IV. Conclusion

Using only the information contained in the (exact or approximate) first-order density matrix, we have described a procedure for extracting general hybrids, polarization parameters, and bond orbitals and thereby constructing an a priori "Lewis structure" for a given molecule.[42] The method is applicable at any level of ab initio or semiempirical theory and is computationally efficient, involving only the diagonalization of small matrices and a symmetric orthogonalization. The method seems to apply (when a single resonance structure is dominant) to a variety of bonding situations, including molecules with lone pairs, multiple bonds, strained rings and "bent bonds", hydrogen bonds, and three-center bonds. The resulting *natural hybrids* appear to be in good agreement with hybrids determined by other methods and to be consistent with known empirical trends such as those summarized in Bent's Rule and with chemical intuition. Moreover, they appear to closely resemble the "best possible" hybrids, as defined by maximal occupancy of the one-electron density matrix.

Although the NHO's possess a number of desirable features for bond orbital studies and are in a certain sense optimal for this purpose, one should note a certain disadvantage inherent in their use. Since the NHO's change continuously with the molecular environment, they are not generally transferable from one molecule to another. For the same reason the NHO's do not necessarily form a suitable fixed basis set for the comparison of one molecule with another or for the analysis of changes within a single molecule. For the latter purposes the "nominal" hybrids retain a distinct conceptual advantage, particularly when the antibond density associated with the two sets of hybrids is similar.

The illustrative numerical applications of this paper were carried out at the semiempirical INDO level of approximate SCF-MO theory. It would be desirable to obtain corresponding ab initio (SCF or CI) natural hybrids for a number of the systems considered here, in order to compare the effects of various approximations at the level of individual atomic hybrids, polarization parameters, and occupancy. We hope to report such studies at a later date.

(42) A Fortran implementation of this procedure, part of the general bond orbital package for INDO-LCBO-MO calculations (BONDO), is being submitted to the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana 47405.

Acknowledgment. We thank Dr. Graham Doggett for calling our attention to McWeeny's paper and Professor J. O. Hirschfelder for support. Financial support from the National Science Foundation (Grant CHE76-22760) is also gratefully acknowledged.

Electronic Control of Stereoselectivity. 4. Effects of Neighboring Fused Bicyclic Frameworks on the Stereochemical Outcome of Diels-Alder Cycloadditions to Cyclopentadiene Rings[1]

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Abstract: The stereochemistry of Diels-Alder cycloadditions to tricyclo[5.2.1.$0^{2,6}$]deca-2,5-diene (**1**), tricyclo[5.2.1.$0^{2,6}$]-deca-2,5,8-triene (**2**), and tricyclo[5.2.2.$0^{2,6}$]undeca-2,5,8-triene (**3**) has been investigated with various dienophiles. In the reactions involving **1** and **2**, single products were obtained in each instance, and unambiguous structural proof was obtained for kinetically favored stereospecific bond formation from the endo surface of the diene moiety. As concerns **3**, the additions were stereoselective only, with exo attack now being favored. These observations cannot be attributed to steric factors, for the behavior of **1** and **3** would be countrasteric in that event. Rather, the stereochemical phenomena are best rationalized in terms of σ orbital mixing with the π_s diene orbital, such interactions serving to tilt the diene orbitals disrotatorily with resultant minimization of the level of antibonding interaction on the endo face of **1** and **2** relative to the exo face. Theory predicts a reduction in stereoselectivity for **3** as is seen.

The norbornane ring system, a focal point of physical organic chemistry for several decades, continues to evade a universally acceptable interpretation of its unique and often complex chemical reactivity. The capture by norbornyl cations of various nucleophiles is widely recognized to occur preferentially from the exo side.[3-5] Similarly, addition reactions to norbornene double bonds proceed with essentially complete exo stereoselection, except in certain cases where C_7 substituents interfere.[6] The first phenomenon was originally attributed to presumed nonclassical characteristics of the cationic species.[7] With the advent of Brown's more recent studies,[8] it has become clear that high percentages of exo product do not require a bridged ion explanation. The demise of the nonclassical electronic interpretation has caused torsional[9] and steric effects[10] to be considered seriously. However,

(1) Part 3: Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186.
(2) (a) Institut für Organische Chemie Darmstadt. (b) The Ohio State University. (c) Institut für Organische Chemie Heidelberg.
(3) Bartlett, P. D. "Nonclassical Ions", W. A. Benjamin: New York, 1965.
(4) Sargent, G. D. *Q. Rev., Chem. Soc.* **1966**, *20*, 301.
(5) Sargent, G. D. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. III, Chapter 24.
(6) (a) Brown, H. C.; Kawakami, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 5521, and earlier papers in this series. (b) Freeman, F. *Chem. Rev.* **1975**, *75*, 439. (c) Wilt, J. W.; Narutis, V. P. *J. Org. Chem.* **1979**, *44*, 4899.
(7) Winston, S.; Trifan, D. *J. Am. Chem. Soc.* **1952**, *74*, 1147, 1154.
(8) Brown, H. C. "The Nonclassical Ion Problem", Plenum Press: New York, 1977.
(9) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 701.
(10) Brown, H. C. *Chem. Ber.* **1966**, *2*, 199.

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neither factor has proven to be completely satisfactory in rationalizing all observations.[11,12] The desirability of clarifying this rather muddled state of affairs has perhaps been expressed most succintly by Brown when he wrote "if there is a hunger for a directed electronic contribution in the *exo*-norbornyl system, one can only hope that someone will demonstrate unambiguously the existence of such a directed electronic effect".[17]

Only in the last few years has the possible existence of electronic factors in norbornyl systems been examined theoretically. Using second-order perturbation theory, Fukui and his co-workers concluded that the σ electrons associated with the strained bridge of norbornene enter into σ–π mixing with the olefinic π orbital.[18] The effect of this rehybridization, although quite small in absolute terms, is thought to cause the HOMO to extend nonequivalently in the exo and endo directions with resultant greater electron density in the exo region. More recently, Houk has advanced the contrasting viewpoint that secondary orbital interactions rather than π asymmetric distortion are responsible for stereoselection.[19] In his analysis, electrophiles are considered not to approach the norbornene endo surface because of destabilization brought on by an antibonding interaction between the $C_1C_6C_5C_4$ bridge and the π orbital. Despite the elegance of these treatments, exo stereoselection clearly remains incompletely understood from the theoretical vantage point. Some quantitative measure of the magnitude of any second-order effects would be particularly welcomed.

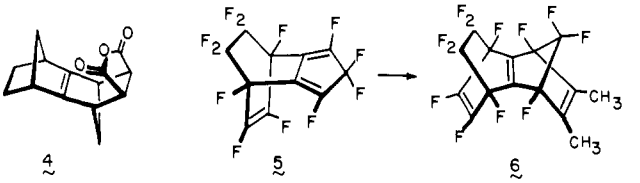
Seemingly, our inability to dissect steric and electronic contributions within norbornane systems is the source of the apparent complications in developing a comprehensive interpretation of their chemistry. To a first approximation, however, the orbital interactions existent in bridged bicyclic systems should have a recognizable impact at more remote sites which are not sterically biased. Diels–Alder cycloaddition to the bridged bicyclic fused cyclopentadienes **1**–**3** is herein considered to be an appropriate

1 **2** **3**

first test of this concept. In each instance, the dienes are differentiated by rather remote substitution only, and molecular models suggest that steric factors should be of little direct stereochemical consequence. Because of the directional nature of the orbitals making up the diene components, exo and endo modes of bond making continue to be available, and the methylene carbon of the five-membered ring serves as the stereochemical marker.

The stereochemistry of $(4 + 2)\pi$ bonding would then be controlled only by the energetic relationships of the two transition states, as modified by electronic interactions, if any, present in the bridged bicyclic moiety. As will be shown, 100% endo stereoselectivity operates in dienophilic additions to **1** and **2**, while the capture of **3** is preferentially exo directed. These results are viewed to be of electronic origin[20] and to constitute justification for consideration of norbornyl and norbornenyl frameworks as quite respectable electronic perturbers of chemical reactivity.

Our attention was directed to **1**–**3** chiefly as the result of the earlier reports by Alder,[21] Kobuke,[22] Feast[23] and their co-workers. Over 20 years ago, the Köln group demonstrated the ability of "isodicyclopentadiene" (**1**) and "dehydroisodicyclopentadiene" (**2**) to serve as 4π components in cycloadditions to maleic anhydride. In the first instance, the *lone* product was considered to be **4** but this assignment is erroneous (see below).[1] Diels–Alder

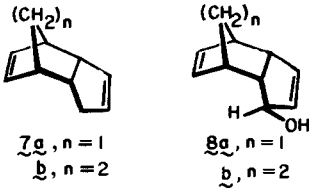


4 **5** **6**

cycloadditions of **1** to methyl propiolate and methyl acrylate, examined by Kobuke and his colleagues, were shown again to proceed stereospecifically and with endo stereoselection. In contrast, the condensation of dodecafluorotricyclo[5.2.2.$0^{2,6}$]-undeca-2,5,8-triene (**5**) with 2-butyne at 120 °C has been reported to give rise predominantly to addduct **6** (77%).[23] The question of possible secondary orbital interaction with the neighboring double bond[24] is opened in this instance and appeared to us to require the detailed tandem study of both **2** and **3**.

Results

Substrate Synthesis. Tricyclo[5.2.1.$0^{2,6}$]deca-2,5-diene (**1**) has been known for many years, and its preparation has previously been described by several research groups.[21,25-27] In contrast, **2** forms the subject of a single literature citation.[21] In our hands, repetition of the allylic oxidation of *endo*-dicyclopentadiene (**7a**)

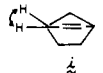


7a, n = 1; **b**, n = 2 **8a**, n = 1; **b**, n = 2

proceeded to give **8a** in acceptable yield (58%). However, distillation of **8a** from activity I alumina which had been pretreated with quinoline (1%) invariably produced **2** in low yield as earlier reported. Attempts to effect this dehydration with iodine proved still more inferior.

To gain access to **3**, use was made of an observation described in an Italian patent[28] that the heating of a mixture of dicyclopentadiene and 1,3-cyclohexadiene affords **7b**. Selenium dioxide oxidation of this hydrocarbon proceeded conventionally to give **8b** which was determined to dehydrate rather efficiently (45%

(11) The existence of a torsional effect exerted between the bridgehead hydrogens and the neighboring olefinic protons in norbornene (see i) should be accentuated, for example, in 1-methylnorbornene. Yet, this bridged olefin reacts with mercuric salts[13] and formic acid[14] to yield approximately equal amounts of the two possible exo products. Torsional strain as in i should have favored attack of the electrophile at C_2. Additionally, hydrochlorination of 1-methylnorbornene affords exo products in inverted ratios, depending on conditions.[14]



i

(12) The steric argument centers on the interference to electrophilic approach caused by the endo hydrogens at C_5 and C_6. However, substantial steric crowding of the exo face by 7,7-dimethyl substitution does not reverse exo stereoselection in oxymercuration[13,15] or hydrochlorination reactions.[16]

(13) Tidwell, T. T.; Taylor, T. G. *J. Org. Chem.* **1968**, *33*, 2615.

(14) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 3901.

(15) Brown, H. C.; Kawakami, J. H.; Ikegami, S. *J. Am. Chem. Soc.* **1967**, *89*, 1525.

(16) Brown, H. C.; Liu, K.-T. *J. Am. Chem. Soc.* **1967**, *89*, 3898, 3900.

(17) Brown, H. C.; Guedin, B. G.; Takeuchi, K.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 610.

(18) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054.

(19) Houk, K. N. In "Reactive Intermediates"; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1978; Vol 1, pp 326–327.

