exchange, was also measured at the same temperatures. The ratio of the line widths was then plotted as function of temperature, so that the ratios could be interpolated, at temperatures where exchange occurs. The use of the ratios guarantees that the results are not affected by variations of the spectrometer resolution at different temperatures. From the interpolated ratios and from the knowledge of the width of the reference line where exchange occurs, accurate values of the line width in absence of exchange were obtained for the pair of the NMe signals. The knowledge of the line widths allowed us to computer-simulate the line-shape in the coalescence region as a function of *both* the rate constant and the chemical shift difference. These two unknowns were thus simultaneously obtained with a satisfactory degree of accuracy, allowing the determination of a $\Delta G^{*} = 19.1$ kcal mol^{-1} for the enantiomerization of **6**. Owing to the additional measurements required when the chiral auxiliary is employed, the errors on ΔG^{*} obtained in these conditions are larger: they were estimated to be ±0.3 kcal mol^{-1}. In the other cases the error is believed[1] to be ±0.15 kcal mol^{-1}.

ESR Measurements. The spectra were recorded with a Varian E-4 spectrometer. The *g* factors were measured by comparison with a sample containing solid DPPH in sodium chloride (*g* 2.0037). The nitroxides **8–16** were obtained by oxidizing the corresponding amines with *m*-chloroperbenzoic acid in toluene. The samples were degassed in vacuo by the usual thaw–freezing technique. The molar ratio amine/peracid was about 5–10:1 and the concentrations of the amines ranged between 10^{-3} and 10^{-2} M. If an excess of peracid was used, a second nitroxide was sometimes observed. For instance in the case of *N*-isopropyl-1-naphthylamine a second ESR spectrum appeared, in addition to the spectrum of **12**. On raising the temperature (+100 °C) this second radical disappeared, whereas at low temperature (−100 °C) it became the dominant species. This second nitroxide had $a_N = 13.5$ G and $a_H(CH) = 3.5$ G and no splittings from the ring hydrogens. Analogous results were obtained with *N*-ethyl-1-naphthylamine (the corresponding secondary species had $a_N = 13.2_5$ G and $a_H(CH_2) = 9.0$ G). Probably an excess of peracid introduces the -OCOAr (Ar = *m*-chlorophenyl) group into position 2 (and in position 4) of the naphthalene ring.[30] The presence of a substituent in position 2 would make the RNO plane more twisted with respect to the naphthalene ring than in the unsubstituted nitroxides **10** and **12**. This feature would account for the increased a_N values and for the absence of ring splittings in the secondary radicals.

Acknowledgment. Thanks are due to Dr. K. U. Ingold (N.R.C., Ottawa) for helpful comments and to Dr. J. E. Anderson (University College, London) for stimulating discussions on the stereodynamics of naphthylamines which were made possible by the N.A.T.O Research Grants Programme. This work received financial support from the Ministry of Public Education, Rome.

Registry No. **1**, 86-56-6; **2**, 83777-94-0; **3**, 110014-40-9; **4**, 110014-41-0; **5**, 110014-42-1; **6**, 110014-43-2; **7**, 110014-44-3; **8**, 61899-23-8; **9**, 110014-45-4; **10**, 110014-46-5; **11**, 110014-47-6; **12**, 110014-48-7; **13**, 110014-49-8; **14**, 41085-50-1; **15**, 110014-50-1; **16**, 110014-51-2; *N*-isopropylmethanamine, 4747-21-1; 1-bromonaphthalene, 90-11-9; *N*-ethyl-1-naphthalenamine, 118-44-5; *N*-(2,2-dimethylpropyl)-1-naphthalenamine, 110014-52-3; *N*-(3-pentyl)-1-naphthalenamine, 110014-53-4; *N*-*tert*-butyl-1-naphthalenamine, 54961-92-1; 1-naphthalenamine, 134-32-7; iodoethane, 75-03-6; 2-iodopropane, 75-30-9; *N*-isopropyl-1-naphthalenamine, 4960-23-0; *N*-methyl-1-naphthalenamine, 2216-68-4; *N*-methyl-1-naphthalenamine-*methyl-d*, 110014-54-5; 4-bromo-1-naphthalenamine, 2298-07-9; *N*-isopropyl-4-bromo-1-naphthalenamine, 110014-55-6; 2,2-dimethylpropanol, 75-84-3; *tert*-butyl alcohol, 75-65-0; 2-*tert*-butyl-1-naphthalenamine, 110014-56-7; *N*-ethyl-2-*tert*-butyl-1-naphthalenamine, 110014-57-8.

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[30] Berti, C.; Colonna, M.; Greci, L.; Marchetti, L. *Tetrahedron* **1977**, *33*, 2321.

π-Facial Selectivity in Diels–Alder Reactions of Hexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-5,7-diene-3,10-dione

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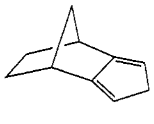
Received March 9, 1987

The reactions of the title diene (**2**) with olefinic dienophiles occur exclusively by attack on the carbonyl-bearing face of the diene component of **2**, while other dienophiles (benzyne, acetylenes, and azo compounds) exhibit mixed π-facial selectivities. X-ray crystal structures of the diene **5** and the diethyl azodicarboxylate adduct **47**, refined to conventional *R* values of 3.8% and 4.0%, respectively, are also reported.

Diels–Alder reactions of isodicyclopentadiene (**1**) and its derivatives have been extensively studied in recent years.[1] The origin of the observed π-facial selectivities has been considered variously as resulting from product stabilities,[1b] polarizability effects,[1c] π-orbital tilting associated with σ/π interactions,[1d] and a combination of torsional and steric effects.[1e]



(1)

We now report a related study of the Diels–Alder reactions of the title diene (**2**) with a variety of dienophiles. This diene can undergo dienophile attack on either the carbonyl-bearing face of the diene to produce **3**, or on the opposite face to produce **4**. Although three Diels–Alder reactions of this diene had been previously reported,[2-4] the stereochemistry of the products was not known until our

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[1] (a) Watson, W. H. *Stereochemistry and Reactivity of Systems Containing Pi Electrons*; Verlag Chemie International: Deerfield Beach, FL, 1983. (b) Hagenbuch, J. P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1818. (c) Mahaim, C.; Vogel, P. *Helv. Chim. Acta* **1982**, *65*, 866. (d) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328. (e) Brown, F. K.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 1971. (f) Paquette, L. A.; Gugelchuk, M.; Hsu, L.-Y. *J. Org. Chem.* **1986**, *51*, 3864 and references cited therein.

