JOC Article

An Annulene-Fused Cyclopentadienide. A Photochromic Cyclopentadienodimethyldihydropyrene Where the Fused Cyclopentadienide Group Resembles Benzene in Its Effect on the Dihydropyrene−Metacyclophanediene Valence Isomerization

Reginald H. Mitchell,* Wei Fan, Danny Y. K. Lau, and David J. Berg*

Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC, Canada V8W 3V6

regmitch@uvic.ca

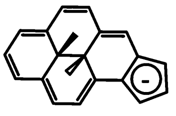
Received October 3, 2003

The synthesis of the green cyclopentadiene-fused dimethyldihydropyrene **12** was achieved in 36% yield in 7 steps from the parent dihydropyrene **3**. Reaction of **12** with KH or $LiCH_2SiMe_3$ gave the [14]annulene-fused cyclopentadienide anion quantitatively. In the ^{1}H NMR spectra, the internal methyl protons of **12** at δ −3.9, change dramatically on formation of anion **5**, becoming deshielded to δ −1.82. This is caused by the reduction in diatropicity of the [14]annulene ring on fusion to the 6π-cyclopentadienide ring. The anion is also a photochromic switch. Irradiation of the closed form **5** with visible light opens it to the open form **5′**, which reverts to the closed form **5** either with UV light or thermally. The switching behavior is between that of the parent **3**/**3′** and the benzannelated system **4**/**4′** and suggests that in its effect on the photoswitching, cyclopentadienide is behaving chemically similar to benzene.

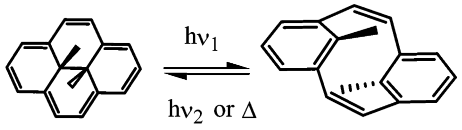
Introduction

The 6π cyclopentadienide anion is the archetypical nonbenzenoid "all-carbon" version of the prototype aromatic benzene.[1] As such it has been of interest ever since its synthesis by Thiele.[2] Its easy conversion to a plethora of "aromatic organometallics" such as ferrocene has only added to the studies performed on this molecule. In 1991, we[3] reported the preparation of the first large annulene-fused cyclopentadienide, the [*a*]-fused dihydropyrene **1**. Chemical shift data were used to estimate the relative aromaticity of the cyclopentadienide anion to be about 50% that of benzene. We have used the chemical shifts of both the internal and external protons of dimethyldihydropyrene as a probe for aromaticity,[4] and have extended such studies to cover a variety of organometallics.[5]

We thought it would be interesting if we could also use the dihydropyrene probe to give a chemical comparison between the cyclopentadienide anion and benzene. One very interesting property of the dimethyldihydropyrenes is the reversible photochromic switching between the dihydropyrene **2** and the metacyclophanediene **2′**.[6]



1



2 **2'**

Benzannelation substantially changes the ease with which this switching can take place.[7] Fusion at the [*a*]-position as in **1** essentially shuts down the photoswitching. However, fusion of aromatic rings at the [*e*]-position, for example **4**, substantially enhances the photoswitching.[7] We thus thought it would be interesting to prepare the [*e*]-fused cyclopentadienide pair **5**−**5′**, and determine whether the cyclopentadienide modifies the **3**−**3′** pair in the same way as benzene does in **4**−**4′**. This paper reports the results of this study.

Results and Discussion

Synthesis of the Diene 12. The synthesis of the cyclopentadiene fused derivative **12** from parent **3**[8] is

---

* Address correspondence to this author. Phone: 250-721-7159. Fax: 250-721-7147.

[1] Garratt, P. J. In *Aromaticity*; Wiley-Interscience: New York, 1986; Chapter 5. Lloyd, D. In *Nonbenzenoid conjugated carbocyclic compounds*; Elsevier: Amsterdam, The Netherlands, 1984; Chapter 2.

[2] Thiele, J. *Ber.* **1901**, *34*, 68.

[3] Mitchell, R. H.; Khalifa, N. A.; Dingle, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 6696−6697.

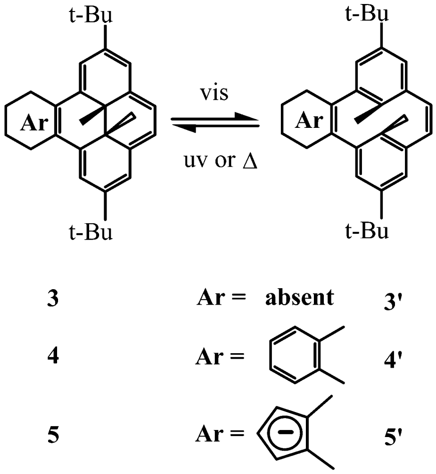
[4] Mitchell, R. H.; Iyer, V. S.; Khalifa, N.; Mahadevan, R.; Venugopalan, S.; Weerawarna, S. A.; Zhou, P. *J. Am. Chem. Soc.* **1995**, *117*, 1514−1532.

[5] Mitchell, R. H.; Chen, Y.; Khalifa, N.; Zhou, P. *J. Am. Chem. Soc.* **1998**, *120*, 1785−1794.

[6] Mitchell, R. H. *Eur. J. Org. Chem.* **1999**, 2695−2703.

[7] Mitchell, R. H.; Ward, T. R.; Chen, Y.; Wang, Y.; Weerawarna, S. A.; Dibble, P. W.; Marsella, M. J.; Almutairi, A.; Wang, Z. Q. *J. Am. Chem. Soc.* **2003**, *125*, 2974−2988.