(20) A theoretical analysis of the Diels–Alder reactivity of 2,3-dimethylenenorbornane has previously been reported by Hardy, M.; Carrupt, P.-A.; Vogel, P. *Helv. Chim. Acta* **1976**, *79*, 1685.

(21) Alder, K.; Flock, F. H.; Janssen, P. *Chem. Ber.* **1956**, *89*, 2689.

(22) Sugimoto, T.; Kobuke, Y.; Furukawa, J. *J. Org. Chem.* **1976**, *41*, 1457.

(23) (a) Feast, W. J.; Musgrave, W. K. R.; Preston, W. F. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1830. (b) Feast, W. J.; Hughes, R. R.; Musgrave, W. K. R. *Ibid.* **1977**, 152.

(24) Jacobson, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 2579.

(25) Katz, T. J.; Rosenberger, M.; O'Hara, R. K. *J. Am. Chem. Soc.* **1964**, *86*, 249.

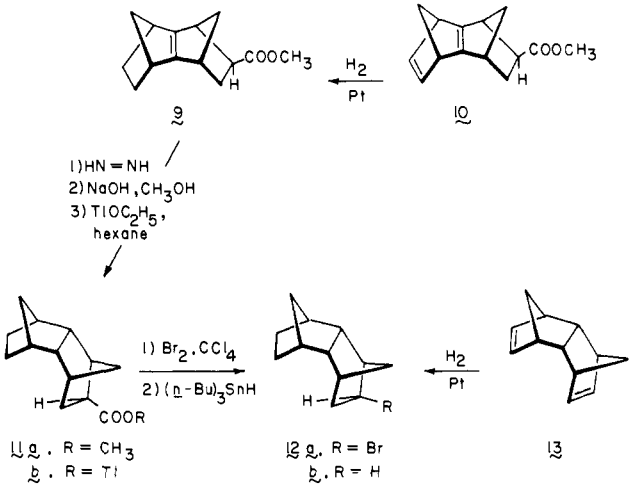
(26) Cesca, S.; Arrighetti, S.; Priola, A.; Duranti, P. V.; Bruzzone, M. *Makromol. Chem.* **1974**, *175*, 2539.

(27) Scroggins, R. T.; Rettig, R. F.; Wing, R. M. *Inorg. Chem.* **1976**, *15*, 1381.

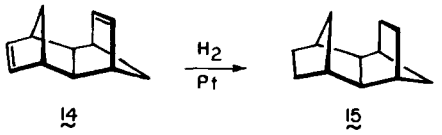
(28) Cameli, N.; Salveti, G.; Sartori, G. Italian Patent 730703, 1966; *Chem. Abstr.* **1968**, *69*, 51740.

yield of **3**). The symmetrical arrangement of the cyclopentadiene double bonds in **3** was clearly evident from its ^{13}C (six lines, two quaternary trigonal carbons) and ^1H NMR spectra (single resonances for each proton pair), as well as the symmetric nature of the derived cycloadducts.

Cycloaddition Reactions of 1 and 2. When carbon tetrachloride solutions of **1** and methyl acrylate were warmed to 42 °C in a sealed tube for 10 h, adduct **9** was obtained as the exclusive

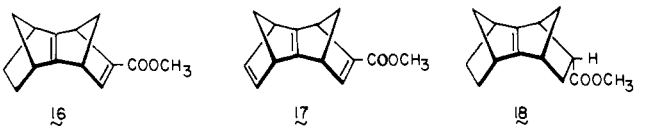


product in 94% yield after purification. Triene **2** was less reactive toward this reagent and required 48 h at 42 °C to provide **10** (88%). Through catalytic hydrogenation, **10** was converted to **9**, the outcome providing a valuable stereochemical correlation point. The dienophile stereoselection experienced in common by the two systems was shown to be endo by diimide reduction of **9** to give **11a**. Under these conditions, exo delivery of hydrogen occurred to the common norbornene double bond. Subsequent degradation of this ester provided hydrocarbon **12b**. The scheme involved conversion of **11a** to its thallium carboxylate **11b**, Hunsdiecker reaction[29] of which with a stoichiometric quantity of bromine produced **12a**; the reductive debromination of **12a** was made available by catalytic hydrogenation of the well-known diene **13**.[30,31] The alternate possibility **15** was similarly prepared from **14**[30-32] and shown to differ substantively in spectral detail from **12b**.



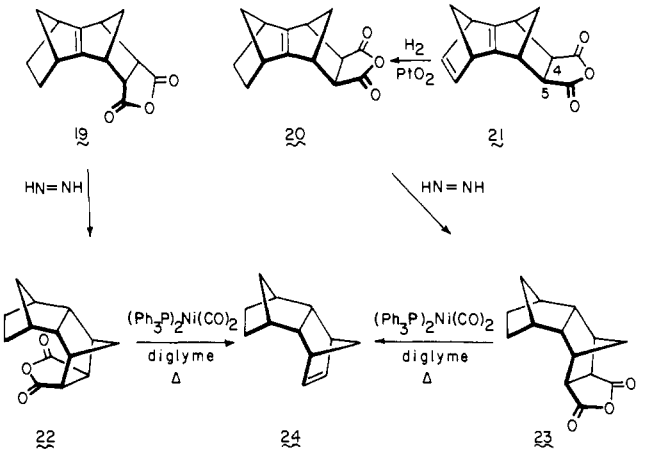
The exo orientation of the carbomethoxyl groups in **9** and **10** follows from equilibration studies described below. These cycloadditions do not, therefore, conform to the Alder endo rule (maximum accumulation of double bonds, etc). This secondary effect is inoperative in these examples because of the moderate reactivity of the dienophile and the obvious steric compression which would be experienced by the relevant functional group as it is brought into the proximity of the ethano bridge. Although such observations are significant, they should not detract attention from the outcome of the primary stereoselection (viz., endo) which is of vastly greater import.

Comparable reaction of **1** (42 °C, 11 h) and **2** (65 °C, 24 h) with methyl propiolate proceeded cleanly to give **16** (93%) and **17** (83%). Structural identification of these adducts followed from

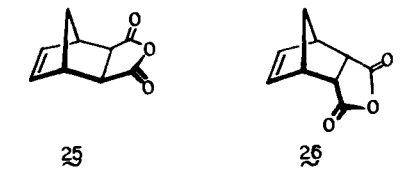


their catalytic hydrogenation to the common reduction product **18** and subsequent base-catalyzed epimerization to **9**. At this point, any original suspicion that the double bond in **2** might perturb stereoselection was dispelled. However, its presence does retard the cycloaddition rate. Approximate 2 M solutions of **1** and **2** were individually treated with 50% excess of methyl acrylate and methyl propiolate at 42 °C, and the times required for 50% consumption of the cyclopentadienes were determined: **9**, 3 h; **10**, 73 h; **16**, 0.7 h; **17**, 18 h. The observed reactivity order conforms expectedly[33] to the frontier orbital energies of **1** and **2** as determined by photoelectron spectroscopy (see below).

Contrary to the published report,[21] we have found **1** to react exothermically with maleic anhydride in benzene with resultant formation of the pair of adducts **19** and **20** (90%) in a 1:2 ratio.



In the case of **2**, only **21** was formed. The differing product distributions appear contrary to steric approach control considerations and are therefore considered to arise from the higher reactivity of **1**. The stereochemistry of **21** was deduced principally on the basis of its spin-decoupled 90-MHz ^1H NMR spectrum (in $CDCl_3$) which is characterized in particular by a narrow doublet (J = 1.03 Hz) at δ 2.43 for H_4 and H_5. The highly shielded nature of this pair of protons is recognizable when comparison is made with the chemical shifts of the α-carbonyl proton in **25** (δ 3.00) and **26** (δ 3.57).[34] This effect is seen to



be directly related to the proximity of H_4 and H_5 in **21** to the distal double bond, this stereochemical designation being supported by the absence of measurable coupling to H_3 and H_6 and the obvious weak interaction with H_{12syn}. In the case of **25**, $J_{5endo,7syn}$ has been determined to be 1.8 Hz while in **26** it is $J_{4,5exo}$ which dominates.[34] Through catalytic hydrogenation, **21** was converted to **20**. The ^1H NMR spectra of **19** and **20** compare closely in detail to those of **25** and **26** (see Experimental Section).

Various attempts to decarboxylate **19** and **20** directly required forcing conditions and generally returned **1** by retro-Diels–Alder fragmentation. Consequently, the two isomers were individually

(29) McKillop, A.; Bromley, D.; Taylor, E. C. *J. Org. Chem.* **1969**, *34*, 1172.

(30) (a) Scharf, H.-D. *Tetrahedron* **1967**, *23*, 3057. (b) Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 3724. (c) Martin, H.-D.; Schwesinger, R. *Chem. Ber.* **1974**, *107*, 3143.

(31) (a) Prinzbach, H.; Sedelmeier, G.; Martin, H.-D. *Angew. Chem.* **1977**, *89*, 111; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 103. (b) Prinzbach, H.; Sedelmeier, G.; Krüger, C.; Goddard, R.; Martin, H.-D.; Gleiter, R. *Angew. Chem.* **1978**, *90*, 297; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 271.

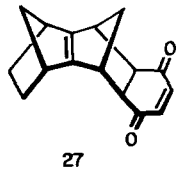
(32) (a) Mantzaris, J.; Weissberger, E. *J. Org. Chem.* **1974**, *39*, 726. (b) Stille, J. K.; Frey, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 4273.

(33) Houk, K. N. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II, Chapter 4.

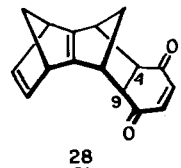
(34) Kamezawa, N.; Sakashita, K.; Hiyamizu, K. *Org. Magn. Reson.* **1969**, *1*, 405.

subjected to diimide reduction and oxidatively decarboxylated with bis(triphenylphosphine)nickel dicarbonyl.[35] Both reaction sequences delivered olefin **24** uniquely, the structure of which was ascertained by reduction to **12b**.

With *p*-benzoquinone as dienophile, the singular adducts **27** (94%) and **28** (88%) were obtained and interrelated by catalytic hydrogenation. As before, the exo stereochemistry of the cyclo-



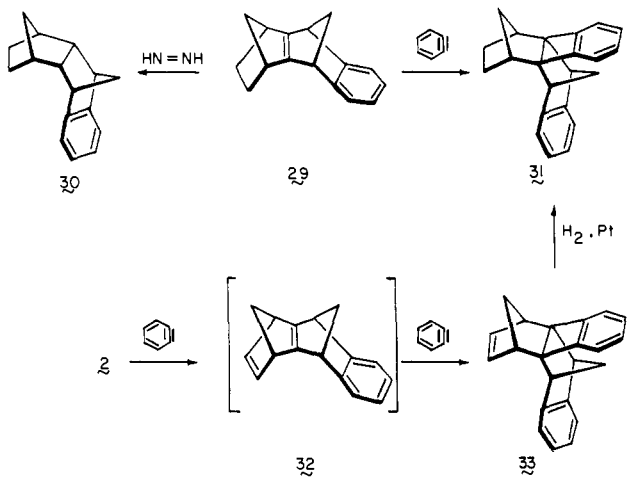
27



28

hexane-1,4-dione moiety was established by ^{1}H NMR spectroscopy. Most revealing is the dramatic downfield shift of H_4; H_9 observed as **28** (δ 1.85) is transformed into **27** (δ 2.40). At this point, it was accepted that long-range shielding of this order of magnitude can materialize only upon (4 + 2)π cycloaddition from the endo surfaces of **1** and **2**.