[2] With maleic anhydride: Filipescu, N.; Menter, J. M. *J. Chem. Soc. B* **1969**, 616.

[3] With benzoquinone: (a) Tolstikov, G. A.; Lerman, B. M.; Galin, F. Z. *Zh. Org. Khim.* **1975**, *11*, 1348. (b) Galin, F. Z.; Afonichev, D. D.; Lerman, B. M.; Kazakov, V. P.; Tolstikov, G. A. *Zh. Org. Khim.* **1978**, *14*, 2308.

[4] With dimethyl acetylenedicarboxylate: (a) Kushner, A. S.; *Tetrahedron Lett.* **1971**, 3275. (b) Mehta, G.; Singh, V.; Rao, K. S. *Tetrahedron Lett.* **1980**, *21*, 1369.

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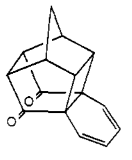
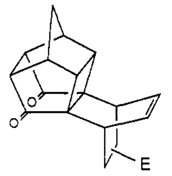
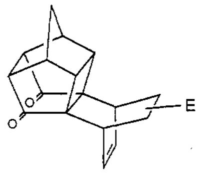
recent crystallographic study.[5]



(2)



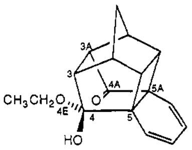
(3)



(4)

Results and Discussion

The title diene (**2**) was prepared according to the literature procedure.[4a] Since π-facial selectivities of Diels–Alder reactions have previously been ascribed to pyramidalization of the diene system,[6] we were interested in carrying out an X-ray crystal structure of the title diene (**2**) in order to determine whether the diene component of this compound is planar. Crystals of **2** suitable for crystallography were not available. However, recrystallization of **2** from ethanol resulted in its conversion to the crystalline monohemiacetal **5**, an X-ray structure of which was determined.



(5)

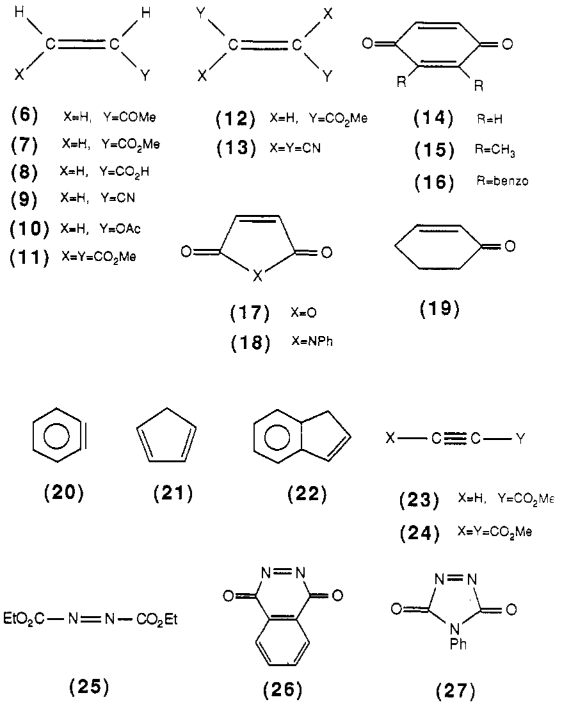
Of particular significance is the fact that the ethanol addition has occurred from the "internal" (endo) face of the carbonyl group. This result is somewhat surprising, since reactions involving the carbonyl group of related cage compounds have been assumed[7] to involve nucleophilic attack on the exo face of the carbonyl group. Although stereospecific exo reduction of such compounds has recently been unambiguously demonstrated,[8] the present result suggests that other reactions (e.g., amine and water additions) may involve attack on the endo face.

The geometry of the diene moiety in **2** and **5** is expected to be very similar, since the structural differences between the two are remote from the diene component. The cyclohexadiene ring is planar,[9] and there is no significant pryamidalization of the diene carbons in this compound.[10] The (nonbonded) O4E–C4A distance [2.612 (2) Å] is considerably longer than that previously[7a] estimated (2.20 Å) for this structural unit and the O4E–C4A–O4A angle (100.2 (1)°) greater than estimated (84°).

Table I. Reaction Conditions and Product Ratios for the Diels–Alder Reactions of 2

dienophile	react. condn, time/temp, °C	products (%) carbonyl face	cyclobutane face
6	4 days/80	**28** (>98)	(<2)
7	5 days/80	**29** (>98)	(<2)
8	7 days/80	**30** (>98)	(<2)
9	8 days/80	**31** (>98)	(<2)
10	6 days/80	no reaction	
11	9 days/80	**32** (>98)	(<2)
12	9 days/80	no reaction	
13	5 days/80	no reaction	
14	3 h/80	**33** (>98)	(<2)
15	24 h/80	**34** (>98)	(<2)
16	24 h/80	**35** (>98)	(<2)
17	24 h/80	**36** (>98)	(<2)
18	1 h/80	**37** (>98)	(<2)
19	6 days/80	no reaction	
20	3 h/40	**39** (90)	**40** (10)
22	6 days/80	no reaction	
23	9 days/80	**44** (>98)	(<2)
24	1 day/80	**45** (55)	**46** (45)
24	6 days/25	**45** (60)	**46** (40)
25	5 days/80	(<2)	**47** (>98)
26	5 h/25	**48** (43)	**49** (57)
27	15 min/0	**50** (64)	**51** (36)

Chart I



In solution, proton NMR studies showed that **5** rapidly redissociates to the diene **2** and ethanol. In the Diels–Alder reactions described below, trial studies showed that the same products were obtained whether **5** or unrecrystallized **2** was used as starting material.

Diels–Alder Reactions. The diene **2** reacted smoothly, albeit slowly, with a variety of dienophiles to produce the Diels–Alder adducts **3** and/or **4**. Table I summarizes the reaction conditions and product ratios for the Diels–Alder reactions with the dienophiles listed in Chart I. Product ratios were determined by 300-MHz ^1H NMR spectral analysis of the crude reaction mixtures. The stereochemistry of the adducts was determined by a variety of methods. As mentioned above, we previously reported unambiguous structure determinations of three adducts

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[5] Coxon, J. M.; O'Connell, M. J.; Steel, P. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 1773.

[6] Angell, E. C.; Fringuelli, F.; Pizzo, F.; Porter, B.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1986**, *51*, 2642 and references cited therein.

