acknowledged for kind and fruitful discussions and suggestions.

Registry No. 1a, 1897-52-5; 1b, 94088-46-7; 1c, 394-47-8; 1d, 96994-73-9; 1e, 143306-27-8; 1f, 19064-24-5; 1g, 1493-27-2; 2a, 93-08-3; 3a, 143306-28-9; 3b, 143306-29-0; 3c, 143306-30-3; 3d, 143306-31-4; 3f, 143306-32-5; 3g, 143306-33-6; 4a, 143306-34-7; 4b, 143306-35-8; 4c, 143306-36-9; 4f, 143306-37-0; 4g, 143306-38-1; 5a, 99-90-1; 5b, 403-42-9; 5c, 98-86-2; 5d, 100-06-1; 5e, 99-93-4; 5f, 93-55-0; 5g, 1078-19-9; 5h, 451-40-1; 5i, 99-92-3; 5j, 611-70-1; 6a, 143306-39-2; 6b, 143306-40-5; 6c, 143306-41-6; 6d, 143306-42-7; 6e, 143306-43-8; 6f, 143306-44-9; 6g, 143306-45-0; 6h, 143306-46-1; 6j, 143306-47-2; 7a, 143306-48-3; 7b, 143306-49-4; 7c, 143306-50-7; 7d, 143306-51-8; 7e, 143306-52-9; 7f, 143306-53-0; 7g, 143306-54-1; 7h, 143306-55-2; 7j, 143306-56-3; 8, 143306-58-5; 9, 143306-57-4; 10, 143306-59-6; 11, 143306-60-9; 12, 143306-61-0; 13, 143306-62-1; 14, 143306-63-2.

Supplementary Material Available: ^{1}H NMR spectra of 1e–f, 3a, 3f–g, 4a, 4f–g, 6c, 6f, 7c, 7f, and 8–14 (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Stereoelectronic Control of Facial Selectivity in the Diels–Alder Cycloaddition of Sterically Unbiased 5,5-Diarylcyclopentadienes

Ronald L. Halterman,* Bridget A. McCarthy,† and Marjorie A. McEvoy†

Department of Chemistry, 620 Parrington Oval, University of Oklahoma, Norman, Oklahoma 73019

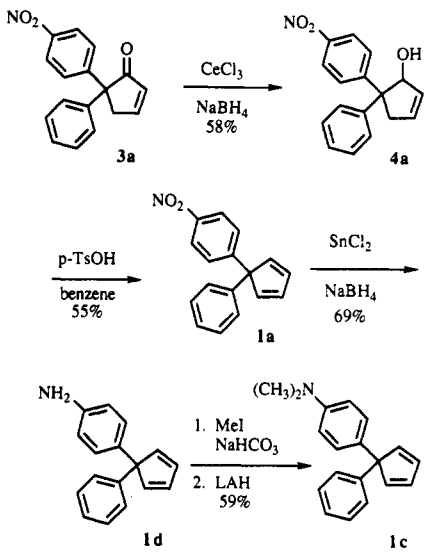
Received February 3, 1992

This study provides strong evidence for stereoelectronic control of diastereoselectivity in the Diels–Alder cycloaddition of sterically unbiased 5-(4-X-phenyl)-5-phenylcyclopentadienes 1 (X = NO_2, Cl, and $N(CH_3)_2$) with dimethyl acetylenedicarboxylate (DMAD) producing diastereomeric norbornyl diesters 2 in cis/trans ratios (diester relative to the substituted arene) varying from 68:32 to 38:62 as determined by ^{1}H NMR spectroscopy. The reactions were carried out under both thermal and Lewis acid catalyzed conditions, giving essentially identical selectivities regardless of the conditions used. Structural assignments were made by ^{1}H NMR lanthanide shift reagent studies of the isolated diastereomers, separable by preparative thin-layer chromatography. In each case the dienophile approached the diene from the side opposite the more electron rich aromatic ring as predicted by Cieplak's theory for explaining stereoelectronic control. The observed ratios correspond to an overall energy difference of 0.65 kcal/mol. A Hammet plot of the log (cis/trans) versus the σ_p parameter produced a linear relationship with a correlation coefficient of 0.98. An efficient synthesis of the diarylcyclopentadienes is described.

The role of stereoelectronic effects in controlling diastereoselectivity has, in recent years, been the subject of a growing amount of research.[1] Although steric interactions are thought to be a major factor which determines selectivity in many organic transformations, among them the synthetically important Diels–Alder reaction, it has been less clear to which degree stereoelectronic factors influence diastereoselectivity. A few investigations into the nature of stereoelectronic control of facial diastereoselectivity in the Diels–Alder reaction have been reported. Franck examined the Diels–Alder reaction of various, sterically biased acyclic dienes containing an chiral allylic alkoxy group.[2] le Noble has reported on the Diels–Alder reaction of sterically unbiased 5-fluoroadamantanethione with 2,3-dimethyl-1,3-butadiene which showed that the diene approached the olefin from the face syn to the electron-withdrawing fluoro substituent, in accord with the product predicted by Cieplak theory.[3,4] Fallis has reported studies of Diels–Alder reactions of sterically biased 5-substituted cyclopentadienes.[5]

We have been engaged in an ongoing investigation of the role of stereoelectronic effects in controlling stereoselectivity in a variety of reaction types involving sterically unbiased, yet electronically biased, substrates. We have reported diastereoselectivity in the sodium borohydride reduction of sterically unbiased 2-(4-X-phenyl)-2-phenylcyclopentanones (X = NO_2, Br, Cl, OH, OH, OCH_3, and NH_2) which gave diastereomeric alcohols with stereoselectivities up to 79:21.[6] More recently we reported the results of the osmium-catalyzed cis-dihydroxylations[7]

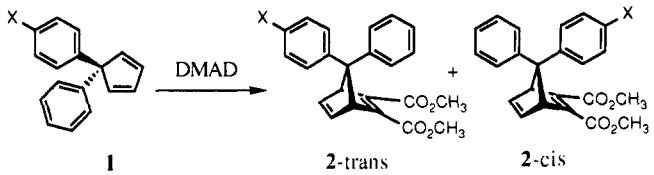
Scheme I



† Work performed at Department of Chemistry, Boston University, Boston, MA.