Benzyne, as traditionally generated from anthranilic acid,[36] reacted with **1** to give **29** (71%) which was transformed into the known **30**[31,37] upon treatment with diimide. With **2**, only a 2:1



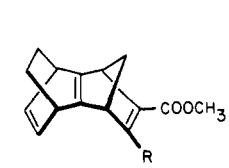
30 **29** **31**

32 **33**

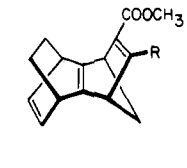
adduct was obtained without regard for the relative amounts of benzyne employed. Evidently, the central double bond of initial adduct **32** is adequately reactive to capture a second benzyne molecule by a [2 + 2] mechanism more rapidly than [4 + 2] addition to **2**. The stereochemical features of **33** were elucidated by treatment of **29** with excess benzyne to give **31** which proved identical to dihydro-**33**.

Cycloaddition Reactions of 3. Reaction of **3** with dimethyl acetylenedicarboxylate at 25 °C resulted in the formation of two products which were separated by preparative thin-layer chromatography on silica gel. The minor product (14%) was identified as **34a** on the basis of the appearance of its ethano bridge protons as a pseudosinglet at δ 1.62 ($CDCl_3$ solution). In major product **35a** (86%), the proximity of the carbomethoxyl-substituted double bond to this bridge induces an appreciable shift differential between the syn and anti protons (m at 1.61–0.60). Experimentally, the product ratio was determined in the unpurified product by integration of the olefinic proton region unique to each isomer. When a mixture of **34a** and **35a** in $CDCl_3$ was heated at 50 °C for 21 h, clean aromatization occurred to give **36a**.

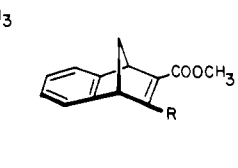
Warming **3** with methyl propiolate at 42 °C gave rise to a comparable distribution of **34b** and **35b** (21:79). Again, the isolation of a pair of stereoisomers permitted structural assignments to be deduced readily from the ^{1}H NMR spectra (see Experimental Section). On thermal fragmentation, **34b**/**35b** cleanly gave **36b**.



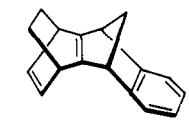
34 a, R = $COOCH_3$
b, R = H



35 a, R = $COOCH_3$
b, R = H



36 a, R = $COOCH_3$
b, R = H



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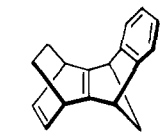

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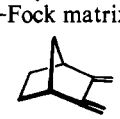
The crossover in stereoselection is not restricted to α,β-unsaturated ester dienophiles, as evidenced by the response to **3** to benzyne (**37**:**38** = 19:81). Under the conditions of this reaction, considerable fragmentation occurred to give dibenzonorbornadiene. However, independent studies showed that **37** and **38** did not aromatize at appreciably different rates.

That **3** does not undergo kinetically favored stereospecific capture from the endo direction as do **1** and **2** must be viewed as suggestive that important electronic perturbations which bear directly on product development are being manifested. The crossover in stereoselectivity cannot be attributed to steric factors because C_1 and C_4 of the cyclopentadiene units in **1**–**3** are too remote from either bridge. Were such a working hypothesis adopted, the behavior of **1** and **3** would have to be implausibly regarded as contrasteric. In their earlier work with **1**, Kobuke et al.[22] suggested a "greater steric attraction by the ethano bridge" or a "greater development of π-orbitals toward the exo side" as proposed originally by Fukui to account for the exo preference of norbornene additions.[18,38] These steric attraction and π-orbital distortion arguments are considered inapplicable for the series **1**–**3**. We now detail a stereoselectivity analysis which utilizes the results of molecular orbital theory and He (1α) photoelectron spectroscopy.

Theoretical Model. Some time ago, Heilbronner and Schmelzer proposed a method which makes possible the quantitative analysis of interactions between various fragments of a molecule, e.g., the interaction between two π or n orbitals located at different sites in a compound or the mixing between π and σ orbitals.[39] The analytical technique begins by transforming the set of occupied canonical molecular orbitals (CMO), obtained by diagonalization of the Fock Hamiltonian, into a set of localized molecular orbitals (LMO). This transformation can be achieved by using the localization procedure given by Edmiston and Ruedenberg.[40] If the molecule contains symmetry elements, the LMOs can be transformed into symmetry-adapted semilocalized molecular orbitals (SLMO).

To determine which of the σ orbitals of a molecule, e.g., **39**, are interacting chiefly with the π orbitals, one must single out from the Hartree–Fock matrix in the localized or semilocalized



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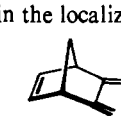


40

basis the off-diagonal elements of rows and columns pertaining to the π orbitals. Diagonalization of the remaining matrix yields the linear combination of the precanonical molecular orbitals (PCMO) (in our example, σ orbitals) ψ_j and their orbital energies $\epsilon_j\psi = F_{\psi_j j}$.

In their analysis of the through-space and through-bond interactions operating in norbornadiene, Heilbronner and Schmelzer

(35) Trost, B. M.; Chen, F. *Tetrahedron Lett.* **1971**, 2603.
(36) Fieser, L. F.; Haddadin, M. J. *Can. J. Chem.* **1965**, *43*, 1599.
(37) MacKenzie, K. *J. Chem. Soc.* **1965**, 4646.
(38) Inagaki, S.; Fukui, K. *Chem. Lett.* **1974**, 509.
(39) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936.
(40) Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457; *J. Chem. Phys.* **1965**, *43*, 597.

Table I. Comparison between Measured Vertical Ionization Potentials, $I_{V,J}$, and Calculated Orbital Energies for 39 and 40 (all values in eV)

compd	$I_{V,J}$[a]	assignment[a]	MINDO/3	SPINDO	EHT	INDO	STO-3G
39	8.41	π_A	−8.96 (π_A)	−9.62 (π_A)	−12.38 (π_A)	−10.33 (π_A)	−7.06 (π_A)
	10.20	π_S	−10.45 (π_S)	−10.92 (π_S)	−13.11 (π_S)	−11.34 (π_S)	−9.51 (π_S)
	10.70	σ	−10.01 (σ_A)	−11.25 (σ_S)	−13.01 (σ_A)	−11.55 (σ_S)	−10.40 (σ_S)
			−10.45 (σ_S)				
40	8.48	π_A	−8.90 (π_A)	−9.50 (π_A)	−12.23 (π_A)	−10.41 (π_A)	−7.07 (π_A)
	9.02	π_{bridge}	−9.00 (π_{br})	−8.33 (π_{br})	−12.38 (π_{br})	−10.61 (π_{br})	−7.60 (π_{br})
	10.35	π_S	−10.44 (π_S)	−10.86 (π_S)	−13.19 (π_S)	−11.39 (π_S)	−9.56 (π_S)
	11.29	σ	−10.40 (σ)	−11.42 (σ_S)	−13.30 (π_A)	−11.79 (σ_S)	−10.80 (σ_S)

[a] See ref 46.

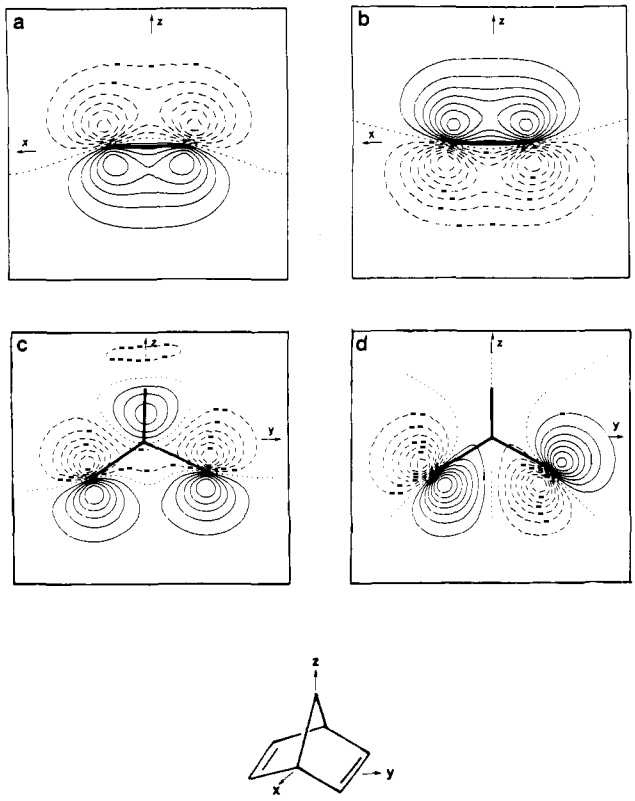


Figure 1. Contour diagrams of a_1 (π') and b_2 (π') in norbornadiene. Full and dashed lines distinguish between amplitudes of different signs; nodes are indicated as short dashes. In a and b, the contours are shown in a plane through the atoms 2 and 3 and perpendicular to the plane defined by atoms 2, 3, and 7. In c and d, the contours are shown in the y,z plane.

found that currently used semiempirical methods (SPINDO, MINDO/2, and CNDO/2) give quite different results concerning the amount of σ contribution. Nevertheless, all methods produce a common shape of the two canonical π orbitals a_1 (π') and b_2 (π') by σ–π interaction. The resulting canonical molecular orbitals can be separated into two "pure" semilocalized π orbitals belonging to the irreducible representations A_1 and B_2 of the molecular point group C_{2v} plus σ contributions which arise from the π/σ nonorthogonality inherent in norbornadiene. As a result of the orbital mixing, the pure π orbitals a_1 (π) and b_2 (π) are rotated with respect to the x,z and y,z planes as shown in Figure 1. The resulting CMO, a_1 (π'), is rotated with respect to the x,z plane in a disrotatory manner in such a way that the amplitude of the wave function on the side of the methylene group is decreased (Figure 1a). In the case of b_2 (π'), the disrotatory motion increases the shape of the CMO syn to the methylene bridge (see Figure 1b).

Superimposed on the rotation of the x,z plane is a second type of π deformation with respect to the x,z plane. Importantly, the a_1 (π') linear combination is seen to be rotated toward the methylene group (Figure 1c). As far as b_2 (π') is concerned, this rotation moves the two π orbitals away from the methylene group (Figure 1d). It should be noted that, in the case of norbornadiene, disrotation is the only possible torsion which conserves the symmetry of the molecule. The different rotations just described result due to admixture of the semilocalized pπ orbitals and the σ frame. This effect must be carefully separated from a nonequivalence due to hybridization,[18,38] viz., a mixing between s and p orbitals. A detailed analysis of the corresponding CMOs of norbornadiene shows that s,p mixing is unimportant and dominated by the p/p interaction of the molecular fragments.

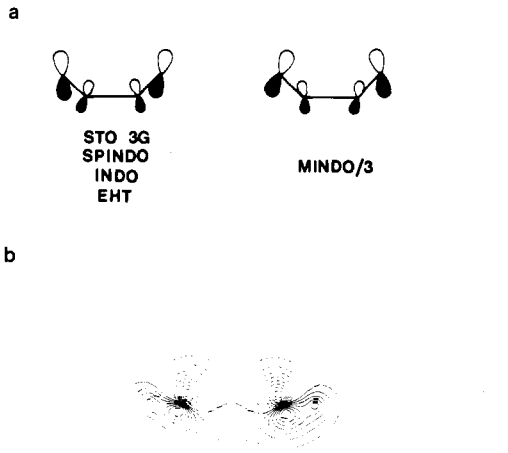


Figure 2. (a) Schematic representation of the π_S orbital in **39** and **40** as obtained with the STO-3G, INDO, SPINDO, and EHT methods (left) and the MINDO/3 method (right). (b) Contour diagram for **40**, showing the deformation of the two terminal π lobes.

Application to the Dienes 39 and 40. To rationalize the stereoselectivity observed in the Diels–Alder reactions of **1–3**, we have carried out extensive calculations on **39** and **40** as simpler model systems. Semiempirical methods (MINDO/3,[41] SPINDO,[42] EHT,[43] together with a recently developed modified INDO[44] version) and ab initio calculations within the STO-3G basis set were employed.[45] In Table I are listed the calculated orbital energies of the highest occupied orbitals, together with the type (π or σ) of the wave function and its symmetry (A or S) with respect to the mirror plane.