[7] (a) Sasaki, T.; Eguchi, S.; Kiriyama, T.; Hiroaki, O. *Tetrahedron* **1974**, *30*, 2707. (b) Dekker, T. G.; Oliver, D. W. *S. Afr. J. Chem.* **1979**, *32*, 45. (c) Marchand, A. P.; Kaya, R. *J. Org. Chem.* **1983**, *48*, 5392. (d) Eaton, P. E.; Or, Y. S.; Branca, S. J.; Ravi Shankar, B. K. *Tetrahedron* **1986**, *42*, 1621.

[8] Marchand, A. P.; LaRoe, W. D.; Sharma, G. V. M.; Suri, S. C.; Reddy, D. S. *J. Org. Chem.* **1986**, *51*, 1622.

[9] Root mean square deviation from the mean plane defined by the six carbon atoms: 0.025 (2) Å (all torsional angles about the C–C bonds being <6°).

[10] The bonding geometry in **5** is similar to that previously reported for related cage compounds,[5,11,12] except that the bond elongations of the C3–C3A and C5–C5A bonds are less extreme than those reported for cage diketones in which there is significant electrostatic repulsion between the two carbonyl groups.

[11] Mehta, G.; Singh, V.; Srikrishna, A.; Cameron, T. S.; Chan, C. *Tetrahedron Lett.* **1979**, 4595.

[12] (a) Marchand, A. P.; Suri, S. C.; Earlywine, A. D.; Powell, D. R.; van der Helm, D. *J. Org. Chem.* **1984**, *49*, 670. (b) Okamoto, Y.; Harano, K.; Yasuda, M.; Osawa, E.; Kanematsu, K. *Chem. Pharm. Bull.* **1983**, *31*, 2526.

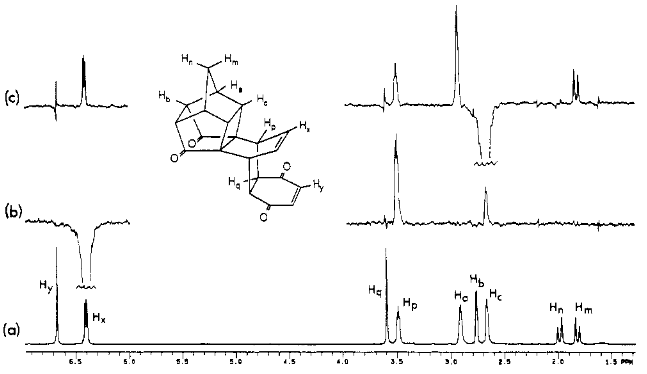
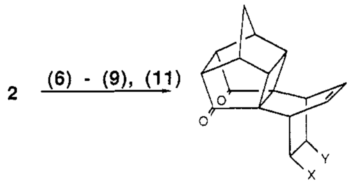


Figure 1. Normal ^{1}H NMR spectrum (a) and NOE difference spectra (b, c) for the benzoquinone adduct of **2**.

Scheme I

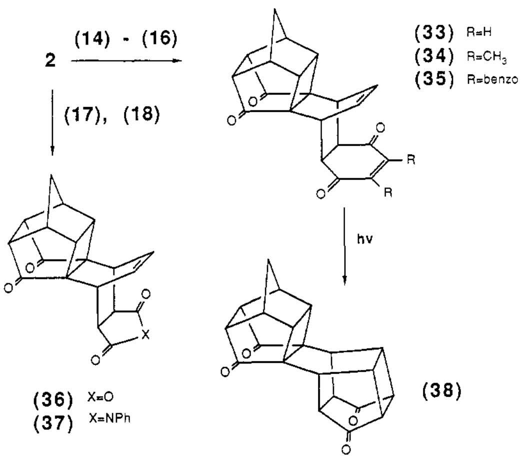


(28) X=H, Y=COMe
(29) X=H, Y=CO$_2$Me
(30) X=H, Y=CO$_2$H
(31) X=H, Y=CN
(32) X=Y=CO$_2$Et

by X-ray crystallography.[5] The stereochemistry of other adducts was determined by spectroscopic or chemical means. In particular, nuclear Overhauser effect difference (NOED) spectroscopy[13] proved particularly useful for distinguishing between **3** and **4**, since spin–spin coupling information is not transmitted through the "spectroscopically silent" propellane carbons of the adducts. A typical example is shown in Figure 1. The normal 300-MHz proton NMR spectrum of the benzoquinone adduct is shown in Figure 1a along with the proton assignments, which were determined on the basis of homonuclear decoupling and NOED experiments. The NOED spectrum resulting from irradiation of the olefinic protons H$_x$ is shown in Figure 1b. This spectrum shows significant enhancement of the signals due to the spatially proximate protons H$_p$ and H$_c$. Similarly, irradiation of H$_c$ (Figure 1c) results in enhancements of the signals for the nearby protons H$_a$, H$_m$, H$_p$, and H$_x$. The mutual enhancements observed between H$_c$ and H$_x$ are clearly only consistent with the structure resulting from dienophile attack on the carbonyl-bearing face of the diene. Detailed assignments of the proton and carbon-13 NMR spectra for all the adducts are given in the supplementary material and are based on two-dimensional proton–proton (COSY) and proton–carbon (HETCOR) correlation spectroscopy and NOED spectra.

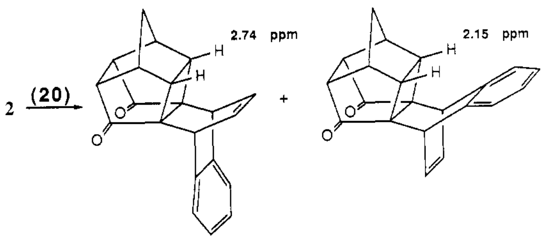
The diene **2** reacted relatively slowly with the electron-deficient monosubstituted alkenes **6–9** and with diethyl maleate (**11**) to give exclusively the Alder adducts **28–32** resulting from dienophile attack on the carbonyl face of the diene (Scheme I). In contrast, the electron-rich alkene **10** and the *trans*-olefin **12** failed to react over extended reaction times. Similarly, no reaction occurred with the tetrasubstituted reactive olefin **13**.