(1) An overview of studies concerning stereoelectronic control can be found in the following papers and references therein: (a) Bodepudi, V. R.; le Noble, W. J. *J. Org. Chem.* **1991**, *56*, 2001–2006. (b) Li, H.; Mehta, G.; le Noble, W. *J. Org. Chem.* **1991**, *56*, 2006–2011. (c) Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 8447–8462. (d) Smith, A. B. III; Dunlap, N. K.; Sulikowski, G. A. *Tetrahedron Lett.* **1988**, *29*, 439–442. (e) Okada, K.; Tomita, S.; Oda, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 459–468.

0022-3263/92/1957-5585$03.00/0



1 2-trans 2-cis

Figure 1. Diels–Alder cycloaddition of 5,5-diarylcyclopentadienes 1 (X = (a) NO_2, (b) Cl, (c) $N(CH_3)_2$).

and peracetic acid epoxidations[8] of the structurally related sterically unbiased 3,3-diarylcyclopentenes. In both the nucleophilic and electrophilic addition reactions a systematic trend of addition opposite the best electron donor was observed. As part of these efforts to assess the magnitude of potential stereoelectronic effects in synthetically useful reactions, we report here the results of the Diels–Alder [4 + 2] cycloaddition of dimethyl acetylenedicarboxylate with the sterically unbiased substrates, 5-(4-X-phenyl)-5-phenylcyclopentadienes (X = NO_2, Cl, and $N(CH_3)_2$), a diastereoselective reaction which also appears to be governed by stereoelectronic control (Figure 1).

Results

Synthesis of 5,5-Diarylcyclopentadienes. The efficient synthesis of the diene substrates **1a** and **1b** proceeded via an acid-catalyzed elimination[9] of the allylic alcohols **4a** and **4b** derived from the Luche reduction[10] of the cyclopentenone **3a** and the known chloro-substituted enone **3b**.[7] Statistical nitration of the known parent enone provided 5-(4-nitrophenyl)-5-phenylcyclopentenone (**3a**).[11] The synthesis of **1a** (X = NO_2) described here is quite analogous to the preparation of **1b** (X = Cl) (Scheme I). The cerium trichloride catalyzed sodium borohydride reduction of nitro-substituted enone **3a** generated the product, 5-(4-nitrophenyl)-5-phenylcyclopent-2-enol (**4a**).[10] Acid-catalyzed elimination of the allyl alcohol **4a** gave the desired nitro-substituted diene **1a**.[9] Selective reduction of the nitro functionality with sodium borohydride in the presence of tin dichloride generated the amino-substituted diene **1d**.[12] Exhaustive methylation of the amino group with methyl iodide followed by lithium aluminum hydride induced loss of methane allowed for the generation of the (dimethylamino)phenyl substrate **1c** as an orange oil.[13]

Diastereoselective Diels–Alder Cycloadditions. The three monosubstituted 5,5-diarylcyclopentadiene substrates 1 were subjected to treatment with 2 equiv of dimethyl acetylenedicarboxylate (DMAD) and stirred at reflux (81 °C) for up to 5 days, depending on the para substituent, until the Diels–Alder cycloaddition was judged complete by thin-layer chromatographic analysis. Addition of water and exhaustive extraction of the aqueous layer with CH_2Cl_2 was performed in order to avoid diastereomeric enhancement due to incomplete product recovery. The combined organic portion was dried and concentrated to provide a diastereomeric mixture of the cycloaddition norbornyl-type products **2**. In all cases the ^1H NMR spectra were taken of these crude norbornyls **2a–c** and the diastereomeric ratios determined from the peak integration. The compounds were purified, and the diastereomers were separated by preparative thin-layer chromatography, enabling full characterization of each product.

Table I. Ratios of the Diels–Alder Cycloadditions with DMAD

X	product	σ_p	% cis	% trans	log (cis/trans)
NO	**2a**	0.778	68	32	0.327
Cl	**2b**	0.227	58	42	0.140
H	**2e**	0.000	(50	50)	0.000
$N(CH_3)_2$	**2c**	−0.83	38	62	−0.213

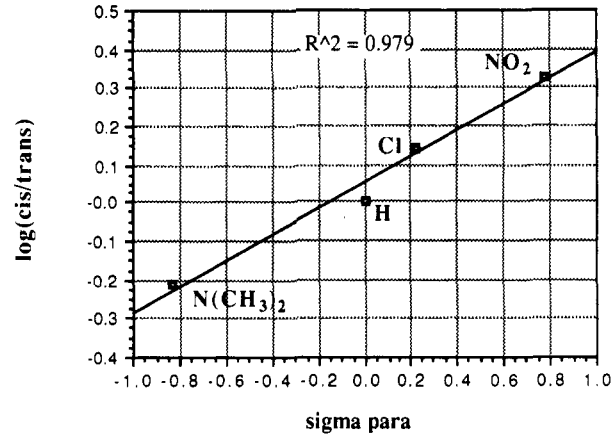
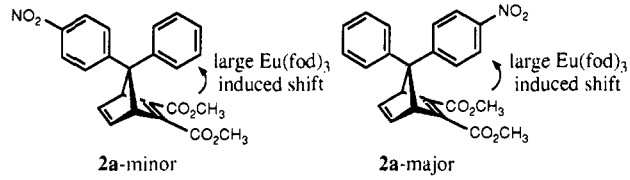


Figure 2. Plot of selectivity vs σ_p values for the reaction with DMAD.



