Thermal Rearrangements and Reactions of 5-Alkyl-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienes

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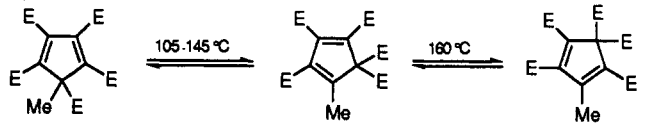
Studies of the thermal reactions of five 5-alkyl-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienes in methanol solvent are described, where the alkyl groups are benzhydryl, methoxymethyl, 1-adamantyl, *p*-methoxybenzyl, and benzyl. The benzyl cyclopentadiene system undergoes thermal [1,5]-sigmatropic rearrangement via methoxycarbonyl migrations while the other cyclopentadienes undergo C–alkyl bond heterolysis to ion-pair intermediates, which are scavenged by solvent. First-order rate constants for solvolysis of the methoxymethyl, 1-adamantyl, and *p*-methoxybenzyl systems in methanol solvent were determined and that for the benzhydryl system was estimated from a single measurement of the half-life.

Introduction

Cyclopentadienes generally undergo thermal rearrangement by [1,5]-sigmatropic migration of a substituent from the tetrahedral carbon center. The migrating group remains continuously and covalently bonded to the rest of the molecule as transfer from one ring atom to another proceeds. Numerous experimental studies[1] support the idea that this process occurs in a concerted manner, but a transition state for cyclopentadiene rearrangements that is more polar than the ground state has been suggested.[2]

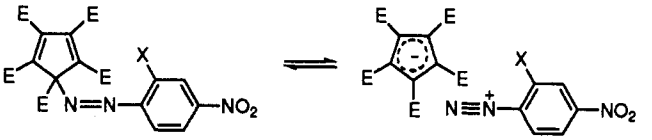
Hoffmann and co-workers investigated the thermal rearrangements of several 5-alkyl-1,2,3,4,5-pentakis-(methoxycarbonyl)cyclopentadienes.[3] The methoxycarbonyl substituent is known to have a high migratory aptitude in [1,5]-sigmatropic rearrangements[4] and this is generally attributed to secondary orbital interactions in the transition state for rearrangement.[5] An example of a "typical" rearrangement of these cyclopentadiene systems is that of 1 (alkyl = Me, Scheme 1).[3b] Between 105 and 145 °C in 1,2-dichlorobenzene, equilibrium was set up between 1 and 2 by [1,5]-sigmatropic methoxycarbonyl shifts. At higher temperatures (160 °C) another methoxycarbonyl shift took place and 1 (34%), 2 (29%), and 3 (37%) were obtained in solution. Hoffmann's investigations suggest that simple 5-alkyl-1,2,3,4,5-pentakis (methoxycarbonyl)cyclopentadienes generally rearrange by [1,5]-sigmatropic methoxycarbonyl migrations.

Scheme 1



1 (E = CO_2Me) 2 3

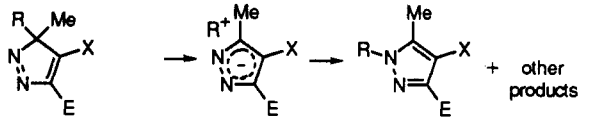
Scheme 2[a]



4a–f (E = CO_2Me) 5a–f

[a] a, X = H; b, X = I; c, X = Cl; d, X = Br; e, X = OMe; f, X = Me.

Scheme 3[a]



6a–e (X = E = CO_2Me)
6f–i (X = H, E = CO_2Me)

[a] a, R = $CHPh_2$; b,f, R = CMe_3; c,g, R = CH_2OCH_3; d,h, R = 1-adamantyl; e,i, R = *p*-$CH_2C_6H_4OMe$.

In contrast to the rearrangement of 1, 5-(arylazo)-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienes **4a–f** undergo stepwise circumambulatory thermal rearrangement *via* reversible formation of ion-pair intermediates (**5a–f**) in benzonitrile.[6] Electron-donating substituents in the ortho position of the arylazo ring were found to enhance the rate of the exchange process, presumably because of the increased stabilization of the intermediate diazonium cation (Scheme 2).