Scheme II



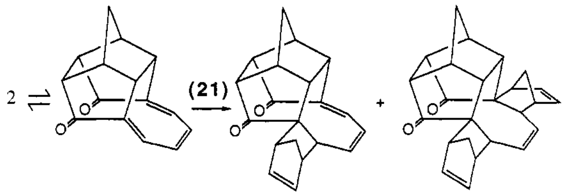
(33) R=H
(34) R=CH$_3$
(35) R=benzo
(36) X=O
(37) X=NPh
(38)

Scheme III



(39) (40)

Scheme IV



(41) (42) (43)

The cyclic dienophiles **14–18** reacted more rapidly with **2** with the same stereoselectivity as above to give the adducts **33–37** (Scheme II). The structure of **33** was shown by X-ray crystallography[5] to be different from that previously proposed.[3] Accordingly, the structure of the known[3] [2+2] photoadduct of **33** should be reassigned as **38**. Although **33** is readily photolyzed to the biscage **38**, the corresponding naphthoquinone adduct **35** failed to form a biscage product on photolysis. The structure of **36** was also confirmed by X-ray crystallography[5] and used to confirm the structure of **32**, to which it was converted by acid-catalyzed reaction with ethanol. The less reactive cyclic dienophile **19** failed to react with **2**.

Benzyne (**20**) reacted with **2** to give a mixture of two adducts, **39** and **40**, which were separated by radial chromatography and distinguished, inter alia, by the relatively high-field position of the cyclobutane ring protons that lie over the shielding region of the benzene ring in **40** (Scheme III).

Reaction of **2** with cyclopentadiene (**21**) has been previously reported.[4b] In our hands, reaction with excess cyclopentadiene produced two adducts, which were separated by radial chromatography and identified as the known monoadduct **42** and the new bisadduct **43** (Scheme IV). The structure of **43** was determined by a combination of one- and two-dimensional NMR techniques. These products are formed from Diels–Alder reactions in which **21** acts as the diene component and the valence tautomer

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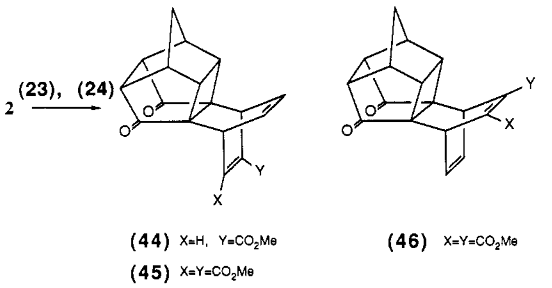
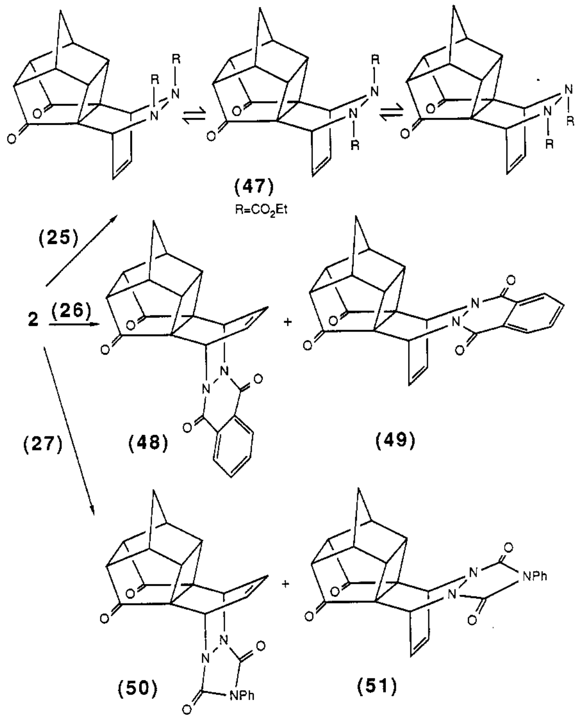
(13) Sanders, J. K. M.; Mersh, J. D. *Prog. Nucl. Magn. Reson. Spectrosc.* 1983, *15*, 353.

Scheme V



Scheme VI



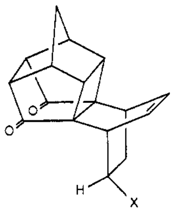
41[4b,11] of the diene 2 acts as the dienophile. In contrast, no reaction occurs with indene (22), which does not undergo reaction as a diene.

Reaction of 2 with the electron-deficient acetylenes 23 and 24 produced the adducts 44–46 (Scheme V). Thus, methyl propiolate (23) reacted stereospecifically to produce a single diastereoisomer resulting from attack on the carbonyl face of the diene, while dimethyl acetylenedicarboxylate (24) reacted more rapidly to give a mixture of the two possible isomers. The reaction of 2 with 24 has been twice previously reported,[4] and in each case only a single product was reported. We have unambiguously determined the structure of 46 by X-ray crystallography,[5] and on the basis of the melting points previously reported, it seems that Kushner[4a] isolated adduct 45 while Mehta et al.[4b] isolated the less soluble minor isomer 46.

Diethyl azodicarboxylate (25) reacted with 2 to give a single adduct, which produced unexpectedly complex NMR spectra. An X-ray crystal structure determination[14] showed this product to be 47, the product resulting from attack on the cyclobutane face of the diene. In the solid state the two nitrogen atoms are pyramidal with one of the two ethoxycarbonyl substituents in an exo configuration and the other endo with respect to the bicyclo[2.2.2]octane skeleton; this is similar to a related structure previously reported.[15] The complexity of the NMR spectra results from slow inversion on the NMR time scale of the nitrogen atoms (see Scheme VI). Similar dynamic effects on the NMR spectra of related compounds are well-known.[17]

Phthalazinedione (26) and the very reactive dienophile *N*-phenyltriazolinedione (27) each reacted with 2 to give a mixture of the two possible diastereoisomers are shown in Scheme VI. In these products, however, the nitrogen atoms are planar, and hence no dynamic NMR effects are observed.

Stereoselectivities. Of the four possible isomers 52–55 from Diels–Alder reactions of 2, only the Alder products (52 and/or 53) are observed in the above reactions. Although anti-Alder adducts are not uncommon[18] (e.g., reactions of 1), the transition states leading to 54 and 55 are destabilized by steric interactions between the dienophile substituent X and either the carbonyl oxygens or the cyclobutane ring protons.[19] These observations are also consistent with the fact that only cis-disubstituted olefins react with 2. Thus, whereas diethyl maleate (11) reacts smoothly, diethyl fumarate (12) and the normally reactive tetrasubstituted dienophile TCNE (14) both fail to react. On the basis of the above it is probable that DEAD (25), which exists principally as the trans isomer,[20] reacts only as the cis isomer with which it is in equilibrium, thereby explaining the relatively slow reactivity of this compared with other nitrogen dienophiles.