2a-minor 2a-major

Figure 3. The aryl protons most effected by the shift reagent for the nitro diester **2a**.

The results of the cycloadditions are summarized in Table I. These Diels–Alder cycloadditions were found to occur with stereoselectivity as high as 68:32 in favor of addition opposite the *unsubstituted* ring for the reaction of the nitro-substituted diene **1a**, and 62:38 in favor of addition opposite the *substituted* ring in the reaction of the (dimethylamino)-substituted diene **1c**. As with the results of our previously published studied,[6-8] there was a preference for the reagent, a dienophile in this case, to approach the substrate 1 from the side anti to the most electron-rich phenyl ring. A graph (Figure 2) of the selectivities, expressed as log (cis/trans), versus the Hammet σ_p values for the substituents (NO_2, Cl, H, $N(CH_3)_2$) can be linearly correlated with a coefficient of 0.98.[14] The value for the nondiastereomeric diphenyl product, neces-

(2) Franck, R. W.; John, T. V.; Olejniczak, K. *J. Am. Chem. Soc.* **1982**, *104*, 1106–1107.
(3) Chung, W.-S.; Turro, N. J.; Srivastava, S.; Li, H.; le Noble, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7882–7883.
(4) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540–4552.
(5) Macauley, J. B.; Fallis, A. G. *J. Am. Chem. Soc.* **1990**, *112*, 1136–1144.
(6) Halterman, R. L.; McEvoy, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 6690–6695.
(7) Halterman, R. L.; McEvoy, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 980.
(8) Halterman, R. L.; McEvoy, M. A. *Tetrahedron Lett.* **1992**, *33*, 753.
(9) Sondheimer, F.; Mechoulam, R.; Sprecher, M. *Tetrahedron* **1964**, *20*, 2473.
(10) Gemal, A. L.; Luche, J.-L. *J. Am. Chem. Soc.* **1991**, *103*, 5454–5459.
(11) (a) Dewar, J. S.; Urch, D. S. *J. Chem. Soc.* **1958**, 3079. (b) Sheehan, M.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3544.
(12) Satoh, T.; Mitsuo, N.; Nishiki, M.; Inoue, Y.; Ooi, Y. *Chem. Pharm. Bull.* **1981**, *29*, 1443–1445.
(13) Cope, A. C.; Ciganek, E.; Fleckenstein, L. J.; Neisinger, M. A. P. *J. Am. Chem. Soc.* **1960**, *82*, 4651–4655.
(14) (a) Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96. (b) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row, Publishers: New York, 1976; pp 60–64; and most textbooks.

Table II. Δδ for Ortho Protons of DMAD Cycloaddition Products 2

X	product	isomer	% Eu(fod)	Δδ (PhX) (ppm)	Δδ (Ph) (ppm)
NO_2	**2a**	major	12.5	0.15	0.05
NO_2	**2a**	minor	29.6	0.16	0.27
Cl	**2b**	major	13.8	0.26	0.16
Cl	**2b**	minor	5.7	0.26	0.50
$N(CH_3)_2$	**2c**	major	14.2	0.30	0.58
$N(CH_3)_2$	**2c**	minor	8.3	0.96	0.50

sarily 50/50, has been added to the experimental data set.

Structure Determination. The stereochemical outcome of the Diels–Alder cycloadditions of the 5,5-diarylcyclopentadienes **1** with dimethyl acetylenedicarboxylate was primarily determined by lanthanide shift reagent studies.[15] The ^1H NMR spectra of both the major and minor products of the cycloaddition reactions **2a–c** were obtained in the presence of the lanthanide shift reagent, $Eu(fod)_3$. The chemical shifts of the hydrogens on the aryl ring syn to the ester groups should be most susceptable to change, and as shown in Figure 3 for the nitro-substituted product **2a**, the major isomer showed larger changes in the chemical shift values of the hydrogens on the substituted arene ring. For the minor isomer the largest changes in the chemical shift values corresponded to the protons on the unsubstituted ring. Similar results were observed for the chloro-substituted product **2b**, and the results were reversed in the case of the (dimethylamino)-substituted product **2c**. The spectral data for the change in chemical shift (Δδ) of the ortho protons on both the substituted (PhX) and unsubstituted (Ph) aryl rings is given in Table II. The experimental evidence presented above is in accord with a preference for approach of the dienophile from the side opposite the more electron rich phenyl ring in agreement with the stereoselectivity predicted by Cieplak theory.[4]

The reactions were also run under Lewis acid catalyzed conditions.[16] The substrates were treated with 4 equiv of aluminum chloride and 2 equiv of DMAD in CH_2Cl_2 at 0 °C for 0.5 h. The reactions were followed to completion by thin-layer chromatography, and the reaction mixtures were quenched with dilute sodium bicarbonate and exhaustively extracted with CH_2Cl_2. The ^1H NMR spectrum for each crude product mixture was recorded and the diastereomeric ratio taken from the electronic integration. The spectra of the products isolated from the Lewis acid catalyzed reactions were not as clean as those recorded for the reactions run under thermal conditions, but the diastereomeric ratios were essentially identical (±3%) under both sets of reaction conditions.