The discovery that 3*H*-pyrazoles **6a–i**, bearing alkyl migrating groups which are relatively stable in cationic form, undergo thermal rearrangement (Scheme 3) by a stepwise mechanism via ion-pair intermediates,[7] raised a question about the generality of rearrangement by such a mechanism. Do cyclopentadienes such as **7a–e** (Scheme

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(2) (a) Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. *Tetrahedron* **1963**, *19*, 1939. (b) Kahn, S. D.; Hehre, N. G.; Rondan, N. G.; Houk, K. N. *J. Am. Chem Soc.* **1985**, *107*, 8291. (c) Replogle K. S.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 5751.

(3) (a) Schmidt, P.; Hoffmann, R. W.; Backes, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 513. (b) Hoffmann, R. W.; Schmidt, P.; Backes, J. *Chem. Ber.* **1976**, *109*, 1918. (c) Hoffmann, R. W.; Backes, J. *Chem. Ber.* **1976**, *109*, 1928.

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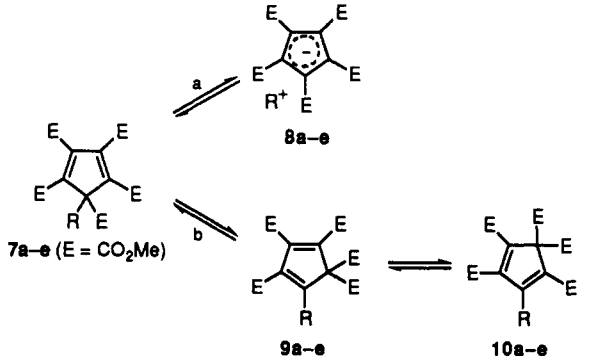
0022-3263/94/1959-0463$04.50/0

Scheme 4[a]



[a] a, R = $CHPh_2$; b, R = CH_2OMe; c, R = 1-adamantyl; d, R = p-$CH_2C_6H_4OMe$; e, R = Bn.

4) dissociate to ion pairs **8a–e** during rearrangement (path **a**) or do they rearrange by "normal" concerted [1,5]-sigmatropic migrations of methoxycarbonyl (path **b**)? To answer that question, investigations of the thermal rearrangements of 1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienes bearing alkyl substituents at C-5 that are relatively stable in cationic form are required. To the best of our knowledge, such systems have never been investigated.

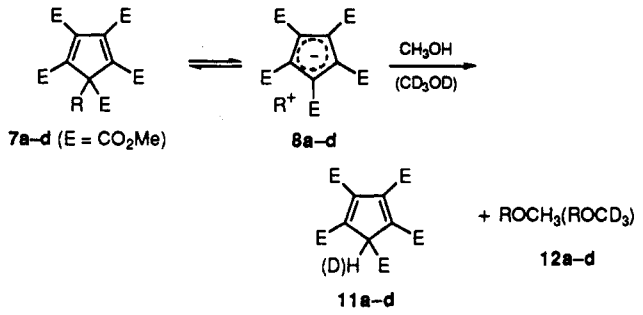
The alkyl substituents chosen in this study were $CHPh_2$, CH_2OMe, 1-adamantyl, p-$CH_2C_6H_4OMe$, and Bn. These groups are known to be relatively stable as cations, from studies of solvolysis reactions of corresponding halides.[8]

Results and Discussion

Compounds **7a–e** were prepared by a modification of a literature procedure for the synthesis of 5-ethyl-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadiene, as described in the Experimental Section.[3b] These compounds were characterized on the basis of their ^1H and ^{13}C NMR spectra as well as by mass spectrometry. Cyclopentadienes **7a–e** are not fluxional on the NMR time scale, at ambient temperature in $CDCl_3$ and benzonitrile solvents, since the methoxycarbonyl proton signals appear in a 2:2:1 intensity ratio according to their 200-MHz ^1H NMR spectra.