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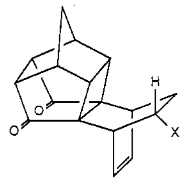
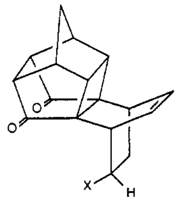
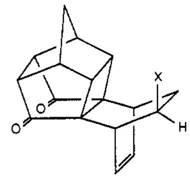


(53)



(54)



(55)

All the olefinic dienophiles studied undergo cycloaddition exclusively from the carbonyl face of the diene component of 2. Calculations based on the crystal structures reported herein suggest that for a normal Diels–Alder transition-state geometry[21] attack from the opposite face

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[14] The bonding geometry in 47 is similar to that reported for related structures.[5,11,12,15,16] However, the geometry does differ from that estimated[7a] for a cage diketone using Dreiding models, the distance between the carbonyl carbons and oxygens being 2.606 (3) and 3.988 (2) Å, respectively, in contrast to the previously estimated[7a] values of 2.44 and 3.52 Å.

(15) Offereins, B.; Altona, C.; Romers, C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 2098.

(16) (a) Sommer, S.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 696. (b) Daub, J.; Hirmer, G.; Jakob, L.; Mass, G.; Pickl, W.; Pirzer, E.; Rapp, K. M. *Chem. Ber.* **1985**, *118*, 1836.

(17) (a) Anderson, J. E.; Lehn, J. M. *Tetrahedron* **1968**, *24*, 123 and 137. (b) Bittner, E. W.; Gerig, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 913. (c) Nelsen, S. F.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 1842. (d) Gunter, H.; Jikeli, G. *Chem. Rev.* **1977**, *77*, 599. (e) Nelsen, S. F.; Frigo, T. B.; Kim, Y.; Thompson-Colon, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 7926.

(18) For example, see: Gallucci, J. C.; Kravetz, T. M.; Green, K. E.; Paquette, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 6592 and references cited therein.

(19) In many cases, the transition states leading to the Alder adducts are further stabilized by secondary orbital interactions. See: Ginsberg, D. *Tetrahedron*, **1983**, *39*, 2095.

(20) Amey, R. L.; Smart, B. E. *J. Org. Chem.* **1981**, *46*, 4090.

would result in unreasonably close interactions between the olefinic protons and the cyclobutane ring protons. In contrast, for the dienophiles benzyne, alkynes, and azo compounds, the stereoselectivity ranges from exclusive carbonyl face attack (for methyl propiolate) to exclusive cyclobutane face attack (for DEAD). We attribute these changes in stereoselectivity to a combination of three factors. First, these dienophiles are considerably more reactive, and hence kinetic differentiation between the two transition states is expected to be reduced. Second, these dienophiles do not possess protons similarly disposed to those in the olefinic dienophiles for interaction with the cyclobutane ring protons as discussed above. Third, in the transition state for carbonyl face attack the dienophiles all possess π- or nonbonding orbital electron density, which will repulsively interact with the electron density of the carbonyl oxygen atoms. Further experiments are currently in progress that are designed to assess the relative importance of these factors on the stereoselectivity observed in the reactions of diene **2**.

Experimental Section

NMR spectra were recorded on a Varian XL-300 spectrometer equipped with a 5-mm probe operating at 299.930 and 75.426 MHz for ^{1}H and ^{13}C, respectively. Spectra were recorded on $CDCl_3$ solutions with tetramethylsilane as internal standard, unless otherwise specified. Difference NOE spectra were obtained in an arrayed experiment with the decoupler offset 10 000 Hz and then cycled with low power over the multiplet peaks of the desired proton for irradiation, a procedure based on that of Kinns and Sanders.[22] COSY spectra were recorded in the normal fashion with the well-established pulse sequence and phase cycling of Bax, Freeman, and Morris.[23] Heteronuclear proton–carbon correlated spectra were recorded in the usual manner.[24] Unless otherwise stated all dienophiles were obtained commercially. Fully assigned ^{1}H and ^{13}C NMR spectra of all the Diels–Alder adducts are provided as supplementary material.

Preparation of 5. The cyclopentadiene–naphthoquinone cage diene **2** was prepared by the literature procedure; mp 108–110 °C (lit.[4a] mp 111–112 °C). Recrystallization of the crude solid (2.0 g) from ethanol–dichloromethane gave colorless prisms (1.3 g) of the monohemiacetal **5**: mp 104–107 °C; IR 3400, 3000, 1740 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.53; H, 6.71.

Diels–Alder Reactions of Diene 2. General Procedure. Equimolar quantities of **2** (3 mmol) and a dienophile were dissolved in benzene (10 mL), and the resulting solutions were refluxed for 1 h–9 days. The crude reaction mixtures were examined by 300-MHz NMR. The adducts either precipitated from the reaction mixture and were filtered, washed several times with benzene, and recrystallized from suitable solvents or were purified by radial chromatography.

(i) Reaction with methyl vinyl ketone (**6**) for 4 days gave 13-acetylheptacyclo$[10.2.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}]$heptadec-15-ene-3,10-dione (**28**), which was recrystallized from benzene as colorless needles: 0.33 g; mp 168–169 °C; IR 1730, 1710 cm^{-1}; mass spectrum, *m/e* 294.1250 (M^+ calcd for $C_{19}H_{18}O_3$ 294.1256). Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.52; H, 6.16. Found: C, 77.42; H, 6.44.

(ii) Reaction with methyl acrylate (**7**) for 5 days gave 13-(methoxycarbonyl)heptacyclo$[10.2.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}]$heptadec-15-ene-3,10-dione (**29**), which was recrystallized from dichloromethane–ethanol as colorless prisms: 0.51 g; mp 151–153 °C; IR 1750, 1730 cm^{-1}; mass spectrum, *m/e* 310.1197 (M^+ calcd for $C_{19}H_{18}O_4$ 310.1205). Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.28; H, 5.74.

(iii) Reaction with acrylic acid (**8**) for 7 days gave 3,10-dioxoheptacyclo$[10.2.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}]$heptadec-15-ene-13-carboxylic acid (**30**), which crystallized from the reaction mixture as colorless prisms: 0.35 g; mp 276–278 °C; IR 3000, 1740, 1700 cm^{-1}; mass spectrum, *m/e* 296.1050 (M^+ calcd for $C_{18}H_{16}O_4$ 296.1049). Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.86; H, 5.51.

(iv) Reaction with acrylonitrile (**9**) for 8 days gave 13-cyanoheptacyclo$[10.2.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}]$heptadec-15-ene-3,10-dione (**31**), which was recrystallized from dichloromethane–benzene as colorless prisms: 0.46 g; mp 197–198 °C; IR 3000, 2250, 1740 cm^{-1}; mass spectrum, *m/e* 277.1104 (M^+ calcd for $C_{18}H_{15}NO_2$ 277.1103). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.60; H, 5.43; N, 4.90.