Comparison of the results obtained by the different calculational methods shows that the STO-3G, SPINDO, and INDO procedures predict the π orbitals to reside on top of the σ orbitals. The MINDO/3 and EH procedures, however, insert the σ orbitals between the π orbitals. This difference causes dramatic changes in the shape of the CMOs, as exemplified below.

To judge which of the methods should be used to evaluate the frontier orbitals, we have compared the results of the calculations with the PE data reported recently for **39** and **40**.[46] These investigations clearly indicate that the π MOs for both compounds are situated on top of the ω MOs as predicted by the STO-3G,

(41) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285. The program actually used that described by Bischof, P. *Ibid.* **1976**, *98*, 6844.
(42) Fridh, C.; Åsbrink, L.; Lindholm, E. *Chem. Phys. Lett.* **1972**, *15*, 282. Åsbrink, L.; Fridh, C.; Lindholm, E. *J. Am. Chem. Soc.* **1972**, *94*, 5501.
(43) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179; *Ibid.* **1962**, *37*, 2872.
(44) Böhm, M. C. Dissertation TH Darmstadt, in preparation.
(45) Hehre, W. J.; Stewart, R. R.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.
(46) Asmus, P.; Klessinger, M. *Tetrahedron* **1974**, *30*, 2477.

Table II. Comparison between Measured Vertical Ionization Potentials, $I_{V,J}$, and Calculated Orbital Energies for 1-3 (all values in eV)

compd	$I_{V,J}$	assignment	MINDO/3	SPINDO	EHT	INDO
1	7.96	π_A	−8.60 (π_A)	−9.27 (π_A)	−12.13 (π_A)	−9.76 (π_A)
	9.68	π_S	−9.80 (π_S)	−10.23 (π_S)	−12.85 (π_S)	−10.27 (π_S)
	10.64	σ	−9.67 (σ_S)	−11.03 (σ_S)	−12.74 (σ_S)	−10.79 (σ_S)
2	8.06	π_A	−8.61 (π_A)	−9.16 (π_A)	−12.12 (π_S)	−9.78 (π_A)
	8.90	π_{bridge}	−8.96 (π_{br})	−9.87 (π_{br})	−12.17 (π_{br})	−9.84 (π_{br})
	9.85	π_S	−9.96 (π_S)	−10.18 (π_S)	−12.94 (π_S)	−10.60 (π_S)
	10.5	σ	−9.73 (σ_S)	−11.17 (σ_S)	−12.81 (σ_S)	−10.86 (σ_S)
3	7.90	π_A	−8.57 (π_A)	−9.21 (π_A)	−12.06 (π_A)	−9.70 (π_A)
	9.10	π_{bridge}	−9.18 (π_{br})	−10.02 (π_{br})	−12.32 (π_{br})	−9.81 (π_{br})
	10.01	π_S	−9.94 (π_S)	−10.38 (π_S)	−13.01 (π_S)	−10.65 (π_S)
	10.3	σ	−9.90 (σ_S)	−11.06 (σ_S)	−12.84 (σ_S)	−10.93 (σ_S)

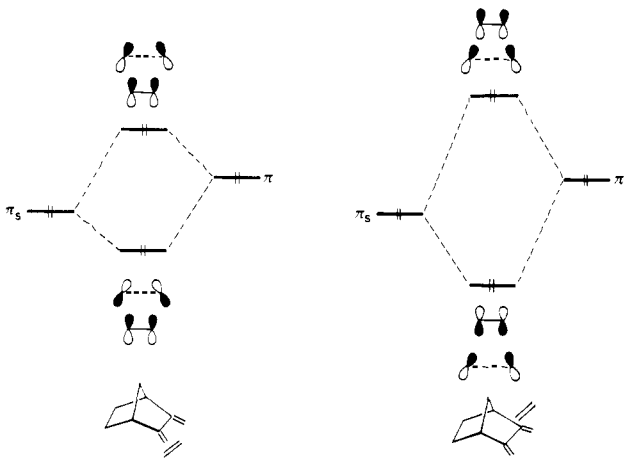


Figure 3. Qualitative diagram of the interaction between π_S of the butadiene unit of **39** and **40** and a π bond. (Left) The situation of the approach of the ethylene anti to the methylene group. (Right) Corresponding syn approach.

SPINDO, and INDO procedures (see Table I). These three theoretical methods reveal that the HOMO (π_A) of **39** and **40** does not interact significantly with the σ frame. The π_s orbital of the butadiene fragment, however, is predicted to admix substantially with the σ frame. As the result of this particular interaction, the π lobes at the terminal carbon atoms of the butadiene moiety in **39** and **40** show a disrotatory movement enhancing the electron density syn to the methano bridge while the π orbitals of the central atoms of the butadiene unit rotate the opposite way as shown schematically in Figure 2a. The rotation of π_S in the case of **40** is shown in the contour diagram of Figure 2b where the deformation of the two terminal π lobes is obvious. It is seen that the rotation leads to significant differences in the electron distribution on the syn and anti side. Various theoretical procedures predict about 20–40% σ concentration of the carbon centers of the dione moiety. As a result of this rotation, one predicts for **39** and **40** that the addition of a dienophile should occur anti to the methano bridge, because the antibonding interaction between π(S) of the butadiene moiety and the HOMO of the dienophile is smaller for anti attack than for syn attack. This state of affairs is outlined schematically in Figure 3. The stereochemical preference is therefore the result of an interaction between the occupied MOs of the reacting partners.

The remarkable rotation of the π lobes within π(S) (CMO) is a result of a strong interaction between the semilocalized π(S) orbital and precanonical σ orbitals of the same symmetry as shown in Figure 4. Consequently, the precise orbital sequencing [π(S) above or below σ(S)] is particularly crucial to our argument. Indeed, the results of the MINDO/3 calculations predict the opposite rotation than the other theoretical procedures. The EHT method places a σ_A orbital between π_A and π_S, in close correspondence to the STO-3G, SPINDO, and INDO predictions. The π_S CMO results as a linear combination (see Figure 4b) of the localized pure "π_S" part and the precanonical σ orbitals displayed in Figure 4a. In Figure 2, the deformation of the π lobes is shown schematically.

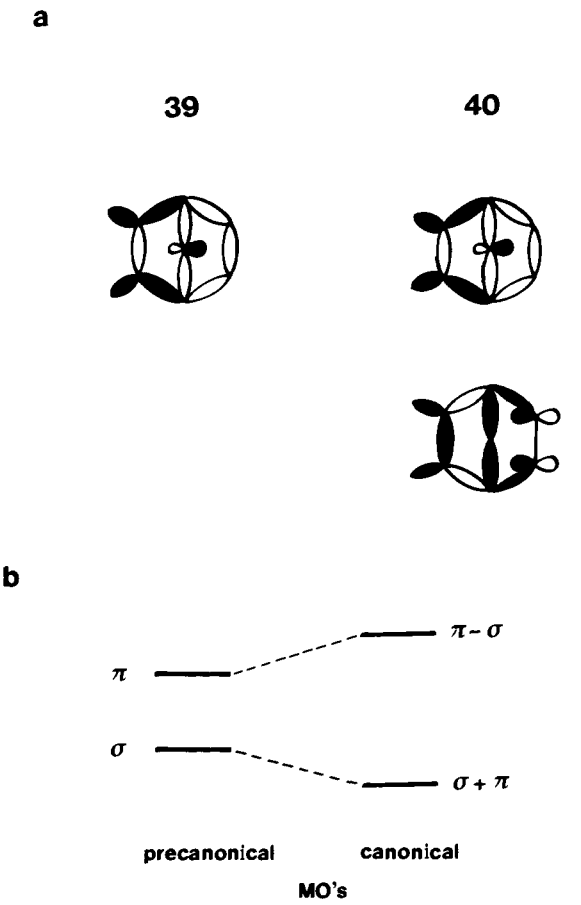


Figure 4. Schematic representation for (a) the most important σ orbitals for the orbital mixing with a_1 (π) and b_2 (π) of **39** and **40** and (b) mixing between the precanonical forms.

Application to 1–3. To judge the reliability of our model calculations on **1–3** the PE spectra of these compounds have been recorded. The first peaks are shown in Figure 5, and the vertical ionization potentials are collected in Table II. Our interpretation of the data assumes the validity of Koopman's theorem ($-\epsilon_J = I_{V,J}$)[47] and the existence of a lowering of the ionization potentials of the π orbitals due to extension of the σ frame, as observed in many examples.[48] In Figure 6, we have correlated the first peaks in the PE spectra of bicyclic compounds **1–3** with the first peaks in the PE spectra of their bicyclic congeners as reported by Klessinger et al.[46] This correlation clearly supports the assumption just made, namely, the anticipated shift toward lower ionization potentials of the π bands in **1–3** due to extension of the σ frame.

A comparison between the PE data and computational results on **1–3** (Table II) indicates that the INDO and SPINDO methods provide MO models suitable to predict the distortion of the π

(47) Koopmans, T. *Physica (Amsterdam)* **1934**, *1*, 104.
(48) See, for example: Brundle, C. R.; Baker, A. D. "Electron Spectroscopy: Theory, Techniques and Applications", Academic Press: London, 1976.

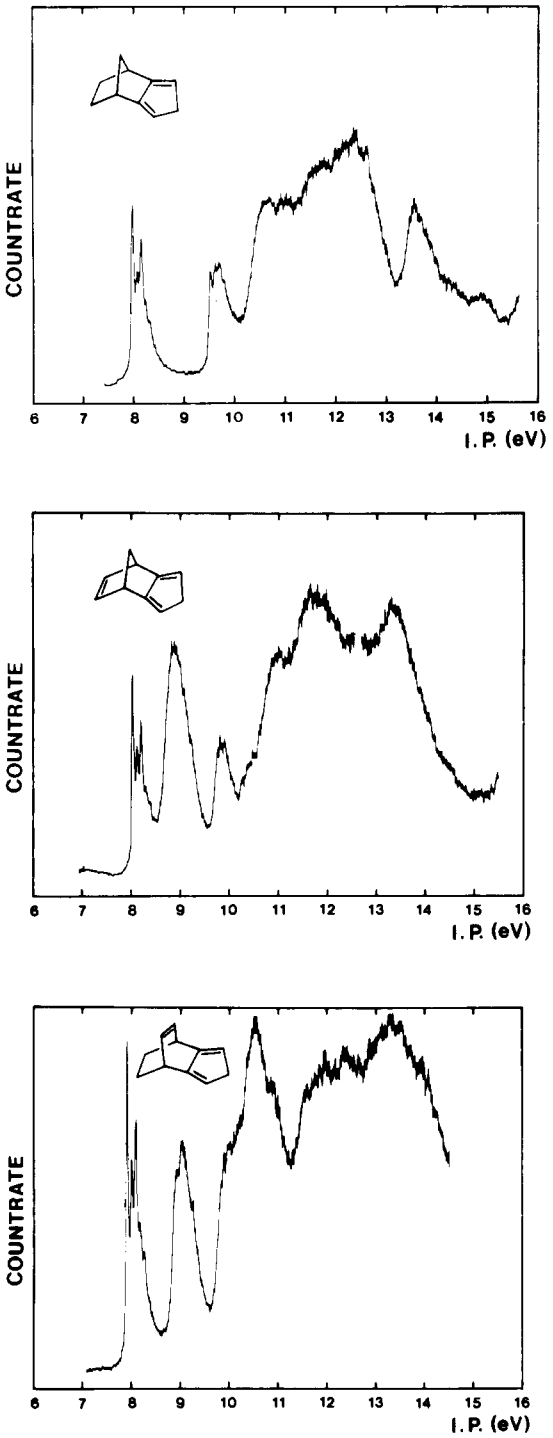


Figure 5. Photoelectron spectra of 1–3.

orbitals as a result of the π/σ interaction. An analysis of the CMOs shows that similar to the case of **39** and **40**, π_A shows negligible π/σ interaction. The π_S orbital, however, interacts significantly with the σ ribbon. The MO wave functions resulting from this π/σ interaction allow us to rationalize the observed stereoselectivity for **3** and **4** described above.