Discussion

We have previously detailed the rationale for utilizing the sterically unbiased diarylcyclopentane derivatives as probes for the examination of stereoelectronic control of asymmetry in diastereoselective reactions[6–8] such as the synthetically important Diels–Alder reaction. Our 5,5-diarylcyclopentadiene system should be able to identify the role of stereoelectronic effects in controlling the facial selectivity of the Diels–Alder cycloaddition since the substituents at the 5-position of the cyclopentadiene are essentially sterically equivalent yet electronically different.

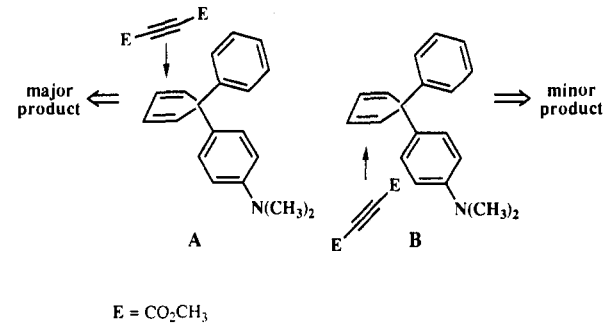


Figure 4. Diastereomeric pathways for approach of a dienophile to the diene **1c**.

In the Fallis cyclopentadiene substrates for his [4 + 2] cycloaddition study the 5-position is occupied by a methyl group and some other group "X" which in most of the substrates differed significantly in bulk from the methyl group.[5] Steric considerations could therefore play a significant part in the determination of stereoselectivity.

We postulate two sterically similar diastereomeric pathways A and B which the dienophile follows upon approach to the cyclopentadiene. The major product results from approach of the dienophile from the face opposite the better electron donor, which in the case of the (dimethylamino)-substituted diene is the substituted aryl ring (pathway A in Figure 4) in accord with the result predicted by Cieplak theory.[4] The minor product necessarily arises from approach of the dienophile syn to the more electron rich aryl ring.

The geometry in the transition state of this Diels–Alder cycloaddition should be somewhat different from that described for the related nucleophilic and electrophilic addition reaction studies[6–8] since the aryl groups are pseudoequatorial in the cyclopentadiene substrate **1**. A deviation from antiperiplanarity to the more electron rich phenyl ring in the approach of the diene could account for the lower stereoselectivity observed in the Diels–Alder reaction with respect to the reductions of the 2,2-diarylcyclopentanones. According to our scheme the dienophile appears to be in a sterically similar environment along either pathway, and any stereoselectivity can be thought of as resulting from electronic differences.

The type of dienophile employed could have a significant effect on the diastereoselectivity observed in the Diels–Alder cycloaddition. The second π-system in the DMAD, perpendicular to an aromatic ring upon approach to the diene, could potentially influence the facial selectivity of the reaction. We are currently examining the effects of varying the dienophile in order to gain a clearer understanding of the forces which direct the approach of the dienophile to the diene.

Conclusion. Evidence for stereoelectronic control in the diastereoselective Diels–Alder cycloaddition of the sterically unbiased 5,5-diarylcyclopentadienes has been provided. The observed selectivities can be rationalized according to the Cieplak notion of σ,σ^* hyperconjugation, where bond formation is predicted to occur opposite the better donor.[7] The level of diastereoselectivity was shown to have been significantly influenced by variation in the electronic nature of the substrate and corresponds to an overall energy difference of 0.65 kcal/mol. This study supports the notion that, in the absence of competing steric factors, stereoelectronic control can significantly alter the stereochemical outcome of the Diels–Alder cycloaddition. Further studies concerned with identifying the effect of dienophile type on the diastereoselectivity of the Diels–Alder reactions of the sterically unbiased 5,5-diarylcyclo-

(15) Wenzel, T. J.; Bettes, T. C.; Sadlowski, J. E.; Sievers, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 5903.

(16) (a) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436. (b) Fray, G. I.; Robinson, R. *J. Am. Chem. Soc.* **1961**, *83*, 249. (c) Inukai, T.; Kojima, T. *J. Org. Chem.* **1967**, *32*, 869.

pentadienes are currently under investigation.

Experimental Section

General Methods. As in ref 7. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded at ambient temperature in $CDCl_3$ unless otherwise specified.

2-(4-Nitrophenyl)-2-phenylcyclopent-4-en-1-one (3a). To a solution of enone **3f** (9.10 mmol, 2.140 g) in a 1:1 solvent mixture of acetic anhydride and nitromethane (30 mL) was added fuming HNO_3 (11.4 mmol, 0.51 mL) diluted in the above solvent mixture (20 mL), and the mixture was stirred at 65 °C for 2.5 days and at rt for an additional day. Water and ether were added, and the layers separated. The organic layer was extracted with ether, dried ($MgSO_4$), and concentrated. The crude product was purified by gravity SiO_2 column chromatography eluting with a 6:4 petroleum ether–ethyl ether solvent mixture. After two such columns pure *p*-nitro enone **3a** was isolated in 31% yield as an orange oil (the major impurity being the ortho isomer which elutes off the column just ahead of the desired para adduct): ^1H NMR 8.16 (d, J = 8.5 Hz, 2 H), 7.91 (m, 1 H), 7.51–7.16 (m, 7 H), 6.32 (m, 1 H), 3.63–3.46 (m, 2 H); ^{13}C NMR 207.23, 162.47, 150.59, 146.51, 141.78, 132.56, 128.90, 128.73, 127.67, 127.28, 123.46, 59.84, 47.03; IR (film) 3060, 2920, 1700, 1510, 1343 cm^{-1}; MS (EI, 70 eV) m/z 279 (M^+, 100), 204 (20).