(v) Reaction with diethyl maleate (**11**) for 9 days gave 13,14-bis(ethoxycarbonyl)heptacyclo$[10.2.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}]$heptadec-15-ene-3,10-dione (**32**), which was recrystallized from benzene as colorless prisms: 0.21 g; mp 191–194 °C; IR 1735 cm^{-1}; mass spectrum, *m/e* 396.1562 (M^+ calcd for $C_{23}H_{24}O_6$ 396.1573). Anal. Calcd for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 69.30; H, 6.17.

(vi) Reaction with benzoquinone (**14**) for 3 h gave octacyclo$[10.6.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,18}]$heneicosa-15,19-diene-3,10,14,17-tetrone (**33**; 0.47 g), which crystallized from the reaction mixture as pale yellow needles: mp >240 °C dec (lit.[3a] mp 265–267 °C); IR 1745, 1720, 1675 cm^{-1}; mass spectrum, *m/e* 332.1039 (M^+ calcd for $C_{21}H_{16}O_4$ 332.1049).

(vii) Reaction with 2,3-dimethylbenzoquinone (**15**)[25] for 24 h gave 15,16-dimethyloctacyclo$[10.6.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,18}]$heneicosa-15,19-diene-3,10,14,17-tetrone (**34**; 0.61 g), which crystallized from the reaction mixture as colorless prisms: mp 280–283 °C dec; IR 1740, 1725, 1670 cm^{-1}; mass spectrum, *m/e* 360.1361 (M^+ calcd for $C_{23}H_{20}O_4$ 360.1362). Anal. Calcd for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.93; H, 5.61.

(viii) Reaction with naphthoquinone (**16**) for 24 h gave nonacyclo$[12.7.2.2^{2,13}.0^{1,14}.0^{3,12}.0^{5,10}.0^{16,20}.0^{17,23}.0^{19,22}]$pentacosa-5,7,9,24-tetrene-4,11,15,21-tetrone (**35**; 0.43 g), which crystallized from the reaction mixture as colorless prisms: mp 291–292 °C; IR 1740, 1695 cm^{-1}; mass spectrum, *m/e* 382.1186 (M^+ calcd for $C_{25}H_{18}O_4$ 382.1205). Anal. Calcd for $C_{25}H_{18}O_4$: C, 78.52; H, 4.74. Found: C, 78.53; H, 5.13.

(ix) Reaction with maleic anhydride (**17**) for 24 h gave 5-oxaoctacyclo$[10.5.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,17}]$eicos-18-ene-3,10,14,16-tetrone (**36**; 0.73 g), which crystallized from the reaction mixture as colorless plates: mp 304–305 °C (lit.[2] mp 299–300 °C); IR 1870, 1840, 1790, 1740, 1725 cm^{-1}; mass spectrum, *m/e* 322.0847 (M^+ calcd for $C_{19}H_{14}O_5$ 322.0841).

(x) Reaction with *N*-phenylmaleimide (**18**) for 1.5 h gave 15-phenyl-15-azaoctacyclo$[10.5.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,17}]$eicos-18-ne-3,10,14,16-tetrone (**37**; 0.80 g), which crystallized from the reaction mixture as colorless plates: mp 344–345 °C; IR 1730 cm^{-1}; mass spectrum, *m/e* 397.1314 (M^+ calcd for $C_{25}H_{19}NO_4$ 397.1314). Anal. Calcd for $C_{25}H_{19}NO_4$: C, 75.55; H, 4.82; N, 3.52. Found: C, 75.27; H, 4.58; N, 3.44.

(xi) Benzenediazonium-2-carboxylate prepared from anthranilic acid (0.67 g, 4.9 mmol) by the method of Crews and Beard[26] was allowed to decompose to benzyne (**20**) in the presence of **2** (1.1 g, 4.5 mmol) in dichloromethane (15 mL) by gentle heating on a steam bath for 3 h. The solvent was removed under reduced pressure to give an oil, which was adsorbed onto silica on a radial chromatograph. Elution with ether–petroleum ether (1:1) gave octacyclo$[10.6.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,18}]$heneicosa-13,15,17,19-tetrene-3,10-dione (**40**), which was recrystallized from dichloromethane–benzene as colorless plates: mp 229–232 °C dec; IR 1735 cm^{-1}; mass spectrum, *m/e* 300.1153 (M^+ calcd for $C_{21}H_{16}O_2$ 300.1150). Further elution gave octacyclo$[10.6.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{15,18}]$heneicosa-13,15,17,19-tetrene-3,10-dione (**39**), which was recrystallized from dichloromethane–benzene as colorless prisms: mp 240–241 °C; IR 1740, 1730 cm^{-1}; mass spectrum, *m/e* 300.1138 (M^+ calcd for $C_{21}H_{16}O_2$ 300.1150). Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.79; H, 5.10.

(xii) To a solution of **2** (0.45 g) in benzene (10 mL) was added freshly cracked cyclopentadiene (**21**; 1 mL). The mixture was refluxed at 85 °C for 7.5 h, after which time solvent was removed

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under reduced pressure to give an oily residue, which was absorbed onto silica on a radial chromatograph. Elution with ether–petroleum ether (1:1) gave heptacyclo[14.2.1.1^{5,8}.0^{2,15}.0^{4,9}.0^{4,18}.0^{13,17}]eicosa-6,10,12-triene-3,14-dione (**42**; 0.24 g) as reported by Mehta.[4b] Further elution gave nonacyclo[18.2.1.1^{5,8}.1^{13,16}.0^{2,19}.0^{4,9}.0^{4,22}.0^{12,17}.0^{17,21}]pentacosa-6,10,14-triene-3,18-dione (**43**; 0.19 g), which was recrystallized from benzene as colorless prisms: mp 144–145 °C; IR 1745 cm^{-1}; mass spectrum, *m/e* 356.1763 (M$^+$ calcd for $C_{25}H_{24}O_2$ 356.1776). Anal. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79. Found: C, 84.35; H, 6.72.

(xiii) A solution of **2** (0.27 g) and methyl propiolate (**23**; 0.4 mL) in benzene (5 mL) was heated under reflux for 9 days. The solvent was removed, the residue was absorbed onto silica on a radial chromatograph, and elution with ether gave unreacted **2** (0.11 g). Further elution gave 13-(methoxycarbonyl)heptacyclo[10.2.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}]heptadeca-13,15-diene-3,10-dione (**44**), which was recrystallized from dichloromethane–ethanol as colorless prisms: 0.10 g; mp 172–174 °C; IR 1760, 1730 cm^{-1}; mass spectrum, *m/e* 308.1029 (M$^+$ calcd for $C_{19}H_{16}O_4$ 308.1049). Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.93; H, 5.41.