If cyclopentadienes **7a–e** were to undergo thermal rearrangement by migration of their respective R groups, such circumambulatory rearrangements might be observed at higher temperatures by ^1H NMR spectroscopy, if they were sufficiently fast on the NMR time scale. Solutions of cyclopentadienes **7a** and **7b** in toluene-d_8 were heated to 80 °C in the NMR probe in an effort to observe any potential rearrangement. These cyclopentadienes contain R substituents which, in cationic form, are the most stable ones in the series of cyclopentadienes **7a–e**. However, at 80 °C three methoxycarbonyl singlets were again observed in the ^1H NMR spectra (500 MHz) of both **7a** and **7b**. Furthermore, there was no observable broadening of the methoxycarbonyl singlets in those ^1H NMR spectra, indicating that rearrangement was either not occurring or too slow at 80 °C. In nitromethane-d_3 at 75 °C the ^1H NMR (500 MHz) spectrum of **7b** also showed three sharp methoxycarbonyl signals, indicating that increased solvent polarity was insufficient to bring rearrangement into the "fast" range.

Scheme 5[a]



[a] a, R = $CHPh_2$; b, R = CH_2OMe; c, R = 1-adamantyl; d, R = p-$CH_2C_6H_4OMe$.

Rearrangement of 7a–e in Methanol. The behavior of cyclopentadienes **7a–e** in methanol solvent was examined to determine if ion-pair intermediates could be trapped in competition with circumambulatory rearrangement. Trapping experiments, unlike NMR probes for line broadening or coalescence, can succeed for either slow or fast reactions. Cyclopentadiene **7a** (R = $CHPh_2$) was dissolved in methanol-d_4, and after 3 min at room temperature, ^1H NMR spectroscopy revealed **7a** (49%), **11** (D analogue, 51%), and **12a** (D analogue, 51%) according to Scheme 5. The rate constant for the overall disappearance of **7a** was estimated from the half-life as 4×10^{-3} s^{-1}, assuming first-order kinetics. Another experiment, with cyclopentadiene **7a** dissolved in methanol, showed that during 20 min at room temperature, it had been converted to **11** and benzhydryl methyl ether in quantitative yield. The identity of the methyl ether was confirmed by comparison of its spectroscopic data with those reported in the literature.[9]

In methanol-d_4 at 40 °C, cyclopentadiene **7b** (R = CH_2OMe) decomposed with an observed rate constant of $(6.2 \pm 0.3) \times 10^{-4}$ s^{-1}. After 2 h at 40 °C, ^1H NMR spectroscopy revealed **11** (D analogue, 100%) and dimethoxymethane-d_3 (100%). Dimethoxymethane-d_3 was confirmed by ^1H NMR spectroscopy and gas chromatography spiking experiments with an authentic sample of dimethoxymethane. Cyclopentadiene **7a** reacted approximately 18 times faster than cyclopentadiene **7b**, assuming a 2.8-fold increase in the observed rate constant for the 15 °C temperature difference.[10]

Cyclopentadiene **7c** (R = 1-adamantyl) also reacted with methanol solvent. The observed rate constant for the decrease in concentration of **7c** in methanol-d_4 at 50 °C was $(5.2 \pm 0.2) \times 10^{-4}$ s^{-1}. During 2 h at 65 °C in methanol, **7c** was quantitatively converted to **11** and 1-adamantyl methyl ether. The 1-adamantyl methyl ether was confirmed by comparison of its spectroscopic data to those of a sample prepared by another route.[11]

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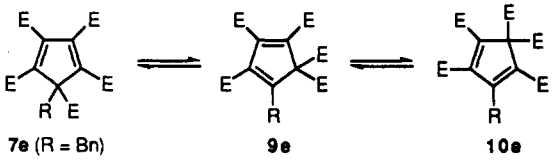
(8) (a) Steitwieser A., Jr. *Solvolytic Displacement Reactions;* McGraw Hill: New York, 1962. (b) Thornton, E. R. *Structure and Mechanism in Organic Chemistry;* 2nd ed.; Cornell University Press: Ithaca, New York, 1969. (d) Hartshorn, S. R. *Aliphatic Nucleophilic Substitution;* Cambridge University Press: New York, 1973. (e) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In *Ions and Ion-Pairs in Organic Reactions;* Szwarc, M., Ed.; Wiley: New York, 1974.