5-(4-Chlorophenyl)-5-phenylcyclopent-2-en-1-ol (4b): Representative Enone Reduction Procedure. A solution of enone **3b** (0.989 mmol, 0.266 g) in methanol (5.5 mL) was added to anhydrous $CeCl_3$ (1.09 mmol, 0.268 g) under N_2, and the temperature was reduced to 0 °C. To this mixture was added $NaBH_4$ (1.09 mmol, 0.0412 g) in one portion from a side arm. After the reaction mixture was stirred at 0 °C for 40 min, water was added, and the resulting mixture was acidified with 1 N HCl. Following an ethyl ether extraction, the organic portion was dried ($MgSO_4$) and concentrated to give the allyl alcohol **4b** as an orange oil in 90% yield. The crude product gave a clean ^1H NMR spectrum showing a diastereomeric ratio of 53:47. Separation of the diastereomers was accomplished by preparative TLC (SiO_2; 8.5:1.5 petroleum ether–ethyl ether; four developments): ^1H NMR major (lower R_f) 7.32–7.16 (m, 9 H), 6.13 (m, 1 H), 5.93 (m, 1 H), 5.39 (broad s, 1 H), 3.46 (dd, J = 16.5 Hz, J = 1.0 Hz, 1 H), 2.86 (d, J = 16.5 Hz, 1 H), 1.36 (broad, s, 1 H); ^1H NMR minor (higher R_f) 7.38–7.27 (m, 5 H), 7.25 (d, J = 6.5 Hz, 2 H), 7.15 (d, J = 8.5 Hz, 2 H), 6.13 (m, 1 H), 5.92 (m, 1 H), 5.45 (broad s, 1 H), 3.42 (d, J = 16.5 Hz, 1 H), 2.93 (dd, J = 16.5 Hz, J = 2.0 Hz, 1 H); ^{13}C NMR (major) 146.75, 142.46, 133.98, 132.33, 131.90, 129.33, 129.09, 128.19, 126.72, 82.38, 59.51, 44.86; ^{13}C NMR (minor) 147.65, 141.72; 134.09, 132.43, 132.30, 130.63, 128.37, 128.08, 127.79, 126.27, 82.42, 59.54, 45.04; IR (film) 3400, 3050, 2910, 1487, 1090 cm^{-1}; MS (EI, 70 eV) m/z 272 (m^+ + 2, 28), 270 (M^+, 48), 252 (32), 228 (29), 226 (74), 201 (100), 165 (80); HRMS (EI 70 eV) m/z (M^+) calcd for $C_{17}H_{15}OCl$ 270.0811, obsd 270.0802.

5-(4-Nitrophenyl)-5-phenylcyclopent-2-en-1-ol (4a). Following the representative enone reduction procedure with nitro enone **3a** (0.874 mmol, 0.244 g) for 0.5 h at 0 °C gave the allylic alcohol **4a**, after purification by column chromatography (SiO_2, CH_2Cl_2), as a yellow oil in 58% yield, as well as the recovery of starting material (0.032 g). Diastereomers separated via preparative TLC (SiO_2, two developments with 8:2 CH_2Cl_2–petroleum ether). The major–minor ratio equals 60:40 by ^1H NMR spectroscopy: ^1H NMR major (higher R_f) 8.16 (d, J = 9.0 Hz, 2 H), 7.49 (d, J = 9.0 Hz, 2 H), 7.33–7.17 (m, 3 H), 7.16 (d, J = 7.0 Hz, 2 H), 6.14 (m, 1 H), 5.94 (m, 1 H), 5.36 (m, 1 H), 3.52 (m, 1 H), 2.85 (m, 1 H); ^1H NMR minor (lower R_f) 8.11 (d, J = 9.0 Hz, 2 H), 7.39 (d, J = 9.0 Hz, 2 H), 7.36–7.24 (m, 5 H), 6.16 (m, 1 H), 5.97 (m, 1 H), 5.49 (broad s, 1 H), 3.44 (d, J = 16.5 Hz, 1 H), 2.99 (dd, J = 16.5 Hz, J = 2.0 Hz, 1 H); ^{13}C NMR (major) 155.70, 146.24, 141.33, 133.92, 132.24, 129.09, 128.87, 128.47, 127.16, 123.83, 82.12, 60.19, 44.48; ^{13}C NMR (minor) 151.44, 146.76, 146.34, 133.96, 132.70, 130.16, 128.54, 127.73, 126.70, 122.95, 82.63, 60.15, 44.75; IR (film) 3410, 1620, 1510, 1350 cm^{-1}; MS (EI, 70 eV) m/z 281 (M^+, 38), 264 (56), 237 (39), 212 (69), 178 (76), 165 (100); HRMS (EI, 70 eV) m/z (M^+) calcd for $C_{17}H_{15}NO_3$ 281.1052, obsd 281.1052.