The canonical pπ orbitals can be described as resulting from two different rotations. With respect to the mirror plane, there exists a disrotation of the π lobes which enhances the amplitude of the π_S wave function syn to the methano bridge. Therefore, attack from the side of the C–C bridge should be favored (see Figure 3). Superimposed on this phenomenon is a second rotation which moves the pπ lobes parallel to the plane of symmetry. This mode of rotation causes in our cases a tilting of the terminal pπ lobes away from the methano bridge and toward the C–C bridge. An approach of a π bond syn to the C–C bridge is more favored

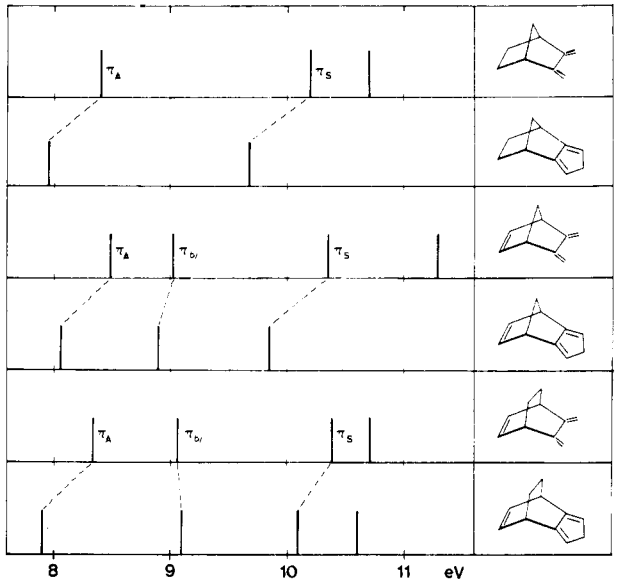


Figure 6. Correlation between the first bands of the PE spectra of 1–3 with the PE results of related bicyclic compounds.

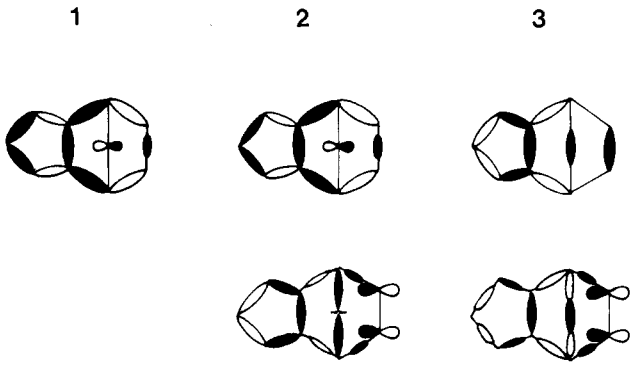


Figure 7. Schematic representation for the most important relay orbitals for mixing a_1 (π) and b_2 (π) of 1–3.

since the repulsive interaction is felt at a smaller distance compared with an approach anti to the C–C bridge. It should be noted that the corresponding CMOs of π_S in the case of **1** and **2** show an important difference in both systems. In the case of **1**, there is only one precanonical σ orbital for π,σ interaction, namely, the high-lying σ_S combination. In the case of **2**, however, there is also a considerable interaction with the PCMO derived from the π bond of the bridge (see Figure 7). This latter PCMO can influence the shape of the π_S orbital of the diene unit via the σ ribbon. Both relay orbitals act in different directions and therefore mitigate the perturbation of the π bond. This is in line with experimental findings that the triene **2** reacts slower compared to the diene **1**. Through the series **1–3**, theory predicts a reduction of stereoselectivity. For **3**, both methods (INDO and SPINDO) predict only a slight preference for attack on the side of the unsaturated C–C bridge. Once again the "π_S" orbital is influenced by two σ orbitals, σ_S and the PCMO of the π bridge (see Figure 7). To estimate the energy difference for exo and endo attack in the case of the dienes **1–3**, we have calculated (eq 1) the four-electron destabilization energies ΔE_{ij}^{exo} and ΔE_{ij}^{endo} between

$$\Delta E_{ij} = \frac{4(\epsilon_{ij}S_{ij} - H_{ij}S_{ij})}{1 - S_{ij}^2}$$

the canonical MOs π_S of the dienes **1–3** and π_1 of ethylene.[49] In the above formula for the four-electron destabilization energy, the expression S_{ij} represents the group overlap integral between

(49) Müller, K. *Helv. Chim. Acta* **1970**, *53*, 1112. Baird, N. C.; West, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 4427. Epiotis, N. D.; Yates, R. L. *Ibid.* **1976**, *98*, 461.

Table III. LCAO Coefficients of the Terminal C Atoms of the π_S Orbital of **1**, **2**, and **3** Together with Their Mean Orbital Energies (ϵ_{ij}), Group Overlap Integrals (S_{ij}), and Four-Electron Destabilization Energies (E_{ij})

	1	**2**	**3**
LCAO coefficients			
2s	−0.008	−0.026	0.003
$2p_x$	−0.081	0.003	0.013
$2p_y$	−0.006	−0.073	−0.007
$2p_z$	0.304	0.258	0.309
ϵ_{ij}[a]	−10.09	−10.18	−10.26
S_{ij}^{exo}	0.0601	0.0507	0.0518
ΔE_{ij}^{exo} [b]	41.47	29.38	30.57
S_{ij}^{endo}	0.0446	0.0382	0.0546
ΔE_{uj}^{endo} [b]	22.82	16.66	34.10
$\Delta\Delta E_{ij} = \Delta E_{ij}^{exo} - \Delta E_{ij}^{endo}$ [b]	18.65	12.72	−3.52

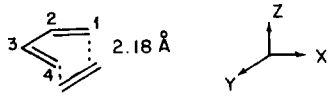
[a] In eV. [b] In kJ/mol.

Table IV. Overlap Integrals between the AO Basis Functions $2s/2p_\pi$, $2p_x/2p_\pi$, $2p_y/2p_\pi$, and $2p_z/2p_\pi$ Utilized to Calculate the Group Overlap Integral

$\langle 2s/2p_\pi \rangle$	0.1428
$\langle 2p_x/2p_\pi \rangle$	0.0861
$\langle 2p_y/2p_\pi \rangle$	0.0569
$\langle 2p_z/2p_\pi \rangle$	0.1373

the two π MOs, π_S and π_1, and the term ϵ_{ij} stands for the average of their one-electron energies taken from PE spectroscopic data. The ϵ_{ij} values for the reaction of **1–3** with ethylene are given in Table III.[50] For the interaction matrix element H_{ij}, the following approximation has been taken from the literature.[52] The geo-

$$H_{ij} = K \cdot S_{ij} \qquad K = -39.7 \text{ eV}$$



metrical parameters to compute S_{ij} were taken from calculated transition-state geometries of Diels–Alder cycloadditions between butadiene and ethylene by using ab initio wave functions of different degrees of sophistication.[53] As shown above, a mean difference of 2.18 Å between the terminal C atoms of the diene and the carbon centers of ethylene has been assumed. In Table IV, the overlap integrals between the atomic orbital basis functions (2s, $2p_x$, $2p_y$, $2p_z$) of the carbon atoms 1 and 4 and the $2p_z$ orbital of the ethylene are given. In Table III, the LCAO coefficients from an EH calculation of the C atoms 1 and 4 for the symmetrical π combination (π_S) of the diene and the group overlap integral between π_S and π_1 for exo and endo attack are given.

Table III clearly displays that in the case of **1** and **2** the four-electron destabilization energy for exo attack exceeds the corresponding contribution for endo attack by more than 12 kJ/mol ($\Delta\Delta E_{ij}$ = 18.65 kJ/mol for **1**, 12.72 kJ/mol for **2**). This explains why only the single endo product is observed. On the other hand, $\Delta\Delta E_{ij}$ is significantly reduced in the Diels–Alder addition between ethylene and the diene **3**. Here a difference between the destabilization energies of 3.52 kJ/mol is predicted, with preference for endo attack. It is clear that this value for $\Delta\Delta E_{ij}$ is not large enough to produce only one cycloadduct. Thus, the difference leads to a stereoselective behavior with predominant bond formation on the exo side. Although these model calculations are only a rough estimate, the computational results are in excellent agreement with experiment.

(50) The PE data of **1–3** are given in Table II; for the π-orbital energy of ethylene, a value of 10.5 was used.[51]

(51) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy", Wiley: London, 1970.

(52) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1.

(53) Burke, L. A.; Leroy, G.; Sana, M. *Theor. Chim. Acta* **1975**, *40*, 313. Townsend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190. Caramella, P.; Houk, K. N.; Domelsmith, L. N. *Ibid.* **1977**, *99*, 4519.

Concluding Remarks

The collective results show that dienophilic addition to an *exo*-2,3-dimethylenenorbornane and norbornene proceeds with an overwhelming kinetic preference for endo attack, at least when the diene forms part of a five-membered ring. Although this stereospecificity finds adequate explanation in the detailed MO treatment presented in the preceding section, it is particularly relevant to the present work that several additional questions are answered. Given the fact, for example, that cyclopentadiene itself is an especially reactive 4π partner in cycloadditions due chiefly to the enforced proximity of C_1 and C_4,[54] one may ask whether a salient stereochemical contrast might materialize when cycloadditions to suitably substituted derivatives of **39** and **40** and to bicyclo[2.2.1]heptyl-fused 1,3-cyclohexadienes are carried out. Although our theoretical treatment predicts total consistency, this point requires experimental verification. Furthermore, some concern must be directed to the magnitude of the energy gap which separates exo and endo approaches to **1** and **2**. At the moment, it is not known whether the prevailing electronic interaction between the diene π orbitals and the σ framework causes a disparity of 2 or 20 kcal/mol. The advantage to endo approach is likely to be small, but some quantitative assessment of this dominating influence in terms of $\Delta H^{\ddagger}$ would prove enlightening.

Also, the deductions reached here suggest that further variations in the bridge segments of bicyclic moieties fused to cyclopentadiene rings might very well cast additional light on the general relationship between electronic perturbation and stereoselection.

We hope to be in a position to report on the outcome of experiments which speak to these issues in the near future.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^1H NMR spectra were determined with Varian T-60, Varian EM-360, and Bruker HX-90 instruments, and apparent splittings are given in all cases. The ^{13}C NMR spectra were recorded on Bruker HX-90 and WP-80 instruments. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-5-ol (8a).[55] A solution of *endo*-dicyclopentadiene (79.3 g, 0.60 mol) in 300 mL of 10% aqueous dioxane containing potassium dihydrogen phosphate (13.5 g, 0.10 mol) was heated to 90 °C with stirring. Selenium dioxide (30.0 g, 0.27 mol) was added in portions during 45 min, and the mixture was heated at this temperature for 2 h and at reflux for 1 h. The cooled reaction mixture was filtered, and the filtrate was taken up in ether and washed several times with 10% sodium bicarbonate solution and brine before drying. After evaporative removal of solvent, the residue was distilled at 20 torr to remove unreacted diene (12 g) and at 0.3 torr to give 51.5 g (68%, based on recovered starting material) of **8a**, bp 78–80 °C [lit.[56] bp 70–80 °C (0.1 torr); lit.[57] bp 67 °C (0.1 torr)].

Tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene (2). After pretreatment of 70 g of alumina (Woelm activity I) with 1% by weight of quinoline, **8a** (20 g, 0.135 mol) was adsorbed onto the solid, and the mixture was heated rapidly to 150 °C under a pressure of 80 torr. These conditions were maintained for 3 h, during which time 2.6 g of a yellow distillate appeared in the ice-cooled receiver, and 0.7 g of clear liquid materialized in the second receiver (dry ice–isopropyl alcohol bath). The two fractions were combined and filtered through 15 g of alumina to give 1.74 g (9.9%) of **2** as a colorless liquid which solidified upon refrigeration: mp 43–44 °C (lit.[21] mp 44 °C); ^1H NMR (CCl_4) δ 6.18 (t, J = 2 Hz, H_3 and H_5), 5.53 (br t, H_8 and H_9), 3.38 (m, H_1 and H_7), 3.15 (dd, J = 3.5, 2 Hz, H_4), 2.20 (dt, J = 8, 1.5 Hz, H_{10s}), 1.97 (m, H_{10a}).

Tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (7b). Freshly distilled samples of *endo*-dicyclopentadiene (3.0 g, 22.7 mmol) and 1,3-dicyclohexadiene (4.0 g, 50.0 mmol) were mixed in a heavy-walled glass tube (25 × 3 cm) which had been prerinsed with pyridine and sealed in vacuo. The tube was heated in a copper tube furnace at 175 °C for 18 h and at 185 °C for 5 h. The pyrolysate was distilled through an 8-cm Vigreux column at 17 mmHg to give 4.9 g of a colorless, mobile liquid, by 85–105 °C.

(54) Sustmann, R.; Schubert, R. *Angew. Chem.* **1972**, *84*, 888; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 840.

(55) This allylic oxidation procedure is that of Cookson, R. C.; Isaacs, N. S.; Szelke, M. *Tetrahedron* **1964**, 717.

(56) Alder, K.; Flock, F. H. *Chem. Ber.* **1954**, *87*, 1916.

(57) Woodward, R. B.; Katz, T. J. *Tetrahedron* **1959**, *5*, 70.

Redistillation of this material furnished 3.18 g of **7b**, bp 85–87 °C (17 mmHg) [lit.[28] bp 80.5 °C (20 torr)].

Tricyclo[5.2.2.0^{2,6}]undeca-3,8-dien-5-ol (8b). A stirred mixture of **7b** (7.3 g, 50 mmol), potassium dihydrogen phosphate (1.6 g, 12 mmol), dioxane (50 mL), and water (5 mL) was heated to 75 °C, and selenium dioxide (3.3 g, 30 mmol) was added in portions during 40 min. Upon completion of the addition, the reaction mixture was warmed to 90 °C during 2 h and heated at reflux for 1 h. Workup in the predescribed manner gave a residue which was first heated at 17 mmHg to recover **7b** (850 mg obtained). Upon reduction of the pressure to 0.4 mmHg, bulb-to-bulb distillation (bp 90–93 °C), and subsequent sublimation of the solid distillate at 60 °C and 0.3 torr, there was isolated 4.94 g (69%, based on recovered **7b**) of alcohol **8b** as a colorless crystalline solid: mp 85.5–86 °C; ^{1}H NMR ($CDCl_3$) δ 6.04 (m, H_3 and H_5), 5.70 (m, H_8 and H_9), 4.29 (br s, –OH), 2.92 (br d, J = 8 Hz, H_5), 2.79 (br m, H_7), 2.54 (br m, H_1), 2.14 (m, H_6), 2.04 (m, H_2), 1.41 (m, H_{10} and H_{11}). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.36; H, 8.70.

Tricyclo[5.2.2.0^{2,6}]undeca-2,5,8-triene (3). A 50-mL two-necked flask equipped with a short-path distillation column (wrapped with heating tape for external heating) connected to an ice-cooled receiver was charged with 8.0 g of Woelm activity I alumina, 0.2 mL of quinoline, and 2.1 g (13.0 mmol) of **8b** and placed in a preheated (152 °C) oil bath. The pressure in the system was immediately reduced to 25 torr, and the heating tape was made to deliver a temperature of 110 °C. During 2.5 h, the hydrocarbon and a small amount of water collected in the receiver. NMR analysis at this point indicated that little or no indene had formed. Passage of the distillate through alumina (30 g) with pentane elution and careful evaporation of solvent gave 820 mg (44%) of **3** as a colorless mobile liquid: bp 95–97 °C (18 torr); ^{1}H NMR ($CDCl_3$) δ 6.23 (AB sextet, J = 7.6, 2.0, and 1.5 Hz, H_8 and H_9), 5.64 (dd, J = 1.2, 0.8 Hz, H_3 and H_5), 3.43 (m, H_1 and H_7), 2.99 (br dd, H_4), 1.60 (br s, H_{10} and H_{11}); ^{13}C NMR ($CDCl_3$) 150.7, 134.4, 116.1, 42.5, 35.2, and 26.3 ppm; m/e calcd 144.0939, obsd 144.0942. Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.38. Found: C, 91.36; H, 8.26.

Cycloaddition of 1 and Methyl Acrylate. A mixture of **1** (0.5 g, 3.79 mmol), methyl acrylate (0.5 g, 1.5 equiv), and carbon tetrachloride (900 μL) was placed in a stoppered flask and stirred magnetically at 42 °C for 10 h. The solvent was removed on a rotary evaporator, and the residue was passed down a silica gel (10 g) column (elution with 20% ethyl acetate in hexane). There was obtained 775 mg (94%) of **9**, whose spectra were identical with those previously reported.[22]

Cycloaddition of 2 and Methyl Acrylate. A solution of **2** (720 mg, 5.54 mmol) and methyl acrylate (620 mg, 7.21 mmol) in carbon tetrachloride (8 mL) was placed in a stoppered vessel and heated at 42 °C for 48 h. After the evaporation of solvent, the residue was chromatographed on Florisil (25 g). Elution with hexane–dichloromethane (1:1) afforded 1.05 g (88%) of **10** as a colorless oil: IR (CCl_4) 3060, 2950, 1732, 1424, 1185, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.39 (m, 2 H), 3.58 (s, 3 H), 3.28 (m, 2 H), 3.07 (m, 1 H), 2.93 (m, 1 H), 2.18–1.38 (series of m, 6 H), 0.79 (ddd, J = 10, 7.5, and 2.0 Hz, 1 H); m/e calcd 216.1150, obsd 216.1154.

This material proved to be air sensitive and was therefore directly hydrogenated.

Catalytic Hydrogenation of 10. A solution of **10** (126 mg, 0.61 mmol) in 5 mL of ethyl acetate was treated with 14 mg of platinum oxide and hydrogenated at 1 atmosphere until the uptake of hydrogen ceased (20 min). The reaction mixture was filtered and evaporated to leave 103 mg of **9**, which proved identical in all respects with the authentic sample.

***exo*-4-Bromo-*syn*,*endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane (12a).** A 1.44-g (6.6 mmol) sample of **9** was subjected to the diimide reduction, saponification, and acidification procedure described by Sugimoto et al.[22] The crude carboxylic acid (810 mg, 4.0 mmol) was dissolved in benzene (15 mL) and thallium ethoxide (0.3 mL, 4.2 mmol) was introduced via syringe. After the solution had been stirred under argon for 15 min, hexane (40 mL) was added, and the white precipitate was filtered and dried in vacuo overnight [1.7 g (104%) of off-white solid, mp 230 °C dec].

The thallium carboxylate (1.23 g, 3.0 mmol) dissolved in carbon tetrachloride (15 mL) was stirred vigorously under argon while a solution of bromine (720 mg, 4.5 mmol) in carbon tetrachloride (5 mL) was added dropwise during 15 min. The bright yellow mixture was heated at reflux until carbon dioxide evolution ceased (3 h). The cooled mixture was filtered, and the filtrate was washed with 10% sodium bisulfite and 10% sodium bicarbonate solutions before drying. Evaporation of solvent left a colorless oil which was filtered through 10 g of silica gel (pentane elution) to give 350 mg (72%) of **12a** as a mobile, colorless liquid homogeneous on TLC: ^{1}H NMR ($CDCl_3$) δ 3.17 (dd, J = 7.5, 5.5 Hz, H_{4endo}), 2.93 (m, H_3), 2.65–1.23 (series of m, 15 H), m/e calcd 161.1330, obsd 161.1337.

***syn*,*endo*-Tetracyclo[6.2.1^{3,6}.0^{2,7}]dodecane (12b). A. Reductive Debromination of 12a.** A solution of **12a** (74 mg, 0.3 mmol) and tri-*n*-butyltin hydride (120 mg, 0.41 mmol) in dry benzene (6 mL) was heated to 60 °C under an argon atmosphere with stirring for 2.5 h. The hydrocarbon product was isolated directly from the cooled reaction mixture by preparative VPC: colorless solid, mp 29–31 °C (lit.[58] mp 51 °C); ^{1}H NMR ($CDCl_3$) δ 2.33–1.88 (series of m, 10 H), 1.82–1.22 (series of m, 8 H); ^{13}C NMR ($CDCl_3$) 48.0, 47.1, 41.4, and 25.3 ppm; m/e calcd 162.1408, obsd 162.1413.

B. Hydrogenation of 13. To a solution of **13** (20 mg, 1.25 mmol) in ethyl acetate (3 mL) was added 18 mg of prereduced platinum oxide, and the mixture was hydrogenated at atmospheric pressure. Upon completion of hydrogen uptake, the catalyst was separated by filtration through Celite, and the filtrate was evaporated to give 158 mg (79%) of **12b** as a colorless solid, mp 29–31 °C, identical with the material obtained in A.

Catalytic Hydrogenation of 14. With application of the procedure described above, 400 mg (2.50 mmol) of **14** was converted into **15** (370 mg, 92%), obtained as a white solid: mp 43–44 °C (lit.[30a] mp 38 °C); ^{1}H NMR ($CDCl_3$) δ 2.17–2.03 (m, 4 H), 1.72–1.35 (series of m, 14 H); ^{13}C NMR ($CDCl_3$) 50.3, 42.2, 41.4, 36.3, 34.3, 31.3, and 24.5 ppm.

Cycloaddition of 1 and Methyl Propiolate. A solution of **1** (2.77 g, 21 mmol) and methyl propiolate (2.0 g, 24 mmol) in carbon tetrachloride (2 mL) was sealed into a heavy-walled glass tube under an argon atmosphere and heated at 42 °C for 11 h. The product was chromatographed on Florisil (60 g, dichloromethane elution) to give 4.21 g (93%) of **16** whose spectral properties were identical with those reported by Sugimoto et al.[22]

Cycloaddition of 2 and Methyl Propiolate. A solution of **2** (750 mg, 5.77 mmol) and methyl propiolate (500 mg, 5.95 mmol) in hexane (4 mL) was sealed into a heavy-walled glass tube under an argon atmosphere and heated at 65 °C for 24 h. The reaction mixture was rapidly filtered through silica gel (elution with hexane followed by dichloromethane), and the filtrate was evaporated to give 1.04 g (83%) of **17** as an air-sensitive pale yellow oil: IR (CCl_4) 3060, 2970, 2875, 1718, 1590, and 1568 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.07 (d, J = 2.5 Hz, 1 H), 6.20 (m, 2 H), 3.61 (s, 3 H), 3.50 (m, 4 H), 2.37–1.88 (series of m, 4 H); m/e calcd 214.0994, obsd 214.0999. This material was catalytically hydrogenated without further purification.