(9) Mayeda, E. A.; Miller, L. L.; Wolf, J. F. *J. Am. Chem. Soc.* **1972**, *94*, 6812.

(10) A 2-fold increase in the observed rate of decomposition for every 10 °C increase in temperature was assumed in order to compare observed rate constants that were not determined at identical temperatures.

(11) Owens, P. H.; Gleicher, G. J.; Smith, L. M., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4122.

Scheme 6



Cyclopentadiene **7d** was found to be much more stable, but it reacted at 100 °C in methanol-d_4 with an observed rate constant of $(3.14 \pm 0.08) \times 10^{-4}$ s^{-1}. During 4 h in methanol at 100 °C, it was converted to **11** (100%) and **12** (100%). The identity of the methyl ether was confirmed by comparison of its spectroscopic data to those of a sample prepared by another route.[12]

It is very unlikely that methanol reacts with cyclopentadienes **7a–d** by the S_N2 mechanism. For **7a**, that mechanism is very unattractive and for **7c** it is impossible. The mechanism of choice is therefore the S_N1 mechanism of solvolysis and the remaining question concerns the type(s) of ion pairing involved. Contact ion pairs, expected from unimolecular bond heterolysis, probably revert to starting material in competition with their evolution to solvent-separated ion pairs. For that reason, the measured rate constants (k_{obsd}) cannot be equated to unimolecular dissociation rate constants. There is no information about the distribution of return events among the three possible pathways for return (collapse at C1, C2, or C3) which, in the absence of labels, are indistinguishable. The species that are scavenged by methanol are presumably solvent-separated ion pairs and free ions. From the products in spent solutions of **7a–d** in methanol, it is clear that sigmatropic rearrangement by migration of their 5-methoxycarbonyl groups is not competitive. In no case could cyclopentadienes **9** and **10** (Scheme 4) be detected by ^{1}H NMR spectroscopy.

The measured rate constants for consumption of the most reactive members of the family **7** in methanol make clear the failure to observe their degenerate rearrangement by ^{1}H NMR spectroscopy. For line broadening to be observed in systems with spin = $^1/_2$ nuclei, the rearrangement rate constant must be in the range of 1 to 10^6 s^{-1} (lifetimes 1 to 10^{-6} s).[13] Even for rearrangement of **7a** and **7b** in a solvent like methanol, the rate constant is too small by several orders of magnitude for detection of the onset of line broadening. It is clear that the arylazo compounds of Mikhailov and co-workers[6] are very much better generators of ion pairs and that stabilization of the cyclopentadienide, by five methoxycarbonyl groups, will need to be augmented with very substantial cation stabilization before degenerate rearrangments of 5-alkyl-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienes will be observable by ^{1}H NMR spectroscopy.

The relative rates of solvolysis of **7a–d** in methanol, estimated by assuming that there is a 2-fold rate increase for every temperature increase by 10 °C, are: **7a**, 2.3×10^3; **7b**, 1.3×10^2; **7c**, 53; **7d**, 1.

Rearrangement of 7e in Methanol-d_4. Cyclopentadiene **7e** (R = Bn), dissolved in methanol-d_4, was heated in a sealed NMR tube at 140 °C for 3 h. ^{1}H NMR spectroscopy of the solution revealed **7e** (63%), **9e** (29%), and **10e** (8%) according to Scheme 6. Benzyl methyl ether could not be detected by ^{1}H NMR spectroscopy or by gas chromatography with an authentic sample of benzyl methyl ether. The mixture of cyclopentadiene isomers could not be separated by centrifugal chromatography and compounds **9e** and **10e** were identified on the basis of ^{1}H NMR spectroscopy. It follows from the structures of the products that cyclopentadiene **7e** undergoes thermal rearrangement by [1,5]-sigmatropic methoxycarbonyl migrations. Thus, the crossover from an ion-pair mechanism to the concerted (sigmatropic) mechanism must come with substituents that lie between *p*-methoxybenzyl and benzyl, in stability as cations. That stability difference is considerable, as reflected in the relative solvolytic reactivities of *p*-anisyl and benzyl chlorides (910 000:1, 67% aqueous acetone, 60 °C) or the corresponding tosylates (25 000:1, 76.6 mol % water in acetone, 25.3 °C).[14] With **7d** as sluggish as it is at 100 °C, it is not totally surprising to find that **7e**, which might dissociate to ions more slowly by a factor of *ca.* 10^4, eschews the ion-pair mechanism in favor of sigmatropic migration of the methoxycarbonyl group.