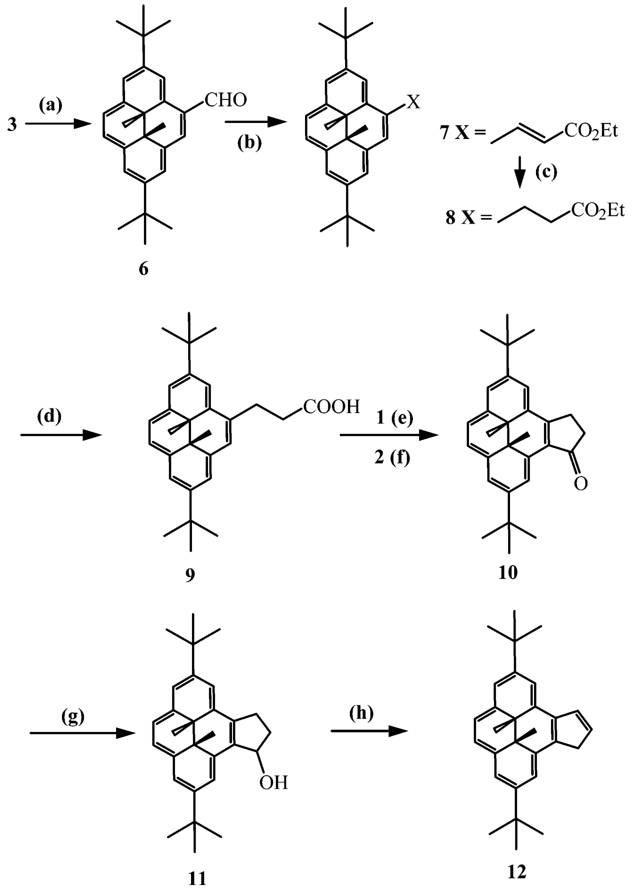
10.1021/jo0354589 CCC: $27.50



shown in Scheme 1. The original[9] formylation of the parent **3** used $SnCl_4$ as the catalyst; however, we found it easier to prepare aldehyde **6** on a larger (3 g) scale using $TiCl_4$, where a 44% yield (88% based on returned **3**) was obtained. Horner−Wittig reaction of aldehyde **6** gave 80% of ester **7**. Interestingly conjugation changes the green color of **3** to red-orange for both **6** and **7** and in the proton spectra of **7**, the *tert*-butyl groups are somewhat more differentiated (δ 1.688 and 1.654) than the internal methyl protons (δ −3.786 and −3.777). Palladium-catalyzed reduction of **7** gave 98% of green saturated ester **8**, which was directly hydrolyzed in 91% yield to give acid **9**. This acid was converted in one pot, first to the acid chloride with oxalyl chloride, and then was cyclized with BF_3 etherate to yield the dark red ketone **10** in 43% yield (65% based on returned acid **9**). Ketone **10** was reduced to alcohol **11**, which was directly eliminated with aq 2 M HCl to yield 88% (from **10**) of the green cyclopentadiene **12**. Since this compound is rather unstable, especially in chlorinated solvents, ketone **10** was stored and converted to **12** as needed. Full characterization of all compounds (except intermediate alcohol **11**) is given in the Experimental Section.

Generation of Anion 5. Reaction of cyclopentadiene **12** with either KH or $LiCH_2SiMe_3$ at 20 °C in THF produces a green solution of anion **5**. There is very little difference in the proton NMR spectra obtained when either base is used, and since the internal methyl protons appear as a singlet at δ −1.82, presumably the cation is rather loosely bound. These protons are, as expected,[3,4] substantially less shielded than those of **12** (δ −3.9), because of the reduced ring current in the [14]annulene ring on annelation with an aromatic species. These protons are also more shielded than those of benzo-derivative **4** (δ −1.58), consistent with a benzene ring having higher aromaticity than the Cp anion.[3] The external protons of **5** are affected by both the reduction in diatropicity of the [14]annulene ring and the dispersion of the negative charge, and so are substantially less deshielded than those of **12**. The relevant data are shown in Table 1. Even the *tert*-butyl protons reflect the reduced ring current in **5** over that of **12**.

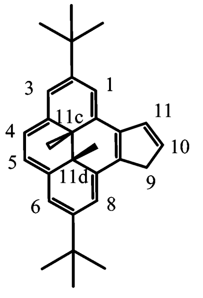
SCHEME 1[a]



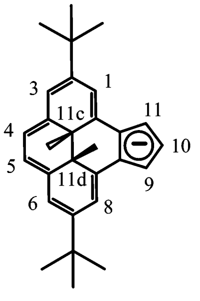
[a] Reagents and conditions: (a) Cl_2CHOCH_3, $TiCl_4$, CH_2Cl_2, 0 °C, 44% (88% based on recovered starting material); (b) $(EtO)_2POCH_2CO_2Et$, NaH, THF, 0 °C, 80%; (c) H_2, 10% Pd/C, EtOAc, 20 °C, 98%; (d) NaOH, THF/H_2O, 100 °C, 91%; (e) $(COCl)_2$, CH_2Cl_2, 20 °C; (f) $BF_3 \cdot OEt_2$, CH_2Cl_2, 20 °C, 43% (65% based on recovered starting material) on steps e and f; (g) $NaBH_4$, MeOH/THF, 20 °C; (h) 2 M aq HCl, THF, 20 °C, 88% on steps g and h.