5-(4-Chlorophenyl)-5-phenyl-1,3-cyclopentadiene (1b): General Diene Synthesis. A solution of allyl alcohol **4b** (0.176 mmol, 0.048 g) in benzene (4 mL) was added to *p*-TsOH–H_2O (0.009 mmol, 0.002 g). The mixture was stirred at reflux for 18 h, at which time saturated sodium bicarbonate was added. Diethyl ether was then added, and the layers separated. The aqueous portion was extracted with diethyl ether, and the organic portions were combined, washed twice with water and twice with brine, dried ($MgSO_4$), and concentrated. The compound was purified by passing the crude product through a short silica plug (7:3 petroleum ether–CH_2Cl_2) to give the diene **1b** as an orange oil in 54% yield: ^1H NMR 7.29–7.13 (m, 9 H), 6.81–6.80 (m, 2 H), 6.42 (d, J = 6.5 Hz, 2 H); ^{13}C NMR 144.58, 141.30, 140.44, 132.36, 129.83, 128.91, 128.35, 127.56, 126.83, 68.14; IR (film) 3056, 1597, 1445, 1065, 1015 cm^{-1}; MS (EI, 70 eV) m/z 254 (M^+ + 2, 31), 252 (M^+, 100), 214 (46); HRMS (EI, 70 eV) m/z (M^+) calcd for $C_{17}H_{13}Cl$ 252.0706, obsd 252.0698.

5-(4-Nitrophenyl)-5-phenyl-1,3-cyclopentadiene (1a). Following the representative diene synthesis with nitro allylic alcohol **4a** (1.891 mmol, 0.532 g) for 4 h, and purification by column chromatography (SiO_2, 7:3 petroleum ether–CH_2Cl_2), gave the diene **1a** as an orange oil in 46% yield: ^1H NMR 8.04 (d, J = 8.5 Hz, 2 H), 7.32 (d, J = 8.5 Hz, 2 H), 7.25–7.18 (m, 5 H), 6.77–6.76 (m, 2 H), 6.44–6.42 (m, 2 H); ^{13}C NMR 149.99, 146.71, 144.01, 140.30, 130.74, 128.62, 128.20, 127.67, 127.27, 123.51, 68.63; IR (film) 3060, 2930, 1600, 1520, 1355 cm^{-1}; MS (CI, 150 eV (NH_3)) m/z 281 (M^+ + NH_4^+, 84), 262 (100); HRMS (CI 150 eV (NH_3)) m/z (M^+ + NH_4^+) calcd for $C_{17}H_{17}N_2O_2$ 281.1290, obsd 281.1290.

5-(4-Aminophenyl)-5-phenyl-1,3-cyclopentadiene (1d). To a mixture of nitro diene **1a** (1.371 mmol, 0.361 g) and $SnCl_2{\cdot}2H_2O$ (6.855 mmol, 1.547 g) in absolute ethanol (5 mL) at 60 °C was added $NaBH_4$ (0.686 mmol), 0.0259 g) in absolute ethanol (2 mL) in a dropwise fashion. The reaction mixture was stirred for 30 min at 60 °C, then cooled to 5–10 °C, and quenched with 5 mL of cold water. Neutralization with 1 M NaOH was followed by extraction of the aqueous layer with excessive quantities of diethyl ether. The combined organic portions were extracted twice with brine, dried ($MgSO_4$), and concentrated. After purification by elution with CH_2Cl_2 through a short silica plug, the amino diene **1d** was recovered in 69% yield as an orange oil: ^1H NMR 7.51–7.38 (m, 5 H), 7.27–7.23 (m, 2 H), 7.03–7.01 (m, 2 H), 6.76–6.71 (m, 2 H), 6.58–6.56 (m, 2 H), 3.67 (broad s, 2 H); ^{13}C NMR 145.03, 144.86, 144.67, 142.41, 128.87, 128.39, 128.02, 127.35, 126.27, 114.80, 67.78; IR (film) 3440, 3060, 2930, 1620, 1515 cm^{-1}. MS (CI, 150 eV (NH_3)) m/z 251 (M^+ + NH_4^+, 3.5), 234 (M^+ + H^+, 100); HRMS (CI, 150 eV (NH_3)) m/z (M^+ + H^+) calcd for $C_{17}H_{16}N$ 234.1283, obsd 234.1288.

5-[4-(Trimethylammonio)phenyl]-5-phenyl-1,3-cyclopentadienyl Iodide (1e). To a mixture of amino diene **1d** (0.943 mmol, 0.220 g) and $NaHCO_3$ (2.829 mmol, 0.238 g) in methanol (9 mL) was added CH_3I (4.883 mmol, 0.304 mL), and the reaction mixture was stirred under N_2 for 24 h at reflux. Another portion of CH_3I (3.213 mmol, 0.200 mL) was then added, and the mixture again was stirred at reflux for 24 h. A final aliquot of CH_3I (3.213 mmol, 0.200 mL) was added, and the mixture was stirred at reflux for 24 h. The reaction mixture was concentrated, and the residue was extracted with CH_2Cl_2 and water, dried ($MgSO_4$), and concentrated. Recrystallization in a CH_2Cl_2–petroleum ether solvent system gave the iodide salt **1e** in 77% yield as tan crystals, which decomposed above 169 °C: ^1H NMR 7.86 (d, J = 8.7 Hz, 2 H), 7.46 (d, J = 8.7 Hz, 2 H), 7.31–7.25 (m, 5 H), 6.82 (d, J = 5.0 Hz, 2 H), 6.48 (d, J = 5.0 Hz, 2 H), 4.01 (s, 9 H); ^{13}C NMR 145.40, 145.26, 143.84, 140.16, 130.48, 129.44, 128.48, 127.55, 127.09, 119.79, 67.90, 57.79; IR (film) 2970, 1580, 1375, 1210 cm^{-1}; MS (CI, 150 eV (NH_3)) m/z 262 (M^+ – I^- – CH_3 + H^+, 100); HRMS (CI, 150 eV (NH_3)) m/z (M^+ – I^-) calcd for $C_{20}H_{22}N$ 276.1753, obsd 276.1763.