Although we first thought of the movement of alkyl groups around the periphery of cyclopentadiene-like rings in terms of a mechanistic continuum,[7b] that description is probably not correct. Sigmatropic rearrangement must have a reaction coordinate that resembles a bending motion of the bond that connects the migrating group to the ring whereas formation of an ion pair by heterolysis of that bond presumably has a reaction coordinate that resembles bond stretching.[7c] Thus, the mechanisms are quite distinct and the use of terms such as "borderline" to describe rearrangments for which a mechanistic assignment cannot be made is not appropriate.

Conclusions

From the evidence presented above, it is clear that cyclopentadienes **7a–d** dissociate, in methanol solvent, to ion pairs (**8a–d**) by C–C bond heterolysis.[15–20] Presumably, collapse of the ion pairs to covalent **7a–d** (degenerate rearrangement) competes with solvent interception of these ion pairs. Such degenerate rearrangements in other solvents could not be observed by ^{1}H NMR spectroscopy because they are much too slow at readily achievable probe temperatures.

The rearrangement of cyclopentadiene **7e** (R = $CH_2C_6H_5$) does not belong in the same mechanistic category as the rearrangement reactions of cyclopentadienes **7a–d**. Cyclopentadiene **7e** rearranges by a concerted mechanism involving [1,5]-sigmatropic methoxycarbonyl group migrations.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Centrifugal chromatography was performed with silica gel (Merck kieselgel 60 PF_{254}) coated plates

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(13) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983, p 122.
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(17) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Miyabo, A. *J. Chem. Soc., Chem. Commun.* **1988**, 923.
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(20) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344 and references therein.

(2-mm or 4-mm thick) spinning in a Chromatotron Model 7924T apparatus. Analytical thin-layer chromatography was performed with silica gel plates (E. Merck, D-Plastikfolien, kieselgel 60 F_{254}). Proton nuclear magnetic resonance (^{1}H NMR) data were obtained on Bruker AC-200 or Bruker AM-500 spectrometers. Chemical shifts are reported in δ units (ppm) relative to the singlet at 7.24 ppm for chloroform in chloroform-*d*. ^{13}C NMR spectra were obtained at 50 MHz on a Bruker AC-200 or at 125 MHz on a Bruker AM-500 spectrometer and are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-*d*. High resolution EI spectra were recorded on a VG ZAB-E double focusing mass spectrometer. Samples were run at 70 eV, source temperature 200 °C, resolution 5000. Samples were introduced by direct insertion probe.

Synthesis of 5-Alkyl-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienes 7a–e. General. The syntheses of 5-alkyl-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienes were adapted from a procedure for the synthesis of 5-ethyl-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadiene.[3b] Pentakis(methoxycarbonyl)cyclopentadiene (0.50 g, 1.43 mmol), Ag_2O (0.16 g, 0.73 mmol), and benzene (9 mL) were stirred for 2 h at room temperature. The halide (2.38 mmol) was then added and the mixture was stirred for 2 h. The solution was filtered and most of the benzene was removed by rotary evaporation. Crude product solutions of **7a** and **7b** were subjected to centrifugal chromatography (silica gel, 4:1 hexane/ethyl acetate). For crude product solutions of **7c** and **7d**, CH_2Cl_2 was added and the solution was washed three times with 10% $NaHCO_3$. The CH_2Cl_2 layer was dried with $MgSO_4$ and filtered. The CH_2Cl_2 was removed by rotary evaporation and the residues were subjected to centrifugal chromatography (silica gel, 7:3 hexane/ethyl acetate) to afford **7a–d** of sufficient purity. In the case of **7e**, pure material was obtained by means of recrystallization from methanol. The isolated yields of **7a–e** were not optimized. Pentakis(methoxycarbonyl)cyclopentadiene, silver(I) oxide, and the following halides were purchased from Aldrich Chemical Co. and used as supplied: bromodiphenylmethane (for **7a**), chloromethyl methyl ether (for **7b**), 1-bromoadamantane (for **7c**), 4-methoxybenzyl chloride (for **7d**) and benzyl bromide (for **7e**).