TABLE 1. Comparison of ^{1}H NMR Chemical Shifts (d_8-THF, δ) of 12, 5(Li$^+$), and 5′(Li$^+$)

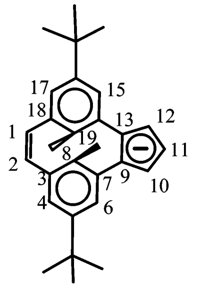
proton	12	5	proton	5′
1, 8	8.81, 8.68	7.62	6, 15	6.88
3, 6	8.53, 8.52	7.02	4, 17	6.53
4, 5	8.39, 8.37	6.87	1, 2	6.26
9	4.32, 4.29	6.98	10	5.88
10	6.86	6.65	11	5.61
11	7.97	6.98	12	5.88
11c,d-Me	−3.89, −3.91	−1.82	8,19-Me	1.33
2,7-*t*-Bu	1.73, 1.72	1.48	5,16-*t*-Bu	1.26



12



5



5'

---

(8) An improved large-scale preparation of **3** is given in the Supporting Information of ref 7.

(9) Miyazawa, A.; Yamato, T.; Tashiro, M. *J. Org. Chem.* **1991**, *56*, 1334−1337.

Interestingly, if the anion is generated in cyclohexane, benzene, or toluene, then a red solution is obtained rather than green, along with much red precipitate. If THF is then added, the solution immediately becomes green, the precipitate dissolves, and the same spectrum is observed as when made in THF. We believe that the same anion is formed in both solvents, but that it is much less soluble in the hydrocarbon solvents, and so aggregates (red), and in the ^{1}H NMR spectrum causes the signals to be rather broad in such solvents. Addition of d_8-THF immediately sharpens the signals, and gives the same spectrum as that when the anion is generated in THF. Such aggregation would be expected to affect ^{7}Li NMR spectra when run in different solvents. Indeed in d_8-THF, the ^{7}Li NMR spectrum of the fully closed anion shows a sharp singlet at δ −1.02, while in d_6-benzene, both a broad and a sharp signal are observed. If the THF sample is exposed to room light, the singlet moves upfield somewhat. Visible light opens the dihydropyrene (DHP) anion **5** to the cyclophanediene (CPD) anion **5′** (see below), and lithium ions would be expected to exchange between these two species, giving a single peak. Irradiation with more intense visible light forms a photostationary state, which is about 85% CPD and 15% DHP (see below), and then the singlet in the ^{7}Li NMR spectrum is observed at δ −2.72. Irradiation with UV light (or more slowly thermally) closes all the CPD form to the DHP form, and moves the signal back to δ −1.0. In d_6-benzene, however, the sharp peak at δ −10.6 and the broad peak at δ 0−4 (max at δ 1.5) behave differently on irradiation. The sharp peak disappears and the broad peak maximum shifts to about δ 1.9. The peak at δ −10 reappears slowly thermally. In THF, the difference in Li chemical shift between the open and closed forms does not appear to be as great (~1.7 ppm), and exchange is rapid, and so only an average signal is seen. In benzene, the sharp peak changes dramatically, suggesting that either exchange is slow (which seems unlikely) or perhaps that the open form of the anion precipitates and becomes part of the broad signal, which dissolves again as it closes thermally.

The UV−visible spectrum of anion **5** at first sight appears actually not to be very different from that of cyclopentadiene **12**, both being dominated by the main dihydropyrene bands around 365 and 395 nm. Closer inspection, however, shows that the 365-nm band of **12** has moved to 350 nm in **5**, and the 350-nm band has intensified somewhat (relative to the 395-nm band) over that of the 365-nm band. In diene **12** there is very little absorption between 540 and 640 nm, while in anion **5** there is extensive tail absorption ($\epsilon \sim 4000-800$) in this region, which probably accounts for the increase in color intensity observed when **12** is converted to **5**. The spectra are shown in the Supporting Information.

Photoswitching Properties. The quantum yield for the visible light opening reaction of dihydropyrene (DHP) **3** to metacyclophanediene (CPD) **3′** is very low, $\phi = 0.0015$.[10] Benzannelation substantially increases this value by 28 times to $\phi = 0.042$ in the **4** to **4′** reaction. Opening of the naphthannelated derivative goes even faster.[7] If chemically, the Cp anion of **5** is resembling benzene, then **5** should also photoopen faster than cyclopentadiene **12**. Indeed the latter cycloalkene-fused dihydropyrene photoopens even slower (if at all) than its parent **3**, since irradiation of a C_6D_6 solution of **12** with light of wavelength >490 nm (from a 500W Tungsten lamp with filter) for 12 h produced no changes in its ^{1}H NMR spectrum. The benzo-derivative **4**, irradiated at the same time and under the same conditions, completely opened to **4′** in 8 min.

For comparison purposes, equimolar solutions of anion **5-Li$^+$** and **4** in d_8-THF were irradiated parallel to each other with the same lamp at the same time. ^{1}H NMR spectra were recorded at intervals, so that the relative rates of opening could be determined. Anion **5** does photoopen to **5′**, but not as fast as the benzo-derivative **4** to **4′**. The relative rate $k_{\mathbf{5-5'}}/k_{\mathbf{4-4'}}$ is about 0.22. It is not obvious why the quantum yields of opening in the dihydropyrenes are as low as they are,[10,13] and many factors may be contributing. However, fusion of an aromatic ring at the [*e*]-position does seem to increase the efficiency of the photoopening reaction. The Cp anion precursor **12** opens extremely slowly or not at all (relative to **3**), and so in the sequence no group fused, Cp anion fused, and benzene fused, the ring-opening reactivity does seem to be in an aromaticity order, with the Cp anion having a (reduced) benzene-like effect on the photochemical opening reaction.

Continued irradiation of **5** allows about 85% opening to **5′**, when a photostationary state appears to be reached. The chemical shifts of the open form, **5′**, are also shown in Table 1 above, and are dramatically different from the closed form **5**. For example, the internal methyl protons move from δ −1.82 to δ +1.33, no longer being in the center of the large annulene ring.