5-[4-(Dimethylamino)phenyl]-5-phenyl-1,3-cyclopentadiene (1c). To a solution of $LiAlH_4$ (2.690 mmol, 0.102 g) in tetrahydrofuran (5.4 mL) was added the diene salt **1e** (0.538 mmol, 0.217 g) as a solid. The reaction mixture was stirred at reflux for 1 h until the evolution of methane ceased, and then it was cooled to 0 °C and 1 M NaOH was added slowly with stirring. The mixture was then extracted with CH_2Cl_2. The organic portion was dried ($MgSO_4$) and concentrated to give the dimethylamino diene **1c** as a dark orange oil in 76% yield, without need for further purification: ^1H NMR 7.29–7.23 (m, 5 H), 7.15 (d, J = 8.5 Hz, 2 H), 6.85–6.84 (m, 2 H), 6.66 (d, J = 8.5 Hz, 2 H), 6.40–6.39 (m, 2 H), 2.93 (s, 6 H); ^{13}C NMR 149.33, 145.20,

144.98, 142.41, 128.87, 128.28, 128.08, 127.47, 126.30, 112.46, 65.16, 40.57; IR (film) 3000, 1615, 1515 cm^{-1}; MS (CI, 150 eV (NH_3)) m/z 262 ($M^+ + H^+$, 100); HRMS (CI, 150 eV (NH_3)) m/z ($M^+ + H^+$) calcd for $C_{19}H_{20}N$ 262.1595, obsd 262.1591.

7-(4-Chlorophenyl)-2,3-dicarbomethoxy-7-phenylbicyclo[2.2.1]hepta-2,5-diene (2b): Representative Diels–Alder Procedure with Dimethyl Acetylenedicarboxylate. Dimethyl acetylenedicarboxylate (DMAD) (0.158 mmol, 0.19 mL) was added to a solution of chloro diene **1b** (0.079 mmol, 0.020 g) in benzene (1.5 mL). The mixture was heated to reflux and stirred for 2.5 days at which time another portion of DMAD was added (0.158 mmol, 0.19 mL), and the solution was stirred at reflux another 24 h. The reaction mixture was extracted with CH_2Cl_2 and water, dried ($MgSO_4$), and concentrated to give the Diels–Alder adduct **2b** as an orange oil in quantitative crude yield, clean by ^1H NMR. The diastereomeric ratio was determined from the ^1H NMR spectrum recorded in C_6D_6 to be 58:42. Separation of the diastereomers was accomplished by preparative TLC (SiO_2; 8:2 petroleum ether–ethyl ether; three developments) and both isomers were colorless oils: ^1H NMR major (higher R_f) 7.03–6.86 (m, 7 H), 6.78 (d, J = 8.0 Hz, 2 H), 6.45 (d, J = 2.0 Hz, 2 H), 4.58 (s, 2 H), 3.32 (s, 6 H); ^1H NMR minor (lower R_f) 7.22–7.04 (m, 3 H), 6.93 (d, J = 8.5 Hz, 2 H), 6.92–6.86 (m, 2 H), 6.61 (d, J = 8.5 Hz, 2 H), 6.47–6.46 (m, 2 H), 4.60–4.59 (m, 2 H), 3.34 (s, 6 H); ^{13}C NMR (major) 164.85, 150.49, 144.43, 142.85, 141.03, 131.83, 128.61, 128.38, 128.02, 126.70, 125.91, 95.85, 59.85, 52.16; ^{13}C NMR (minor) 164.79, 150.46, 143.71, 143.55, 141.18, 131.49, 128.55, 128.42, 128.24, 126.52, 126.31, 95.95, 59.89, 52.31; IR (film) 3060, 2960, 1710, 1630, 1440, 1267, 1098 cm^{-1}; MS (EI, 70 eV) m/z 394 (M^+, 3), 365 (7), 363 (20), 337 (32), 335 (97), 165 (100); HRMS (EI, 70 eV) m/z (M^+) calcd for $C_{23}H_{19}ClO_4$ 394.0972, obsd 394.0960.