(xiv) A solution of **2** (0.5 g) and dimethyl acetylenedicarboxylate (**24**; 0.28 mL) in benzene (5 mL) was heated under reflux for 1 day. The solvent was removed to give a residue from which the major product 13,14-bis(methoxycarbonyl)heptacyclo[10.2.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}]heptadeca-13,15-diene-3,10-dione (**45**) was recrystallized from chloroform–benzene: 0.25 g; mp 269–272 °C (lit.[4a] mp 275–278 °C); IR 1760, 1745, 1715 cm^{-1}; mass spectrum, *m/e* 366.1086 (M$^+$ calcd for $C_{21}H_{18}O_6$ 366.1103). Crystals from the mother liquor were recrystallized several times to give 13,14-bis(methoxycarbonyl)heptacyclo[10.2.2.1^{5,8}.0^{2,6}.0.0^{2,11}.0^{4,9}.0^{7,11}]heptadeca-13,15-diene-3,10-dione (**46**) as colorless prisms from chloroform–benzene: 0.18 g; mp 189–190 °C (lit.[4b] mp 186–187 °C); IR 1760, 1745, 1710 cm^{-1}; mass spectrum, *m/e* 366.1100 (M$^+$ calcd for $C_{21}H_{18}O_6$ 366.1103).

(xv) To a stirred solution of **2** (1.1 g) in benzene (15 mL) was added diethyl azodicarboxylate (**25**;[27] 0.8 mL), and the mixture was refluxed at 85–90 °C for 5 days. After removal of solvent the residue was absorbed onto silica on a radial chromatograph. Elution with ether gave 13,14-bis(ethoxycarbonyl)-13,14-diazaheptacyclo[10.2.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}]heptadec-15-ene-3,10-dione (**47**), which was recrystallized from benzene–dichloromethane as colorless prisms: 0.2 g; mp 212–213 °C; IR 3000, 1740, 1695 cm^{-1}; mass spectrum, *m/e* 398.1464 (M$^+$ calcd for $C_{21}H_{22}N_2O_6$ 398.1478). Anal. Calcd for $C_{21}H_{22}N_2O_6$: C, 63.31; H, 5.57; N, 7.03. Found: C, 63.39; H, 5.72; N, 7.33.

(xvi) 1,4-Phthalazinedione (**26**) was prepared as follows:[28] to a stirred suspension of 1,4-phthalohydrazide (0.72 g, 4.50 mmol) in dichloromethane (50 mL) was added *N*-bromosuccinamide (1.60 g, 9.00 mmol). After 5 min a solution of **2** (1.9 g, 4.46 mmol) in dichloromethane (5 mL) was added, and the resulting solution was stirred for 5 h at room temperature. The organic layer was washed successively with sodium thiosulfate solution (10%, 50 mL) and water (2 × 50 mL), dried over sodium sulfate, and concentrated under reduced pressure to give a residue from which the major product 3,12-diazanonacyclo[12.7.2.2^{2,13}.0^{1,14}.0^{3,12}.0^{5,10}.0^{16,20}.0^{17,23}.0^{19,22}]pentacosa-5,7,9,24-tetrene-4,11,15,21-tetrone (**49**) was recrystallized from acetone as a colorless powder: 80 mg; mp 295 °C; IR 1750, 1735, 1635 cm^{-1}; mass spectrum, *m/e* 384.1123 (M$^+$ calcd for $C_{23}H_{16}N_2O_4$ 384.1110). Crystals from the mother liquor were recrystallized several times from chloroform to give 3,12-diazanonacyclo[12.7.2.2^{2,13}.0^{1,14}.0^{3,12}.0^{5,10}.0^{16,20}.0^{17,23}.0^{19,22}]pentacosa-5,7,9,24-tetrene-4,11,15,21-tetrone (**48**) as colorless needles: 50 mg; mp >380 °C dec; IR 1760, 1740, 1640 cm^{-1}; mass spectrum, *m/e* 384.1121 (M$^+$ calcd for $C_{23}H_{16}N_2O_4$ 384.1110).

(xvii) To a stirred ice-cooled solution of **2** (0.5 g) in dichloromethane (10 mL) was slowly added dropwise a solution of 4-phenyl-1,2,4-triazaoline-3,5-dione (**27**;[29] 0.39 g) in dichloromethane (15 mL) until a faint red coloration persisted. The solution was stirred for an additional 15 min, and the solvent was removed to give a residue from which the major product 15-phenyl-13,15,17-triazaoctacyclo[10.5.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,17}]eicos-18-ene-3,10,14,16-tetrone (**50**) was recrystallized from benzene–chloroform as colorless prisms: 90 mg; mp 300–301 °C; IR 1740, 1705, 1500, 1400, 1370 cm^{-1}; mass spectrum, *m/e* 399.1217 (M$^+$ calcd for $C_{23}H_{17}N_3O_4$ 399.1219). Crystals from the mother liquor were recrystallized several times to give 15-phenyl-13,15,17-triazaoctacyclo[10.5.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,17}]eicos-18-ene-3,10,14,16-tetrone (**51**) as colorless needles from benzene–chloroform 60 mg; mp 311–312 °C; IR 1740, 1710, 1405, 1375 cm^{-1}; mass spectrum, *m/e* 399.1224 (M$^+$ calcd for $C_{23}H_{17}N_3O_4$ 399.1219).