The UV closing reaction, e.g. **3′** to **3**, is fast for most of the systems studied.[7] Anion **5′** is no exception. When equimolar solutions of **4′** and **5′** in d_8-THF were irradiated side by side with a pencil mercury lamp, anion **5′** actually closed at about 1.5 times the rate of the benzo-derivative **4′**.

The Thermal Closing Reaction. Although Woodward−Hoffmann forbidden, the closing reaction, e.g. **3′** to **3**, also occurs thermally.[6,7,11] Benzannelation substantially slows the thermal closing reaction: At 46 °C, $\tau_{1/2} = 1.88$ h for **3′**, while for **4′** $\tau_{1/2} = 5.75$ h. For anion **5′**, the corresponding $\tau_{1/2}$ is 2.1 h (determined from the ^{1}H NMR changes, see the Experimental Section). The thermal closing can also be followed by the change in the ^{7}Li NMR spectra, and then at 46 °C a $\tau_{1/2}$ of 2.3 h is obtained, in excellent agreement with the proton value. The anion thus thermally closes faster than the benzo-compound **4′** but not as fast as the parent **3′**. In this case, the thermal closing rates are more affected by changes in solvation than in the purely hydrocarbon counterparts such as **3′** and **4′**. This is reflected in a larger value of $\Delta S^{\ddagger}$ for **5′** (−12(±0.4) cal K^{-1} mol^{-1}, derived from both ^{1}H and ^{7}Li data) than for **4′** (+3.8 cal K^{-1} mol^{-1}) or **3′** (+4.3 cal K^{-1} mol^{-1}). We do not yet fully understand the

---

[10] Sheepwash, M. A.; Mitchell, R. H.; Bohne, C. *J. Am. Chem. Soc.* **2002**, *124*, 4693−4700.

[11] Schmidt, W. *Helv. Chim. Acta.* **1971**, *54*, 862−868. Schmidt, W. *Tetrahedron. Lett.* **1972**, *12*, 581−584.

[12] Dr. R. V. Williams (University of Idaho), who has considerable experience in DHP calculations, is attempting to model this process.

[13] Sheepwash, M. A.; Ward, T. R.; Wang, Y.; Bandyopadhyay, S.; Mitchell, R. H.; Bohne, C. *Photochem. Photobiol. Sci.* **2003**, *2*, 104−122.

thermal closing reaction,[7] but one of the factors that enters in to ΔH(**5**−**5′**) is the aromaticity of the [*e*]-fused ring. In comparing DHP's with different fused rings, systems in which the aromaticity (actually the bond localization energy of the fusion bond) of the fused ring is less have a smaller ΔH_f between the open and closed forms. Here, $\Delta H^{\ddagger}$ for the closing of **5′** is smaller (20.7(±0.4) kcal mol^{-1}) than that for the closing of **4′** (23.9 kcal mol^{-1}), which is consistent with the reduced aromaticity of the cyclopentadienide anion relative to benzene.[3] However, it must be stressed that this is only one of the contributing factors,[7] since $\Delta H^{\ddagger}$ for the closing of the parent **3′** is 23.3 kcal mol^{-1}. The E_{act} value for the thermal closing reaction is also reduced: **5′** (21.1(±0.4) kcal mol^{-1}), **4′** (24.5 kcal mol^{-1}), and **3′** (24.0 kcal mol^{-1}). Since the closing reaction breaks Woodward−Hoffmann rules, it is likely that it is not concerted, yet finding the true nature of the transition state by calculation is proving to be a substantial challenge.[12] We hope that as we acquire more data on a variety of annelated systems, we will better be able to comment on this process in the future.

At 20 °C, $\tau_{1/2}$ for the closing reaction is 46−47 h (^{1}H and ^{7}Li data), and so is thermally stable enough to be studied; for example, ^{13}C NMR data are given in the Experimental Section, and its UV spectrum is shown in the Supporting Information.

Photoswitching of Ketone 10. While, as stated above, the quantum yield for the photoopening reaction of the parent **3** to **3′** is low, $\phi = 0.0015$, we have shown[10] that for 4-acetyl-**3** the quantum yield is greater, $\phi = 0.0038$; likewise that for 4-acetyl-**4** ($\phi = 0.095$) was greater than that for **4** ($\phi = 0.042$).[13] Since in ketone **10** the cyclopentanone is in essence a restricted acetyl group, we thought its photoopening would be interesting. Indeed, ketone **10** photoopens considerably faster than **3**, in fact about half as fast as **4**. Substitution of a carbonyl group next to the dihydropyrene ring evidently has an interesting acceleration of the photoopening reaction, which is different from that of an alkene (see below) and which we will pursue in the future. Unfortunately, when **10** is photoopened and then photoclosed with UV, some decomposition occurs, and so not many cycles are possible. We noted above that in **12**, which has alkenyl substitution on **3**, the photoopening reaction appears to be shut down completely. This effect of alkenyl substitution has been noticed in the dithenylcyclopentene photochromes,[14] but fortunately does not extend to the cyclically conjugated anion **5**.

Conclusions

The cyclopentadienide-fused DHP-CPD switch **5**/**5′** is photochromic and is intermediate in behavior between the parent switch **3**/**3′** and the benzannelated switch **4**/**4′**. As far as we know, it is the first cyclopentadienide that has been built in to a photochromic switch. While not quantifiable in this work, it does appear that chemically, the Cp anion is affecting the DHP-CPD switch in a similar but weaker fashion than does benzene. Thus in both the photoopening reaction and the thermal closing reaction, the following "aromaticity order" sequence is observed: no aromatic ring fused, Cp anion fused, and benzene fused.