7-(4-Nitrophenyl)-2,3-dicarbomethoxy-7-phenylbicyclo[2.2.1]hepta-2,5-diene (2a). Following the representative Diels–Alder procedure with DMAD with nitro diene **1a** (0.0919 mmol, 0.0242 g) for 5.5 days gave a quantitative crude yield of the Diels–Alder adduct **2a** as an orange oil. The diastereomeric ratio was determined by ^1H NMR spectroscopy in C_6D_6 to be 68:32. Separation of the diastereomers was accomplished by preparative TLC (SiO_2; 8:2 petroleum ether–ethyl acetate; four developments), and both isomers were colorless oils: ^1H NMR (C_6D_6) major (higher R_f) 7.75 (d, J = 8.7 Hz, 2 H), 7.19–6.93 (m, 5 H), 6.77 (d, J = 7.3 Hz, 2 H), 6.49 (broad s, 2 H), 4.61 (broad s, 2 H), 3.40 (s, 6 H); ^1H NMR (C_6D_6) minor (lower R_f) 7.70 (d, J = 8.7 Hz, 2 H), 7.19–6.91 (m, 5 H), 6.61 (d, J = 8.7 Hz, 2 H), 6.46–6.45 (m, 2 H), 4.61 (broad s, 2 H), 3.38 (s, 6 H); ^{13}C NMR (major) 164.62, 151.69, 150.43, 146.09, 143.13, 140.85, 128.64, 127.52, 126.82, 126.45, 123.87, 96.04, 59.61, 52.29; ^{13}C NMR (minor) 164.54, 152.45, 150.15, 145.80, 142.49, 141.42, 128.80, 127.68, 126.83, 126.64, 123.68, 95.80, 59.69, 52.19; IR (film) 2920, 1708, 1519, 1345, 1280 cm^{-1}; MS (EI, 70 eV) m/z 405 (M^+, 3), 373 (21), 346 (100), 286 (15), 239 (37), 165 (44); HRMS (EI, 70 eV) m/z (M^+) calcd for $C_{23}H_{19}NO_6$ 405.1213, obsd 405.1212.

7-[4-(Dimethylamino)phenyl]-2,3-dicarbomethoxy-7-phenylbicyclo[2.2.1]hepta-2,5-diene (2c). Following the representative Diels–Alder procedure with DMAD with the dimethylamino diene **1c** (0.109 mmol, 0.0286 g) for 5 days gave a quantitative crude yield of the Diels–Alder adduct **2c** as an orange oil. The diastereomeric ratio was determined by ^1H NMR spectroscopy in C_6D_6 to be 62:38. The diastereomers were separated via preparative TLC (SiO_2, 7:3 petroleum ether–diethyl ether; three developments), and both isomers were colorless oils: ^1H NMR (C_6D_6) major (higher R_f) 7.39 (d, J = 7.5 Hz, 2 H), 7.12–7.08 (m, 2 H), 6.91–6.86 (m, 3 H), 6.64–6.62 (m, 2 H), 6.42 (d, J = 8.5 Hz, 2 H), 4.80 (t, J = 2.0 Hz, 2 H), 3.34 (s, 6 H); 2.45 (s, 6 H); ^1H NMR (C_6D_6) minor (lower R_f) 7.26 (d, J = 8.7 Hz, 2 H), 7.04–6.98 (m, 3 H), 6.89–6.86 (m, 2 H), 6.57–6.56 (m, 2 H), 6.46 (d, J = 8.7 Hz, 2 H), 4.79 (t, J = 2.0 Hz, 2 H), 3.35 (m, 6 H), 2.37 (m, 6 H); ^{13}C NMR (major) 165.10, 150.79, 145.08, 141.03, 140.80, 128.88, 128.30, 127.57, 126.38, 125.68, 112.18, 96.40, 60.18, 52.02, 40.46; ^{13}C NMR (minor) 165.11, 150.66, 145.92, 141.24, 141.14, 128.13, 127.33, 126.82, 126.55, 125.26, 112.52, 96.30, 60.19, 52.00, 40.48; IR (film) 2960, 1620, 1513, 1430 cm^{-1}; MS (EI, 70 eV) m/z 403 (M^+, 6.8), 209 (8.8), 84 (100); HRMS (EI, 70 eV) m/z (M^+) calcd for $C_{22}H_{25}NO_4$ 403.1783, obsd 403.1784.

Lanthanide Shift Reagent Study of Products (2) from Diels–Alder Reaction of Cyclopentadienes (1) with DMAD. Both the major and minor products of the Diels–Alder cycloaddition with DMAD, isolated by preparative TLC, were subjected to lanthanide shift reagent $Eu(fod)_3$. The technique, as described here for the minor isomer of the chloro adduct **2b**, was similar to that used for the nitro- and (dimethylamino)-substituted adducts **2a** and **2c**. A sample of the minor isomer of cycloaddition product **2b** (0.068 mmol, 0.0269 g) in deuterated benzene (C_6D_6) was subjected to increasing amounts of a 0.026 M solution of Eu(fod) in C_6D_6, and after each carefully measured addition of shift reagent solution, the ^1H NMR spectrum was recorded. The overall change in chemical shift of the ortho protons on both the substituted (PhX) and unsubstituted (Ph) rings was determined by comparison of the ^1H NMR spectrum recorded in the absence of shift reagent to that taken of the sample when the amount of shift reagent added to the sample reached 5.7% with respect to the cycloaddition adduct **2b**. The procedure was repeated for the major isomer. The change in chemical shift ($\Delta\delta$) of the ortho protons for each diastereomer as determined by ^1H NMR (400 MHz, C_6D_6) is listed as follows: product isomer (% $Eu(fod)_3$, $\Delta\delta$ (PhX) ppm, $\Delta\delta$ (Ph) ppm). **2b** (X = Cl) major (13.8, 0.26, 0.16); **2b** (X = Cl) minor (5.7, 0.26, 0.50); **2a** (X = NO_2) major (12.5, 0.15, 0.05); **2a** (X = NO_2) minor (29.6, 0.16, 0.27); **2c** (X = $N(CH_3)_2$) major (14.2, 0.30, 0.58); **2c** (X = $N(CH_3)_2$) minor (8.3, 0.96, 0.50).

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and the National Science Foundation for a REU-NSF summer fellowship for B.A.M. (1989).

Supplementary Material Available: ^1H and/or ^{13}C NMR spectra of compounds 1–4 (26 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.