1,2,3,4,5-Pentakis(methoxycarbonyl)-5-(1,1-diphenylmethyl)cyclopentadiene (7a): 25% yield; mp 108–110 °C (7:3 hexane/ethyl acetate); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35–7.17 (m, 10 H, 2 Ph), 5.60 (s, 1 H, CH), 3.81 (s, 6 H, 2 COOMe), 3.63 (s, 3 H, COOMe), 3.36 (s, 6 H, 2 COOMe); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.70, 162.66 (2), 161.48 (2), 143.76 (2), 142.67 (2), 139.12 (2), 129.27 (4), 128.00 (4), 127.11 (2), 71.45, 53.30, 52.80, 52.65 (2), 52.06 (2), signals for magnetically equivalent carbons labeled on the basis of relative intensities; MS *m/z* (M^+) for $C_{28}H_{26}O_{10}$ calcd 522.1526, found 522.1514.

1,2,3,4,5-Pentakis(methoxycarbonyl)-5-(methoxymethyl)cyclopentadiene (7b): 39% yield; mp 119–120 °C (7:3 hexane/ethyl acetate); ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.23 (s, 2 H, CH_2), 3.88 (s, 6 H, 2 COOMe), 3.83 (s, 6 H, 2 COOMe), 3.68 (s, 3 H, COOMe), 3.26 (s, 3 H, OMe); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.76, 162.55 (2), 161.92 (2), 141.78 (2), 141.67 (2), 71.84, 68.71, 59.87, 53.21, 52.72 (2), 52.56 (2); MS *m/z* (M^+) for $C_{17}H_{20}O_{11}$ calcd 400.1006, found 400.0995.

5-(1-Adamantyl)-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadiene (7c): 22% yield; mp 124–125 °C (7:3 hexane/ethyl acetate); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.86 (s, 6 H, 2 COOMe), 3.81 (s, 6 H, 2 COOMe), 3.64 (s, 3 H, COOMe), 1.95 (bs, 3 H, CH), 1.88 (bs, 6 H, 3 CH_2), 1.65 (bs, 6 H, 3 CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.65, 163.31 (2), 162.61 (2), 144.51 (2), 140.70 (2), 74.77, 52.60 (2), 52.46 (2), 52.21, 42.55, 38.09 (3), 36.35 (3), 28.94 (3); MS *m/z* (M^+) for $C_{25}H_{30}O_{10}-H$ calcd 489.1761, found 489.1756.

5-(4-Methoxybenzyl)-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadiene (7d): 31% yield; mp 88.5–89.5 °C (7:3 hexane/ethyl acetate); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.92 (d, J = 8.7 Hz, 2 H, CH_{ortho}), 6.69 (d, J = 8.7 Hz, 2 H, CH_{meta}), 3.87 (s, 6 H, 2 COOMe), 3.77 (s, 6 H, 2 COOMe), 3.74 (s, 3 H, COOMe), 3.71 (s, 2 H, CH_2), 3.69 (s, 3 H, OMe); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.33, 162.34 (2), 162.11 (2), 158.60, 142.87 (2), 141.70 (2), 130.19 (2), 125.45, 113.18 (2), 68.48, 55.06, 53.30, 52.66 (4), 37.26; MS *m/z* (M^+) for $C_{23}H_{24}O_{11}$ calcd 476.1319, found 476.1296.

