or ESCA) that methyl substitution can have a dramatic impact on the electronic properties of a series of complexed transition metals including titanium, zirconium, hafnium, and iron.^{1a,2} In terms of substituents, most attention has been devoted to the use of the pentamethylcyclopentadienyl moiety.^{3,4} By comparison, relatively little is known about cyclopentadienyl ligands bearing electron-withdrawing substituents.⁵ In view of the desirability of cyclopentadienyl complexes bearing electron-withdrawing substituents for certain catalytic processes,⁶ we found it surprising that the (trifluoromethyl)cyclopentadienyl group had not been developed as a transition-metal ligand. We now report the synthesis of a series of η^5 -(trifluoromethyl)cyclopentadienyl (CF_3Cp) complexes. In addition, we have demonstrated through the use of ESCA that the CF_3Cp ligand exercises a powerful electron-withdrawing effect on the complexed transition metal.

(Trifluoromethyl)cyclopentadiene (**1**) was prepared according to the method of Olsson and Wennerström.⁷ Since it was well established that **1** gave 6,6-disubstituted fulvenes on treatment with base, we chose to prepare the thallous salt **2**, through reaction of **1** with thallous ethoxide⁸ at -10 to -15 °C in diethyl ether for 15 min. The very insoluble CF_3CpTl (**2**) was isolated by filtration,

(1) (a) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470. (b) Gassman, P. G.; Macomber, D. W.; Willing, S. M. *J. Am. Chem. Soc.* **1985**, *107*, 2380. (c) Gassman, P. G.; Campbell, W. H.; Macomber, D. W. *Organometallics* **1984**, *3*, 385.

(2) See also: Calabro, D. C.; Hubbard, J. L.; Blevins, C. H., II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839 and references therein. Miller, E. J.; Landon, S. J.; Brill, T. B. *Organometallics* **1985**, *4*, 533.

(3) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.

(4) For general references, see: Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. Wolczanski, P. T.; Bercaw, J. E. *Ibid.* **1980**, *13*, 121. McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451. Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Ibid.* **1978**, *100*, 3939. Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *Ibid.* **1981**, *103*, 1265. Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *Ibid.* **1979**, *101*, 892. King, R. B. *Coord. Chem. Rev.* **1976**, *20*, 155. Schmidt, G. F.; Brookhart, M. J. *Am. Chem. Soc.* **1985**, *107*, 1443. Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508. Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *Ibid.* **1985**, *107*, 8091.

(5) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1. Conway, B. G.; Rausch, M. D. *Organometallics* **1985**, *4*, 688.

(6) Bönnerman, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248.

(7) Olsson, T.; Wennerström, O. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 293.

(8) Purchased from Aldrich Chemical Co. and used without purification.