Methyl *syn*-Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-2-ene-*endo*-4-carboxylate (18). A solution of **17** (1.0 g, 4.67 mmol) in ethyl acetate (30 mL) containing 30 mg of platinum oxide was hydrogenated at 1 atmosphere for 24 h. The catalyst was separated by filtration, and the product was chromatographed on silica gel (elution with 5% ether in hexane) to give 925 mg (92%) of **18**, whose spectra were identical with those reported earlier.[22]

Cycloaddition of 1 and Maleic Anhydride. To a solution of **1** (1.6 g, 12.1 mmol) in benzene (8 mL) was added 1.2 g (12.2 mmol) of maleic anhydride in small portions over a period of 20 min (exothermic). The resultant lime-yellow solution gradually became colorless on standing for an additional 25 min. The solution was evaporated under reduced pressure to give 2.51 g (90%) of a viscous colorless oil, the ^{1}H NMR spectrum of which indicated **19** and **20** to be present in a 1:2 ratio. Separation of the isomers was achieved by preparative layer chromatography on silica gel (dichloromethane elution). Adduct **19** was obtained as a colorless crystalline solid: mp 91–93 °C (lit.[21] mp 98 °C); ^{1}H NMR ($CDCl_3$) δ 3.60 (m, 2 H), 3.45 (m, 2 H), 2.93 (m, 2 H), 1.73 (m, 4 H), 1.23 (m, 4 H); ^{13}C NMR ($CDCl_3$) 171.67 (s), 154.09 (s), 50.20 (d), 48.84 (t), 47.77 (t), 44.96 (d), 42.72 (d), and 24.76 (t) ppm; IR (KBr) 1871 and 1780 cm^{-1}; m/e calcd 230.0943, obsd 230.0948.

Adduct **20** was isolated as colorless platelets: mp 106–109 °C; ^{1}H NMR ($CDCl_3$) δ 3.48 (m, 2 H), 3.08 (m, 2 H), 2.80 (d, J = 2.0 H), and 1.88–0.62 (series of m, 8 H); ^{13}C NMR ($CDCl_3$) 171.87, 153.71, 60.40, 48.83, 45.80, 42.20, and 26.22 cm^{-1}; IR (KBr) 1869 and 1782 cm^{-1}; m/e calcd 230.0943, obsd 230.0948.

Cycloaddition of 2 with Maleic Anhydride. Maleic anhydride (800 mg, 8.0 mmol) was added to a solution of **2** (1.3 g, 10.0 mmol) in benzene (5 mL) and a lime-yellow coloration developed immediately. After the reaction mixture stood for 24 h, it deposited crystals which were isolated by decantation and washed with pentane. There was obtained 1.1 g of **21** as colorless crystals, mp 123–127 °C (lit.[21] mp 127 °C). The supernatant and pentane washings were combined and evaporated at reduced pressure to give an additional 560 mg of **21** (total yield 91%): ^{1}H NMR ($CDCl_3$) δ 6.55 (m, 2 H), 3.49 (m, 4 H), 2.43 (d, J = 1.03 Hz, 2 H), 2.24 (d with further splitting, J = 5.6 Hz, 1 H), 2.10 (d with further splitting, J = 5.6 Hz, 1 H), 1.72 (d with further splitting, J = 11.0 Hz, 1 H), 1.46 (d with further splitting, J = 11.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 172.2, 161.9, 139.0, 70.4, 48.7, 47.8, 46.3, and 42.6 ppm; m/e calcd 228.0786, obsd 228.0790.

(58) Bruck, P.; Thompson, D.; Winstein, S. *Chem. Ind.* (*London*) **1960**, 405.

Hydrogenation of 21. A stirred suspension of platinum oxide (21 mg) in ethyl acetate was prehydrogenated, and a solution of **21** (210 mg, 0.9 mmol) in 2 mL of ethyl acetate was added. Hydrogen uptake (1 mol equiv) was complete in 30 min at 1 atmosphere. The mixture was filtered, and the filtrate was evaporated to give **20** (203 mg), identical in all respects with the material obtained earlier.

***syn,endo*-Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (24). A. By Reduction–Oxidative Decarboxylation of 19.** To a stirred suspension of 14.5 g (75 mmol) of potassium azodicarboxylate in 150 mL of dichloromethane containing 2.3 g (10 mmol) of **19** was added dropwise 8.5 g (142 mmol) of glacial acetic acid during 1 h. After stirring was continued for an additional hour, the precipitated solids were separated by filtration, and the filtrate was evaporated. Chromatography of the residue on silica gel (140 g) with elution involving hexane–ethyl acetate (5:1) gave 730 mg (32%) of **22**: IR (CCl_4) 2962, 2900, 1780, 1748, 1300, 1294, and 1188 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.65 (br s, 2 H), 2.77 (m, 2 H), 2.81–0.88 (series of m, 12 H); ^{13}C NMR ($CDCl_3$) 174.00, 48.07, 46.08, 43.62, 43.33, 41.53, 40.87, and 25.03 ppm; *m/e* calcd 232.1099, obsd 232.1104.

A solution of **22** (630 mg, 2.72 mmol) and bis(triphenylphosphine)-nickel dicarbonyl (850 mg, 1.33 mmol) in diglyme (20 mL) was slowly heated to 170 °C during 1 h, at which point diglyme was seen to begin to distill. After 3 h, 10 mL of triglyme was added, the distillation was continued at a bath temperature of 190 °C with the pressure in the flask reduced to 160 torr for 1 h, and the distillate was collected in a dry ice–isopropyl alcohol bath. The combined distillates were taken up in pentane (40 mL), and the organic phase was washed with water (4 × 25 mL), dried, and carefully concentrated through a short path still at atmospheric pressure. There was isolated 121 mg (28%) of **24**:[58] ^{1}H NMR ($CDCl_3$) δ 5.93 (m, 2 H), 2.55 (m, 2 H), 2.38 (m, 2 H), 1.98 (m, 2 H), 1.80–1.02 (br m, 4 H), 1.17 (m, 4 H); ^{13}C NMR ($CDCl_3$) 131.6, 59.2, 48.7, 47.1, 44.7, 39.8, and 24.8 ppm.

B. By Reduction–Oxidative Decarboxylation of 20. Diimide reduction of **20** (3.3 g, 14.3 mmol) was performed in dichloromethane (200 mL) by using 20.7 g (107 mmol) of potassium azodicarboxylate and 12 g (200 mmol) of glacial acetic acid in the predescribed manner. Without purification, the sample of **23** (2.1 g, 9.0 mmol) was dissolved in diglyme (50 mL) containing 2.7 g (4.28 mmol) of bis(triphenylphosphine)nickel dicarbonyl, and the mixture was heated at 170 °C for 2.5 h. At this point, triglyme (25 mL) was added. Distillation and workup in the predescribed manner afforded 810 mg (35% overall) of **24**.

Hydrogenation of 24. A solution of **24** (121 mg) in 5 mL of ethyl acetate containing platinum oxide (8 mg) was hydrogenated at atmospheric pressure for 25 min. Product isolation in the usual manner afforded a colorless mobile liquid which was identical with authentic **12b**.

Cycloaddition of 1 and *p*-Benzoquinone. *p*-Benzoquinone (1.1 g, 0.01 mol) and **1** (1.4 g, 0.01 mol) were dissolved in chloroform (4 mL), and the solution was stored at 5 °C for 6 h. The solvent was evaporated under vacuum, and the residue was maintained overnight under a pressure of 0.3 torr. There was obtained 2.3 g (94%) of **27** which was further purified by sublimation at 90 °C and 0.1 torr: pale yellow solid, mp 104–106 °C; IR (CCl_4) 1672 and 1607 cm^{-1}; ^{1}H NMR δ 6.67 (s, 2 H), 3.33 (br s, 2 H), 3.06 (m, 2 H), 2.40 (br s, 2 H), 1.93–0.62 (series of m, 8 H); ^{13}C NMR ($CDCl_3$) 199.0, 153.8, 141.9, 50.6, 49.0, 45.9, 43.0, and 25.3 ppm; *m/e* 240.1150, obsd 240.1155. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.94; H, 6.69.

Cycloaddition of 2 and *p*-Benzoquinone. A solution of **2** (500 mg, 3.8 mmol) and *p*-benzoquinone (410 mg, 3.8 mmol) in chloroform (3 mL) was refrigerated overnight. The reaction mixture was worked up in the manner described above to give 800 mg (85%) of **28** which was sublimed at 70 °C and 0.1 torr. Analytically pure **28** was obtained as pale yellow crystals: mp 109–110 °C; IR (CCl_4) 1670 and 1606 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.63 (s, 2 H), 6.41 (dd, J = 2.5, 1.0 Hz, 2 H), 3.38 (m, 2 H), 3.28 (m, 2 H), 2.15 (dt, J = 10.5, 1.5 Hz, 2 H), 1.85 (br s, 2 H), 1.36 (m, 2 H); ^{13}C NMR ($CDCl_3$) 200.20, 159.9, 142.00, 138.20, 70.09, 50.07, 48.61, 44.30, and 43.39 ppm; *m/e* calcd 238.0994, obsd 238.0998. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.59; H, 6.00.

Hydrogenation of 28. A solution of **28** (120 mg) in ethyl acetate (5 mL) containing suspended platinum oxide (24 mg) was hydrogenated at atmospheric pressure for 30 min. Product isolation as before yielded 112 mg of **27**.

Benzyne Addition to 1. A solution of **1** (14.2 g, 0.108 mol) in anhydrous dimethoxyethane (25 mL) was heated to reflux while solutions of anthranilic acid (15.0 g, 0.109 mol) in dimethoxyethane (40 mL) and isoamyl nitrite (18 mL) in the same solvent (10 mL) were added simultaneously from two dropping funnels over 30 min. The brown reaction mixture was stirred at the reflux temperature until gas evolution ceased (20 min). The resulting slurry was concentrated in vacuo, and the residue was chromatographed on alumina (grade A, 480 g) with pentane elution. There was obtained 15.9 g (71%) of **29** as a clear colorless oil which solidified on standing in the refrigerator under argon. An analytical sample was obtained by preparative VPC (6 ft × 0.25 in. 5% SE-30 on Chromosorb G) at 190 °C: IR (CCl_4) 3050, 2980, 2873, 1502, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.28–6.71 (m, 4 H), 3.76 (m, 2 H), 3.03 (m, 2 H), 2.36 (m, 2 H), 1.63–0.83 (series of m, 6 H); ^{13}C NMR ($CDCl_3$) 158.7 (s), 150.0 (s), 124.0 (d), 66.9 (t), 49.4 (d), 43.4 (d), and 23.8 (t) ppm; *m/e* calcd 208.1252, obsd 208.1258.

Diimide Reduction of 29. A solution of **29** (940 mg, 4.5 mmol) in dioxane (10 mL) was added to a solution of potassium azodicarboxylate (3.2 g, 16 mmol) in methanol (20 mL), and the mixture was stirred vigorously while acetic acid (3.0 mL) was added during 20 min. After stirring was continued for an additional 20 min, the product was isolated by the conventional workup procedure. VPC analysis (6 ft × 0.25 in. 5% SE-30 on Chromosorb G, 195 °C) of this material indicated a 5:1 mixture of two components to be present. Isolation of the major hydrocarbon showed it to be identical in all respects with authentic **30**:[31,37] IR (neat) 3045, 2945, 762, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.03 (AA′XX′, 4 H), 3.09 (m, 2 H), 2.62 (m, 2 H), 2.10 (m, 2 H), 1.98 (m, 2 H), 1.43 (dt, J = 9.8, 1.5 Hz, 2 H), 0.77 (m, 4 H).

The minor component, a colorless liquid, is thought to be an ene product: ^{1}H NMR ($CDCl_3$) δ 7.01 (m, 5 H), 3.02 (m, 3 H), 2.28–0.96 (series of m, 12 H).