5-Benzyl-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadiene (7e): 45% yield; mp 116–117 °C (MeOH); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.19–7.00 (m, 5H, Ph), 3.87 (s, 6 H, 2 COOMe), 3.76 (s, 8 H, 2 COOMe, CH_2), 3.70 (s, 3 H, COOMe); ^{13}C NMR (50 MHz, $CDCl_3$) δ 176.29, 162.30 (2), 162.06 (2), 142.70 (2), 141.82 (2), 133.40, 129.09 (2), 127.81 (2), 127.28, 68.13, 53.35, 52.69 (2), 52.67 (2), 38.01; MS *m/z* (M^+) for $C_{22}H_{22}O_{10}$ calcd 446.1213, found 446.1218.

Thermal Reactions of 7a–e in Methanol or Methanol-d_4. Reaction of 7a. Cyclopentadiene **7a** (0.0124 g, 0.024 mmol) and toluene (2.52 μL, internal standard) were dissolved in 0.5 mL of methanol-d_4. After 3 min at ambient temperature ^{1}H NMR spectroscopy (200 MHz) revealed **7a** (49%), **11** (D analogue, 51%), and **12a** (D analogue, 51%). After 20 min at ambient temperature, ^{1}H NMR spectroscopy (200 MHz) revealed **11** (D analogue, 100%) and **12a** (D, analogue 100%). In another experiment, cyclopentadiene **7a** (0.200 g, 0.038 mmol) was dissolved in methanol (1.0 mL), and after 20 min, the volatiles were removed in vacuo and the residue was dissolved in $CDCl_3$. ^{1}H NMR spectroscopy revealed **11** (100%) and benzhydryl methyl ether (100%). The $CDCl_3$ was removed in vacuo and the residue was subjected to centrifugal chromatography (silica gel, 3:2 hexane/ethyl acetate) to give **11** (77%) and **12a** (82%). Compound **11a** was confirmed by the comparison of its spectroscopic data to those reported in the literature for benzhydryl methyl ether.[9]

Reaction of 7b. Cyclopentadiene **7b** (0.0076 g, 0.019 mmol) and toluene (2.00 μL, internal standard) were dissolved in methanol-d_4 and placed in an NMR tube. The tube was then heated at 40 °C and the rate of disappearance of **7b** was monitored by ^{1}H NMR spectroscopy (200 MHz). Concentration vs time data (7 points) were obtained by normalizing the integrated intensity of the CH_2 singlet of **7b** for 2 half-lives against the integrated intensity of the methyl singlet of toluene. The resultant plot of $\ln([\mathbf{7b}]/[\mathbf{7b}]_0)$ vs t yielded an observed rate constant of $(6.2 \pm 0.3) \times 10^{-4}$ s^{-1} (correlation coefficient = 0.9934) for the decrease in concentration of **7b**. After 2 h at 40 °C, ^{1}H NMR spectroscopy (200 MHz) revealed **12b** (D analogue, 100%) and **11** (D analogue, 100%). Bulb-to-bulb distillation (0.01 mmHg) separated the volatiles from **11**. The presence of dimethoxymethane-d_3 in the volatiles was confirmed by gas chromatography and ^{1}H NMR spectroscopy spiking experiments with an authentic sample of dimethoxymethane.

Reaction of 7c. Cyclopentadiene **7c** (0.0085 g, 0.0174 mmol) and toluene (1.75 μL, internal standard) were dissolved in methanol-d_4 (0.5 mL) and placed in an NMR tube. The tube was then heated at 50 °C and the rate of disappearance of **7c** was monitored by ^{1}H NMR spectroscopy (200 MHz). Concentration vs time data (6 points) were obtained by normalizing the integrated intensity of the COOMe singlet of **7c** at 3.50 ppm against the integrated intensity of the methyl singlet of toluene for 2.6 half-lives. The resultant plot of $\ln([\mathbf{7c}]/[\mathbf{7c}]_0)$ vs t yielded an observed rate constant of $(5.2 \pm 0.2) \times 10^{-4}$ s^{-1} (correlation coefficient = 0.9966) for the decrease in concentration of **7c**. After 3 h at 50 °C the solution consisted of **11** (D analogue, 100%) and **12c** (D analogue, 100%). In another experiment, cyclopentadiene **7c** (0.0100 g, 0.0205 mmol) was dissolved in 0.5 mL of methanol. After 2 h at 65 °C, the solvent was removed in vacuo and the residue was subjected to centrifugal chromatography (silica gel, 4:1 hexane/ethyl acetate) to give **11** (67%) and 1-adamantyl methyl ether (73%). The spectral data for 1-adamantyl methyl ether were identical to those of a sample prepared by another route.[11]