Experimental Section

General Information. See the Supporting Information. Note: For NMR data, H-1,2 means H-1 and H-2, while H-1/2 means H-1 or H-2.

2,7-Di-*tert*-butyl-4-formyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (6). This is a modified procedure of Miyazawa[9] suitable for a larger scale. TiCl$_4$ (12.00 mL. 100 mmol) was added with stirring under N$_2$ to a solution of dihydropyrene **3**[8] (6.88 g, 20.0 mmol) and Cl$_2$CHOCH$_3$ (2.40 mL, 28.0 mmol) in CH$_2$Cl$_2$ (650 mL) at 0 °C. The resulting red-brown solution then was stirred at 20 °C for 5 h, and then added slowly to ice−water (700 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (500 mL) and then the combined organic layers were washed with water, dried (MgSO$_4$), and evaporated. The resulting brown solid was chromatographed over silica gel. Unchanged green **3** (3.45 g, 10.0 mmol, 50%) was eluted first with hexanes. Then hexanes−CH$_2$Cl$_2$ (1:1) eluted the product **6** (3.24 g, 44%) as dark red-orange (almost brown) crystals, mp 192−194 °C (lit.[9] mp 193−194 °C), identical with an authentic sample.

Ethyl 3-[4′-(2′,7′-Di-*tert*-butyl-*trans*-10b′,10c′-dimethyl-10b′,10c′-dihydropyrenyl)]propenoate (7). Triethyl phosphonoacetate [(EtO)$_2$POCH$_2$CO$_2$Et] (8.90 mL, 45 mmol) was added to a stirred suspension of 60% NaH (4.32 g, 180 mmol) in dry THF (450 mL) under N$_2$ at 0 °C. After 1 h, a solution of aldehyde **6** (5.58 g, 15.0 mmol) in dry THF (500 mL) was added dropwise, and then the mixture was allowed to stir without further cooling for an additional hour. Saturated NH$_4$Cl solution (500 mL) was then added, and the solution was extracted with CH$_2$Cl$_2$ (4 × 500 mL). The combined organic extracts were washed well with water, dried, and evaporated to a dark brown solid. This was chromatographed over silica gel, with hexane−CH$_2$Cl$_2$ (1:3) as eluant to yield 5.3 g (80%) of ester **7** as dark reddish brown crystals from MeOH, mp 165−166 °C. ^{1}H NMR (360 MHz) δ 9.16 (d, $J = 15.6$ Hz, 1H, H-3), 8.89 (s, 1H, H-3′), 8.69 (s, 1H, H-5′), 8.483 (s, 1H, H-1′), 8.475 (s, 1H, H-6′/8′), 8.46 (s, 1H, H-8′/6′). 8.42 (AB, $J = 8.2$ Hz, 1H, H-9′), 8.38 (AB, 1H, H-10′), 6.83 (d, $J = 15.6$ Hz, 1H, H-2), 4.37 (q, $J = 7.1$ Hz, 2H, −OCH_2CH$_3$), 1.69 and 1.65 (s, 9H each, *t*-Bu), 1.41 (t, $J = 7.1$ Hz, 3H, OCH$_2$CH_3), −3.777 and −3.786 (s, 3H each, CH$_3$-10c′,10b′); ^{13}C NMR (90.6 MHz) δ 167.92 (C-1), 147.73/146.47 (C-2′/7′), 141.55 (C-3), 138.94/137.12/136.88/136.46 (C-3a′/5a′/10a′/10d′), 124.73 (C-9′/10′), 124.64 (C-4′), 123.87 (C-10′/9′), 122.32/121.70/121.55 (C-1′/6′/8′), 119.73 (C-5′), 117.02 (C-2), 115.93 (C-3′), 60.33, 36.43/35.88 (C(CH$_3$)$_3$), 31.84/31.75 (C(CH$_3$)$_3$, 31.45 (C-10b′), 29.87 (C-10c′), 15.34/15.21 (10b′,10c′-CH$_3$), 14.49; IR (KBr) ν 1700, 1608, 1286, 1169, 1158, 1034, 970, 886, 867, 674, 660 cm^{-1}; HRMS *m*/*z* calcd for C$_{31}$H$_{38}$O$_2$ 442.2872, found 442.2874. Anal. Calcd: C, 84.12; H, 8.65. Found: C, 83.83; H, 8.79.

Ethyl 3-[4′-(2′,7′-Di-*tert*-butyl-*trans*-10b′,10c′-dimethyl-10b′,10c′-dihydropyrenyl)]propanoate (8). Palladium on activated charcoal (300 mg, 10%) was added to the unsaturated ester **7** (3.98 g, 9.00 mmol) in EtOAc (500 mL) and then the mixture was stirred under H$_2$ (1 atm) at 20 °C for 3 h, during which time the mixture turned green. The catalyst was removed on Celite, which was washed with CH$_2$Cl$_2$ (3 × 75 mL), and then the combined solutions were evaporated to give a green residue. This was chromatographed over silica gel with hexane−CH$_2$Cl$_2$ as eluant to yield 3.92 g (98%) of the saturated ester **8** as a green oily solid. This could not be crystallized satisfactorily, though by ^{1}H NMR it was sufficiently pure to be used directly in the next step. ^{1}H NMR (500 MHz) δ 8.66 (s, 1H), 8.47 (s, 1H), 8.44 (s, 1H), 8.43 (s, 1H), 8.364 (AB, $J = 8$ Hz, 1H), 8.359 (AB, 1H), 8.34 (s, 1H), 4.08 (t, $J = 7$ Hz, 2H), 3.93 (q, $J = 7$ Hz, 2H), 2.96 (t, $J = 7$ Hz, 2H), 1.68 and 1.65 (s, 9H each), 1.14 (t, $J = 7$ Hz, 3H), −3.97 and −4.02 (s, 3H each);

---

(14) Bens, A. T.; Frewert, D.; Kodatis, K.; Ktyschi, C.; Martin, H−D.; Trommsdorff, H. P. *Eur. J. Org. Chem.* **1998**, 2333−2338.