Table II. Crystal Data and X-ray Experimental Details

	5	47
formula	$C_{17}H_{18}O_3$	$C_{21}H_{22}N_2O_6$
MW	270.3	398.4
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	7.011 (1)	8.782 (3)
b, Å	8.977 (2)	14.335 (4)
c, Å	11.216 (2)	14.726 (3)
α, deg	108.13 (1)	90
β, deg	90.09 (1)	98.75 (2)
γ, deg	103.40 (1)	90
V, Å^3	650.5	1832.3
D_{calcd}, g cm^{-3}	1.38	1.44
D_{measd}, g cm^{-3}	1.35	1.42
Z	2	4
F(000)	288	840
radiation	Mo Kα	Mo Kα
wavelength, Å	0.71069	0.71069
temp, °C	−140	−140
crystal dimens, mm	0.61 × 0.39 × 0.21	0.45 × 0.42 × 0.14
scan mode	$\theta/2\theta$	$\theta/2\theta$
2θ range, deg	3–50	4–50
no. of unique reflcns	2280	3249
no. of obsd. reflcns	2047	2400
no. of parameters	184	262
g	0.000 18	0.0006
R, %	3.8	4.0
R_w, %	4.5	5.2

Esterification of Maleic Anhydride Adduct. To a solution of the adduct **36** in ethanol (50 mL) was added concentrated sulfuric acid (0.2 mL). The solution was refluxed at 80 °C for 24 h. The reaction mixture was poured into a saturated solution of sodium carbonate (25 mL), and the aqueous phase was extracted with chloroform (2 × 25 mL). The organic extracts were washed, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was absorbed onto silica on a radial chromatograph. Elution with ether gave 10-ethoxy-10-hydroxy-13,14-bis(ethoxycarbonyl)heptacyclo[10.2.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}]heptadec-15-en-3-one as colorless prisms from benzene: 0.15 g; mp 98–100 °C; IR 3500, 3000, 1740 cm^{-1}; mass spectrum, *m/e* 442.1987 (M$^+$ calcd for $C_{25}H_{30}O_7$ 442.1991). Further elution gave the adduct **32** (0.30 g) with identical physical and spectral properties to those described above.

X-ray Structure Determination. Table II lists crystal data and X-ray experimental details for **5** and **47**. The measured densities were determined by flotation in aqueous potassium iodide solutions. Intensity data were collected with a Nicolet R3m four-circle diffractometer by using monochromatized Mo Kα radiation. Cell parameters were determined by least-squares refinement, the setting angles of 25 accurately centered reflections ($2\theta > 23°$) being used. Throughout the data collections the intensities of three standard reflections were monitored at regular intervals, and this indicated no significant crystal decomposition. The intensities were corrected for Lorentz and polarization effects, but no correction was made for absorption. Reflections with $I > 3\sigma(I)$ were used for structure solution and refinement.

Both structures were solved by direct methods and refined by blocked cascade least-squares procedures. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to the isotropic equivalent to their carrier atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. The magnitude of residual electron density in final Fourier syntheses was <0.3 e·Å^{-3}. All calculations (including diagrams) were performed on a Nova 4X computer using

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SHELXTL.[30] Tabulations of atom coordinates, thermal parameters, bond lengths and angles are available as supplementary material.

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Registry No. **2**, 24402-96-8; **5**, 110097-65-9; **6**, 78-94-4; **7**, 96-33-3; **8**, 79-10-7; **9**, 107-13-1; **11**, 141-05-9; **14**, 106-51-4; **15**, 526-86-3; **16**, 130-15-4; **17**, 108-31-6; **18**, 941-69-5; **20**, 462-80-6; **21**, 542-92-7; **23**, 922-67-8; **24**, 762-42-5; **25**, 1972-28-7; **26**, 20116-64-7; **27**, 4233-33-4; **28**, 110097-66-0; **29**, 110116-43-3; **30**, 110097-67-1; **31**, 110097-68-2; **32**, 110097-69-3; **33**, 106499-32-5; **34**, 110097-70-6; **35**, 110097-71-7; **36**, 106499-31-4; **37**, 110097-72-8; **39**, 110171-14-7; **40**, 110097-73-9; **42**, 110171-15-8; **43**, 110097-74-0; **44**, 110097-75-1; **45**, 33773-13-6; **46**, 33724-42-4; **47**, 110097-76-2; **48**, 110171-16-9; **49**, 110097-77-3; **50**, 110097-78-4; **51**, 110171-17-0; 10-ethoxy-10-hydroxy-13,14-bis(ethoxycarbonyl)heptacyclo[10.2.2.$1^{5,8}$.$0^{2,6}$.$0^{4,9}$.$0^{7,11}$]heptadec-15-en-3-one, 110097-79-5.

Supplementary Material Available: ORTEP diagrams and tables of fractional coordinates, thermal parameters, bond distances, and bond angles for **5** and **47** and full assignments of ^{1}H and ^{13}C NMR spectra of the Diels–Alder adducts (17 pages). Ordering information is given on any current masthead page.

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Homochiral Pinene-Fused Cyclopentadienes. Synthesis and π-Facially Selective Course of Diels–Alder Cycloadditions and Metallocene Formation[1]

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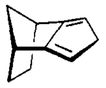
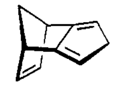
Homochiral (1*R*)-(−)-9,9-dimethyltricyclo[6.1.1.$0^{2,6}$]deca-2,5-diene (**3**) has been synthesized and its Diels–Alder reactions with *N*-phenylmaleimide, *p*-benzoquinone, dimethyl acetylenedicarboxylate, and (*Z*)-1,2-bis(phenylsulfonyl)ethylene investigated. As expected, [4 + 2] cycloaddition occurs preferably from the less-hindered π-surface, although to varying degrees. Reaction of **3** or the anion of **3** with $Fe(CO)_5$ and $TiCl_4$, respectively, is shown to provide only a single metallocene in each instance, complexation occurring from the direction syn to the methano bridge. The ligand transfer reactions of the 4-(dimethylamino)-substituted fulvene **4** with the hexafluorophosphates **29** and **35** gave rise to isomeric pairs of complexes. Above-plane coordination was again shown to predominate. Thus, **3** and **4** consistently undergo binding predominantly or exclusively from one π-face, in striking contrast to the behavior of isodicyclopentadiene (**1**) and isodicyclopentatriene (**2**).


1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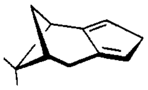
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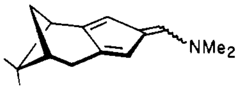
4

Isodicyclopentadiene (**1**) and its dehydro derivative **2** were recognized several years ago to be plane-nonsymmetric dienes offering considerable latitude for the study of π-facial selectivity.[3-5] The remarkable stereochemical outcome of Diels–Alder,[6,7] [6 + 4],[8] and [3 + 4] cycloadditions[8b,9] to **1** has fostered controversy as to the root cause of the phenomena.[10-13] The course of metal complexation to these systems has also been documented.[1,14] More recently, appreciable attention has been directed toward other conjugated dienes with topologically dis-

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[1] Paper 38 in the series dealing with isodicyclopentadienes and related molecules. For 37, see: Paquette, L. A.; McKinney, J. A.; McLaughlin, M. L.; Rheingold, A. L. *Tetrahedron Lett.* **1986**, *27*, 5599.

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