Reaction of 7d. Cyclopentadiene **7d** (0.0104 g, 0.0219 mmol) and toluene (1.75 μL, internal standard) were dissolved in methanol-d_4 (0.5 mL) and placed in an NMR tube. The tube was then heated at 100 °C and the rate of disappearance of **7d** was monitored by ^{1}H NMR spectroscopy (200 MHz). Concentration vs time data (9 points) were obtained by normalizing the integrated intensity of the COOMe singlet of **7d** at 3.77 ppm against the integrated intensity of the methyl singlet of toluene for 2.5 half-lives. The resultant plot of $\ln([\mathbf{7d}]/[\mathbf{7d}]_0)$ vs t yielded an observed rate constant of $(3.14 \pm 0.08) \times 10^{-4}$ s^{-1} (correlation coefficient = 0.9980) for the decrease in concentration of **7d**. After 4 h at 50 °C, the solution consisted of **11** (D analogue, 100%) and **12d** (D analogue, 100%). In another experiment, cyclopentadiene **7d** (0.0200 g, 0.0420 mmol) in methanol (1.0

mL), in a sealed tube, was heated at 100 °C for 4 h. The solvent was removed in vacuo and the residue dissolved in chloroform-*d*. ^{1}H NMR spectroscopy revealed **11** (100%) and **12d** (100%). The chloroform-*d* was removed in vacuo and the residue was subjected to centrifugal chromatography (silica gel, 3:2 hexane/ethyl acetate) to give **11** (71%) and **12d** (82%). The spectral data for *p*-methoxybenzyl methyl ether were identical to those of a sample prepared by another route.[12]

Reaction of 7e. Cyclopentadiene **7e** (0.030 g, 0.067 mmol) was dissolved in methanol-d_4 (0.5 mL) and the solution was then degassed (three freeze–pump–thaw cycles) and sealed into an NMR tube. The tube was heated at 140 °C for 3 h after which ^{1}H NMR spectroscopy (200 MHz) revealed **7e** (63%), **9e** (29%), and **10e** (8%), from the carbomethoxy and methylene signals of **9e** and **10e**, which could be identified in that solution. This mixture of isomers could not be separated by column chromatography and assignments were made on the basis of analogy. Hoffmann and co-workers[3b] had reported the ^{1}H NMR spectra ($CDCl_3$) of the products of [1,5]-methoxycarbonyl migrations in 5-methyl-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadiene as well as the order of their appearance, the first methoxycarbonyl migration being faster than the second. Those experiments were repeated by us, to verify the results. The same order of reactivities was assumed for the analogous methoxycarbonyl group migrations starting with **7e**, to afford first **9e** and, more slowly, **10e**.

4-Benzyl-1,2,3,5,5-pentakis(methoxycarbonyl)cyclopentadiene (9e): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.18–7.00 (m, 5H, Ph), 4.37 (s, 2 H, CH_2), 3.95 (s, 3 H, COOMe), 3.83 (s, 3 H, COOMe), 3.74 (s, 3 H, COOMe), 3.36 (s, 6 H, 2 COOMe).

3-Benzyl-1,2,4,5,5-pentakis(methoxycarbonyl)cyclopentadiene (10e): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.16–7.01 (m, 5H, Ph), 4.24 (s, 2 H, CH_2), 3.83 (s, 3 H, COOMe), 3.79 (s, 6 H, 2 COOMe), 3.77 (s, 3 H, COOMe), 3.51 (s, 3 H, COOMe).

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