Benzyne Addition to 2. By the method described previously, 1.12 g (8.6 mmol) of **2** in 30 mL of dimethoxyethane was allowed to react with 2.2 equiv of benzyne as generated by the aprotic diazotization of anthranilic acid (1.38 g, 10 mmol) with isoamyl nitrite (1 mL). The reaction mixture was concentrated in vacuo and chromatographed on basic alumina (30:1) with elution by hexane–ethyl acetate (50:1). There was obtained 7% of unreacted **2** and 71% of **33**, a white solid: mp 104.5–106 °C (from ethanol–hexane, 1:1); ^{1}H NMR ($CDCl_3$) δ 7.01 (AA′BB′, 4 H), 6.88 (m, 4 H), 4.98 (AB, 2 H), 3.17 (m, 2 H), 2.62 (m, 2 H), 1.78 (m, 2 H), 1.35 (m, 2 H); ^{13}C NMR ($CDCl_3$) 148.4, 146.5, 131.9, 127.9, 125.9, 122.4, 119.5, 64.4, 58.7, 57.6, 45.7, and 43.3 ppm; *m/e* calcd 282.1408, obsd 282.1414.

Catalytic Hydrogenation of 33. To 3 mL of ethyl acetate containing 11 mg of prereduced platinum oxide was added a solution of **33** (62 mg, 0.30 mmol) in the same solvent (2 mL). Stirring at atmospheric pressure led to completed uptake of hydrogen after 15 min. The mixture was filtered through Celite, and the filtrate was concentrated to give 56 mg of **31**, the ^{1}H NMR spectrum of which was superimposable upon that of the sample prepared below.

Benzyne Addition to 29. By the method originally used to prepare **29** itself, 1.04 g (5.0 mmol) of **29** was allowed to react with 1.3 g (9.4 mmol) of anthranilic acid and 1 mL of isoamyl nitrite in 25 mL of dimethoxyethane. The resulting product mixture was chromatographed on alumina (100 g) with pentane elution. There was obtained 170 mg (16.5%) of unreacted **29**, followed by 990 mg of **31**, a colorless solid: mp 116–117 °C (from ethanol–hexane); IR (CCl_4) 3045, 3025, 2965, 1450, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.22–6.85 (m, 8 H), 3.30 (m, 2 H), 2.35 (m, 2 H), 1.75 (m, 2 H), 1.37 (m, 2 H), 0.90 (m, 4 H); ^{13}C NMR ($CDCl_3$) 149.3, 147.3, 127.8, 124.8, 123.3, 119.6, 61.7, 47.2, 45.9, 39.6, and 24.5 ppm; *m/e* calcd 284.1465, obsd 284.1570. Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.98; H, 7.18.

Cycloaddition of 3 and Dimethyl Acetylenedicarboxylate. To a vigorously stirred solution of **3** (245 mg, 1.70 mmol) in benzene (4 mL) was added in one portion a solution of dimethyl acetylenedicarboxylate (310 mg, 2.18 mmol) in the same solvent (2 mL). Upon completion of the addition, the solvent was removed in vacuo, and the residue was filtered through 5 g of silica gel to give 455 mg (94%) of a mixture of **34a** and **35a**, whose isomers were separated by preparative layer chromatography on silica gel (elution with ethyl acetate–hexane, 2:3). A ratio of 14:86 was determined to be present by integration of the olefinic region of the ^{1}H NMR spectrum of the original mixture.

For **34a**, a colorless viscous oil: ^{1}H NMR ($CDCl_3$) δ 6.10 (dt, J = 5.0, 2.5 Hz, 2 H), 3.81 (m, 4 H), 3.73 (s, 6 H), 2.53 (dt, J = 5.5, 1.0 Hz, 1 H), 2.18 (dt, J = 5.5, 1.0 Hz, 1 H), 1.62 (br s, 4 H); ^{13}C NMR ($CDCl_3$) 165.9, 158.4, 152.4, 134.4, 70.6, 55.0, 51.9, 38.6, and 25.9 ppm; *m/e* calcd 286.1205, obsd 286.1211.

For **35a**, a colorless viscous oil: ^{1}H NMR ($CDCl_3$) δ 6.43 (sextet, 2 H), 3.98 (s, 6 H), 4.03–3.68 (m, 4 H), 3.53 (dt, J = 5.5, 0.8 Hz, 1 H), 2.18 (dt, J = 5.5, 0.8 Hz, 1 H), 1.61–0.60 (m, 4 H); ^{13}C NMR ($CDCl_3$) 166.0, 155.7, 151.7, 134.9, 70.0, 54.5, 52.0, 38.6, and 23.7 ppm; *m/e* calcd 286.1205, obsd 286.1211.

Cycloaddition of 3 and Methyl Propiolate. Into an NMR tube was placed 100 mg (0.704 mmol) of **3**, 88 mg (1.05 mmol) of methyl propiolate, and 170 μL of $CDCl_3$. The tube was placed in a 42 °C oil bath, and the progress of reaction was monitored at regular intervals. After 540 min, the distribution was seen to consist of 14% of **3**, 31% of **34b**,

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and 55% of **35b**. This mixture was subjected to preparative layer chromatography on silica gel (elution with 30% ethyl acetate in hexane). There was isolated 8 mg of unreacted **3** and 73 mg of a mixture of **34b** and **35b** which was not further separated: ^{1}H NMR ($CDCl_3$) δ 7.43 (overlapping d, J = 2.8 Hz, 1 H), 6.22 and 6.01 (m, 2 H, ratio 79:21), 4.23-3.58 (m, 7 H, including methoxyl singlets), 2.53-1.93 (m, 2 H), 1.56 (br s, 0.84 H), 1.52-1.17 (m, 1.58 H), 0.73 (m, 0.79 H), 0.62 (m, 0.79 H); m/e calcd 228.1150, obsd 228.1155. This material was directly subjected to thermal aromatization. A third band was determined to be **36b** (45 mg, 32%).

Aromatization of 34a and 35a. Dimethyl Benzonorbornadiene-2,3-dicarboxylate (36a). Into an NMR tube was placed 165 mg of a mixture of **34a** and **35a** and 0.4 mL of $CDCl_3$. The tube was immersed in a 50 °C bath and monitored periodically by ^{1}H NMR. After 21 h, the aromatization process was essentially complete, and the contents of the tube were subjected to preparative layer chromatography on silica gel. Elution with 30% ethyl acetate in hexane gave 120 mg (80%) of **36a** as a colorless viscous oil: IR (neat) 2950, 1708, 1615, 1426, 1253, and 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.25 and 6.98 (AA'BB', 4 H), 4.22 (t with further splitting, J = 1.5 Hz, 2 H), 3.77, (s, 6 H), 2.57 (dt, J = 7.8, 1.5 Hz, 1 H), 2.28 (dt, J = 7.8, 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 164.5, 150.9, 147.9, 124.9, 122.2, 67.8, 52.9, and 51.5 ppm; m/e calcd 258.0892, obsd 258.0897. Anal. Calcd for $C_{15}H_{14}O_2$: C, 69.76; H, 5.46. Found: C, 69.60; H, 5.52.

Aromatization of 34b and 35b. Methyl Benzonorbornadiene-2-carboxylate (36b). A solution of the **34b/35b** mixture (72 mg, 0.32 mmol) in benzene (4 mL) was heated at 50 °C for 24 h and filtered through silica gel (5 g) (elution with 20% ethyl acetate in hexane) to give 44 mg (69%) of **36b** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.50 (d, J = 3.7 H, 2 H), 7.16 and 6.85 (m, 4 H), 4.15 (m, 1 H), 3.95 (m, 1 H), 3.67 (s, 3 H), 2.37 (m, 2 H); m/e calcd 200.0837, obsd 200.0843.

Benzyne Addition to 3. A solution of **3** (130 mg, 0.90 mmol) in dimethoxyethane (1 mL) was heated at reflux with stirring while 144 mg (1.05 mmol) of anthranilic acid dissolved in 5 mL of dimethoxyethane and 0.3 mL of isoamyl nitrite in 2 mL of dimethoxyethane were added simultaneously from separate addition funnels over a period of 10 min. The reaction mixture was heated at reflux for an additional 10 min and concentrated in vacuo. The residue was filtered through alumina (20 g) with hexane elution to give 165 mg of a white solid, ^{1}H NMR analysis of which showed it to consist of **37** (16%), **38** (69%), and dibenzonorbornadiene (15%). Preparative layer chromatography on basic alumina (elution with 15% dichloromethane in hexane) permitted the isolation of pure **38** as a white solid which decomposes with gas evolution above 80 °C: ^{1}H NMR ($CDCl_3$) δ 7.17 and 6.88 (m, 4 H), 6.36 (sextet, 2 H), 3.91 (m, 4 H), 2.03 (br s, 2 H), 1.07 (d with further splitting, J = 6.5 Hz, 2 H), 0.18 (d with further splitting, J = 6.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 150.8, 134.8, 123.8, 121.6, 66.4, 51.8, 39.1, and 24.7 ppm; m/e calcd ($M^+ - C_2H_4$) 192.0939, obsd 192.0943.

Hydrocarbon **37** was not obtained in a form adequately free from **38** to allow complete ^{1}H NMR assignment to be made. ^{13}C ($CDCl_3$) assignments by subtraction of the signals for **38** and dibenzonorbornadiene are 155.7, 133.1, 123.5, 121.4, 67.0, 52.0, 38.2, and 25.8 ppm.

Dibenzonorborandiene by Aromatization of 37 and 38. A sample of the **37/38** mixture in $CDCl_3$ was heated at 45 °C for 16 h. Evaporation of the solvent gave dibenzonorbornadiene in quantitative yield as a white powder: mp 154.5-156 °C (lit.[60] mp 153.5 °C); ^{1}H NMR ($CDCl_3$) δ 7.35 and 6.80 (AA'BB, 8 H), 4.19 (t, J = 1.5 Hz, 2 H), 2.63 (t, J = 1.5 Hz, 2 H); ^{13}C NMR 150.5, 125.1, 121.7, 67.7, and 51.5 ppm; m/e calcd 192.0939, obsd 192.0943.

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Chiral Perturbation of Olefins by Deuterium Substitution. The Optical Activity and Circular Dichroism Behavior of (1*S*)-[2-^{2}H]Norbornene and Deuterated Apobornenes

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Abstract: The deuterated, optically active hydrocarbons **11**, **13**, **16**, and **21** of known absolute configuration have been prepared and their absorption and circular dichroism spectra determined. These compounds represent the first examples of olefins which owe their chirality solely to isotopic substitution. The three apobornenes were prepared from *d*-10-camphorsulfonic acid (**7**) via (+)-ketopinic acid (**8**) and (1*S*)-1-bromo-α-fenchocamphorone (**9**). Replacement of the bridgehead bromine substituent by H or D was efficiently achieved by irradiation with tri-*n*-butyltin hydride or deuteride in refluxing benzene containing AIBN. (1*S*)-[2-^{2}H]norbornene (**21**) was made available by degradation of the (+)-carboxylic acid **17** to (+)-norbornen-2-one (**19**), followed by catalytic hydrogenation, Shapiro reaction on the tosylhydrazone, and a deuterium oxide quench. The contributions of the C-D bonds to the observed Cotton effects are analyzed, and comparisons between the effects of a deuterium atom and a methyl group on chiroptical activity are made.

Since the discovery of deuterium by Urey and co-workers in 1932,[2] many chiral compounds owing their optical activity to the presence of this isotope have been prepared.[3,4] Nonetheless, gaps in our knowledge of asymmetric perturbation by deuterium have managed to persist throughout this period. Recently, intense interest has materialized in clarifying certain of these questions. In particular, research activity in several laboratories during the last 5 years dealing with otherwise intrinsically symmetric carbonyl compounds has provided elegant experimental demonstration of the usual (though not invariant[10]) antioctant (dissignate) behavior of the isotope.[5-10] While conformationally flexible systems such

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