^{13}C NMR (125.8 MHz) δ 173.72, 145.99, 145.00, 137.13, 137.07, 136.92, 132.86, 132.02, 124.64, 123.01, 122.61, 120.85, 120.54, 120.49, 117.10, 60.59, 37.02, 36.33, 36.13, 32.25, 32.13, 30.13, 29.95, 29.43, 14.81, 14.61, 14.39; HRMS *m*/*z* calcd for $C_{31}H_{40}O_2$ 444.3028, found 444.3029.

3-[4′-(2′,7′-Di-*tert*-butyl-*trans*-10b′,10c′-dimethyl-10b′,10c′-dihydropyrenyl)]propanoic Acid (9). The crude saturated ester **8** from above (3.52 g, 7.92 mmol) in THF (400 mL) was mixed with 2 M NaOH (740 mL) and refluxed for 16 h under argon. The solution was cooled and then neutralized with 2 M HCl (740 mL) and then was extracted with CH_2Cl_2. The combined organic extracts were washed, dried, and evaporated to a green residue. This was chromatographed over silica gel with CH_2Cl_2 as eluant to yield 3.0 g (91%) of the acid as a green solid by evaporation from CH_2Cl_2, mp 161−162 °C. ^{1}H NMR δ (500 MHz) 11.5−10.0 (v br s, 1H, −COOH), 8.66 (s, 1H), 8.48 (s, 1H), 8.45 (s, 1H), 8.44 (s, 1H), 8.373 (AB, J = 8.7 Hz, 1H), 8.369 (AB, 1H), 8.35 (s, 1H), 4.00−3.89 (m, 2H), 3.09−2.96 (m, 2H), 1.66 and 1.68 (s, 9H each), −3.96 and −4.01 (s, 3H each); ^{13}C NMR (125.8 MHz) δ 178.20, 146.06, 145.08, 137.11, 137.09, 136.95, 132.83, 131.50, 124.48, 123.35, 123.09, 122.70, 120.91, 120.62, 117.01, 36.44, 36.36 (C-2), 36.14, 32.25/32.13 ($C(CH_3)_3$), 30.15/29.94 (C-10b,c), 29.02 (C-3), 14.84, 14.64; IR (KBr) ν 3300−2600 (br, −COOH), 1706, 883, 668 cm^{-1}; HRMS *m*/*z* calcd for $C_{29}H_{36}O_2$ 416.2715, found 416.2710. Anal. Calcd: C, 83.61; H, 8.71. Found: C, 83.55; H, 8.77.

2,7-Di-*tert*-butyl-*trans*-11c,11d-dimethyl-9,10,11c,11d-tetrahydro-11-oxo-11H-cyclopenta[*e*]pyrene (10). Oxalyl chloride (5.27 mL, 60 mmol) was added at 20 °C under argon with stirring to a solution of acid **9** (5.00 g, 12 mmol) in dry CH_2Cl_2 (700 mL). After the solution was stirred for 6 h, the solvent was evaporated (under vacuum) and the green residue was pumped upon for an additional 30 min to remove all chlorinating reagent. The oily residue was then redissolved in dry CH_2Cl_2 (1 L) and $BF_3{\cdot}OEt_2$ (3.05 mL, 24 mmol) was added, and the mixture was stirred at 20 °C for 12 h. Ice−water was then added and the organic extracts were washed, dried, and evaporated to a reddish brown solid. This was chromatographed on silica gel with hexane−CH_2Cl_2 (1:1) to elute 2.06 g (43%, 65% based on returned acid) of the dark red ketone **10**. Elution with CH_2Cl_2 then eluted returned acid **9** (1.66 g, 33%).

Ketone **10** as crystallized by evaporation of a hexane−CH_2Cl_2 solution had mp 185−187 °C. ^{1}H NMR (500 MHz) δ 9.84 (s, 1H, H-1), 8.72 (d, J = 1.0 Hz, 1H, H-8), 8.50 (s, 1H, H-6), 8.40 (s, 1H, H-3), 8.35 (AB, J = 7.26 Hz, 1H, H-5), 8.25 (AB, 1H, H-4), 3.97 and 3.87 (each dt, J = 17.2, 5.9 Hz, 2H, H-9), 3.10 (∼t, J = 6 Hz, 2H, H-10), 1.677 and 1.669 (s, 9H each, 2,7-$C(CH_3)_3$), −3.71 and −3.74 (s, 3H each, 11c,d−CH_3); ^{13}C NMR (125.8 MHz) δ 208.95 (C-11), 150.47 (C-2), 149.26 (C-11f), 144.55 (C-7), 139.73 (C-3a), 136.31 (C-5a), 133.02 (C-11b), 130.49 (C-11e), 125.98 (C-11a), 125.05 (C-5), 124.04 (C-6), 122.45 (C-4), 120.85 (C-8), 120.63 (C-3), 119.09 (C-1), 37.52 (C-10), 36.47 (2-$C(CH_3)_3$), 35.95 (7-$C(CH_3)_3$), 31.93 (2-$C(CH_3)_3$), 31.78 (7-$C(CH_3)_3$), 31.33 (C-11c), 30.44 (C-11d), 24.66 (C-9), 15.40 (11c-CH_3), 14.77 (11d-CH_3); IR (KBr) ν 1681, 1462, 1261, 1211, 883 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ϵ_{max}) nm 340 (32 000), 365 (32 000), 400 (39 000), 485 (6400), 510 (7100), 605 (1300), 670 (4400); HRMS *m*/*z* calcd for $C_{29}H_{34}O$ 398.2610, found 398.2612. Anal. Calcd: C, 87.39; H, 8.60. Found: C, 87.44; H, 8.58.

2,7-Di-*tert*-butyl-*trans*-11c,11d-dimethyl-11c,11d-dihydro-9*H*-cyclopenta[*e*]pyrene (12). $NaBH_4$ (200 mg, mmol) was added to a stirred solution of ketone **10** (180 mg, 0.45 mmol) in MeOH−THF (1:1, 180 mL) under argon at 20 °C and stirring was continued for 2 h, when the solution had become green. Ice−water was then added, followed by CH_2Cl_2. The organic extracts were washed, dried, and evaporated to alcohol **11** as a green solid. This was dissolved in degassed THF (30 mL), and under argon, degassed aq HCl (2 M, 30 mL) was added with stirring at 20 °C. The mixture was stirred for 1 h and then ice−water and CH_2Cl_2 were added. The organic extracts were washed, dried, and evaporated and the green residue was flash chromatographed over silica gel under argon with hexanes as eluant and on evaporation gave 150 mg (88%) of yellow-green cyclopentadiene **12**, mp ∼184 °C dec. This compound is not very stable, especially in chlorinated solvents, and is best generated from ketone as required. ^{1}H NMR (500 MHz, C_6D_6) δ 8.89 (d, J = 1.0 Hz, 1H, H-1), 8.71 (d, J = 1.2 Hz, 1H, H-8), 8.60 (s, 1H, H-3), 8.59 (s, 1H, H-6), 8.45 and 8.43 (AB, J = 7.7 Hz, 2H, H-4/5), 7.90 (dt, J = 5.6, 1.9 Hz, 1H, H-11), 6.63 (dt, J = 5.6, 2.1 Hz, 1H, H-10), 4.04 and 4.09 (dt, J = 23, 2 Hz, 2H, H-9), 1.68 (s, 9H, 7-$C(CH_3)_3$), 1.65 (s, 9H, 2-$C(CH_3)_3$), −3.48 (s, 3H, 11c-CH_3), −3.51 (s, 3H, 11d-CH_3) [for ^{1}H data in d_8-THF see Table 1]; ^{13}C NMR (125.8 MHz, C_6D_6) δ 145.21 (C-7), 144.47 (C-2), 139.03 (C-11a), 137.36 (C-5a), 136.65 (C-11f), 136.61 (C-3a), 133.53 (C-10), 131.85 (C-11), 131.27 (C-11e), 129.40 (C-11b), 123.64 (C-4), 123.03 (C-5), 121.24 (C-3), 120.60 (C-6), 117.54 (C-1), 116.37 (C-8), 38.82 (C-9), 36.09 (7-$C(CH_3)_3$), 36.05 (2-$C(CH_3)_3$), 32.15 (7-$C(CH_3)_3$), 32.08 (2-$C(CH_3)_3$), 31.46 (C-11c), 31.40 (C-11d), 15.44 (11c-CH_3), 15.13 (11d-CH_3); IR (KBr) ν 3030, 883, 867, 730, 690, 668, 634 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ϵ_{max}) nm 365 (41 000), 395 (36 000), 470 (7500), 490 (9000), 675 (1300) [note: in THF the last two maxima shift to 495 and 670 nm]; HRMS *m*/*z* calcd for $C_{29}H_{34}$ 382.2660, found 382.2665. Anal. Calcd: C, 91.04; H, 8.96. Found: C, 90.79; H, 9.21.

Generation of Lithium [or Potassium] Cyclopentadienide 5. Diene **12** (5 mg, 0.013 mmol) was dissolved in d_8-THF (0.6 mL) in a sealable NMR tube under nitrogen. $LiCH_2SiMe_3$ (1.3 mg, 0.014 mmol) [or KH (∼0.6 mg, 0.014 mmol)] was added at 20 °C, and the tube was sealed and shaken. The anion formed immediately as a dark green solution. ^{1}H NMR (500 MHz, d_8-THF) δ 7.62 (d, J = 1.5 Hz, 2H, H-1,8), 7.02 (d, J = 1.5 Hz, 2H, H-3,6), 6.98 (d, J = 3.4 Hz, 2H, H-9,11), 6.87 (s, 2H, H-4,5), 6.65 (t, J = 3.4 Hz, 1H, H-10), 1.48 (s, 18H, 2,7-$C(CH_3)_3$), −1.82 (s, 6H, 11c,d-CH_3); ^{13}C NMR (90.6 MHz, d_8-THF) δ 143.94 (C-2,7), 138.73 (C-11b,e), 138.38 (C-3a,5a), 122.53 (C-11a,f), 117.55 (C-4,5), 113.16 (C-3,6), 112.55 (C-10), 107.78 (C-1,8), 99.08 (C-9,11), 37.87 (C-11c,11d), 35.76 (2,7-$C(CH_3)_3$), 31.69 (2,7-$C(CH_3)_3$), 18.97 (11c,d-CH_3). When d_8-Toluene or d_6-Benzene was used as the solvent, similar proton spectra with much broader lines were observed. When d_8-THF was added, normal spectra were obtained. UV−vis (cyclohexane) λ_{max} (ϵ_{max}) nm 345 (35 000), 350 (36 000), 390 (28 000), 395 (29 000), 490 (8000), 655 (780) (tail absorption between 500 and 700, see the Supporting Information).

Photoopening of Dihydropyrene Anion 5 to Cyclophanediene Anion 5′. The NMR sample of **5** from above was placed inside a cold water jacket and irradiated with a 500-W tungsten lamp with use of a 490-nm filter such that the sample was irradiated with visible light of >490 nm wavelength. After ∼30 min of irradiation, a photostationary state was reached where NMR indicated about 85% of the open form, the CPD anion **5′**, had formed: ^{1}H NMR (300 MHz, d_8-THF) δ 6.88 (d, J = 2 Hz, H-6,15), 6.53 (d, J = 2 Hz, H-4,17), 6.26 (s, H-1,2), 5.88 (d, J = 4 Hz, H-10,12), 5.61 (t, J = 4 Hz, H-11), 1.33 (s, 8,19-CH_3), 1.26 (s, 2,7-$C(CH_3)_3$); ^{13}C NMR (360 MHz, d_8-THF) δ 148.65, 144.29, 139.20, 137.76, 132.54, 125.84, 124.98, 122.50, 104.25, 103.52, 34.60, 32.17, 20.85; for the UV−vis spectrum of the 85% photostationary state see the Supporting Information.

For the relative rate studies, in separate NMR tubes, anion **5** was prepared from **12** (1.8 mg, 4.7 × 10^{-3} mmol) and $LiCH_2SiMe_3$ (1 mg) in d_8-THF (0.6 mL) such that for the anion $c = 8 \times 10^{-3}$ M, and for the benzo-derivative **4**, $c = 8 \times 10^{-3}$ M from 1.9 mg of **4** in 0.6 mL of d_8-THF. The tubes were sealed under argon and irradiated side by side at the same time, as above, but the tubes were monitored after selected periods of time by ^{1}H NMR. The apparent relative rate constants (assuming constant and excess light flux) for the photoopening reaction were obtained with use of the following equation: $\ln(c_0/c_t) = kt$, where c_0 is the mole fraction of the closed form at the beginning of the experiment (1 in this case), and c_t is the mole fraction of the closed form at each time = closed/(closed + open). The plot of $-\ln(c_t)$ vs t (s) was linear (available in the Supporting Information), and yielded apparent rate constants of 8.0×10^{-4} s^{-1} for **5** and 36×10^{-4} s^{-1} for **4**. The relevant data are the ratio of these constants, $k_{\mathbf{5}}/k_{\mathbf{4}}$, which was found to be about 0.22.

The Photoclosing Reaction of 5′ to 5. The samples above which had been irradiated to open both **5** and **4** to **5′** and **4′**, respectively, as far as possible, were then placed side by side in front of a pencil Hg UV lamp with a short wave filter. Their ^{1}H NMR spectra were then monitored at selected time intervals of irradiation, and the results were plotted as above for the photoopening such that the apparent rate of photoclosing for **5** was 2.5×10^{-4} s^{-1} and that for **4** was 1.6×10^{-4} s^{-1}, leading to a ratio of rates, $k_{\mathbf{5'}}/k_{\mathbf{4'}}$, of 1.5. The graphs are shown in the Supporting Information.

The Thermal Closing Reaction of 5′ to 5. The sample above (in d_8-THF), which had been irradiated to open **5** to **5′**, was placed in a constant-temperature bath at 34 °C and subsequently 39.5 and 54 °C, and ^{1}H NMR was used to follow the thermal closing reaction at each temperature. As before, the mole ratio (c_t), **5′**/(**5′** + **5**), was determined by integration at each time interval, t. Plotting $-\ln(c_t)$ vs t then gave the first-order rate constant (k) for the closing reaction. At these three temperatures, the values of k found were 2.33, 4.50, and 21.2×10^{-5} s^{-1}. Likewise by using the ^{7}Li NMR spectra at 30, 40, 50, and 60 °C, the mole fraction open was plotted against time and fitted to an exponential plot, yielding rate constants of 1.52, 3.79, 14.6, and 34.9×10^{-5} s^{-1}. The ^{1}H and ^{7}Li data could be treated separately (and in fact yield the same results with slightly higher error bars), but since they measure the same rate constants and are in the same solvent, they are better combined, and so a Eyring plot yielded $\Delta H^{\ddagger} = 20.7(\pm 0.4)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -12.4(\pm 0.4)$ cal K^{-1} mol^{-1} and an Arrhenius plot yielded $E_{act} = 21.1(\pm 0.4)$ kcal mol^{-1}. The graphs are shown in the Supporting Information. Also shown there is a plot of the temperature dependence of the ^{7}Li chemical shift for both the closed form **5** and the open form **5′**. Fortunately, the shift difference is greatest at lower temperatures, which makes observing the change in chemical shift possible at the slower reaction rates at lower temperatures.

Photoopening of the Ketone 10. This was carried out exactly as described for **5** above. The ratio of the photoopening rate constants, $k_{\mathbf{10}}/k_{\mathbf{4}}$, is 0.45. The graphs are shown in the Supporting Information.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for financial support.

Supporting Information Available: General experimental information; the UV−vis spectra of anion **5** and alkene **12**; graphs of the photoopening, photoclosing, and thermal closing rate data (^{1}H and ^{7}Li) for **4** and **5**, and Eyring and Arrhenius plots for **5**; a graph of the temperature dependence of the ^{7}Li chemical shift for **5** and **5′**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0354589