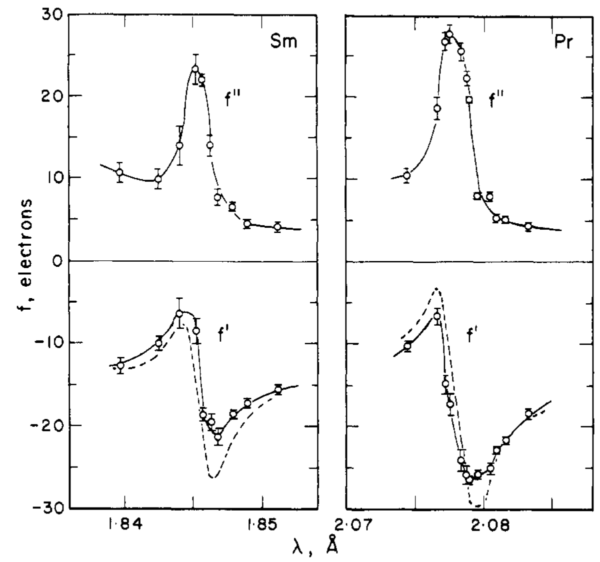

Figure 1. Anomalous scattering terms f' and f'' near the L_3 edges for samarium (left) and praseodymium (right). The broken lines are calculated from f'' by a dispersion relation.

praseodymium in a molecule of 800 000 daltons would be a somewhat similar case, since, according to Wilson statistics, the percentage effects of anomalous scattering depend on the ratio of changes in f to the square root of the number of atoms.[16]

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Electronic Control of Stereoselectivity. 3. Stereoselection Operative in [4 + 2]π Cycloadditions to Cyclopentadiene Rings Fused at C_2,C_3 to Bicyclic Frameworks[1]

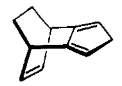
Sir:

Exo addition to norbornene double bonds in the absence of sterically interfering C_7 substituents is so commonplace that transformations based upon this stereoselection have played a pivotal role in organic synthesis. Although exo attack has frequently been attributed to dominant steric control, the possible contribution of electronic factors has recently been addressed.[2,3] Using second-order perturbation theory, Fukui concluded that the higher energy of the norbornene π orbital leads to σ–π mixing in bonding fashion with all lower lying orbitals, the result giving rise to somewhat greater π-electron density in the exo region.[2] Houk's contrasting view is based upon an antibonding interaction between the $C_1C_6C_5C_4$ bridge and the π orbital, with resultant repulsion of electrophiles approaching the endo surface because of destabilizing secondary orbital interactions.[3]

Unambiguous demonstration of the existence of a directed electronic effect (exo) in norbornyl systems has long been awaited. Complications arise because of present inabilities to dissect steric factors which dictate exo stereoselection as well. We have reasoned that the orbital interactions existent in bridged bicyclic systems should have a recognizable impact at more remote sites which are not sterically biased.[4] The present study, which centers about the stereochemistry of Diels–Alder additions to **1–3**, provides evidence sufficient to justify consideration of norbornyl and norbornenyl frameworks as respectable electronic perturbers and constitutes amplification of earlier observations made by the research groups of Alder and Sugimoto.[5] Specifically, the examples presented herein suggest that electronic rather than steric factors govern the highly stereoselective approach of dienophiles to **1** and **2**. These factors are diminished in **3** which shows lower stereoselectivity in reactions with dienophiles.


1


2


3

Heating carbon tetrachloride solutions of **1** (42 °C, 10 h) and **2** (42 °C, 48 h) with methyl acrylate in sealed tubes afforded adducts **4** and **5**, respectively, as exclusive products in purified yields of 94 and 88%. Proof of the dienophile approach to the endo faces of **1** and **2** was gained by conversion of **5** into **4** and subsequent diimide reduction to give **7a** (Scheme I). Delivery of hydrogen to the norbornene-type double bond materialized expectedly from the exo direction as shown by conversion of **7a** into the thallium carboxylate **7b**, treatment

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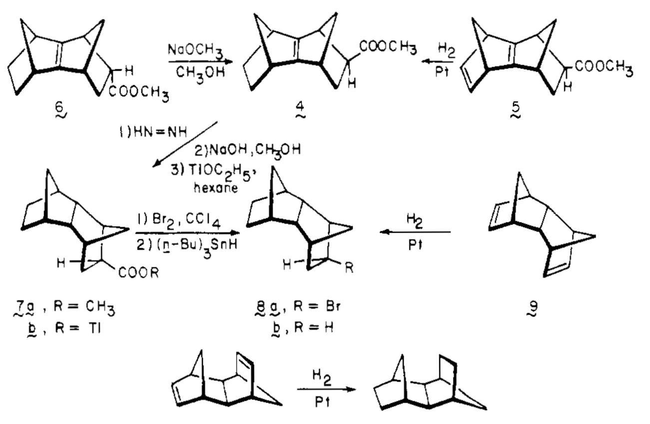
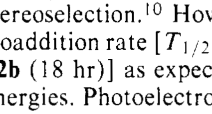
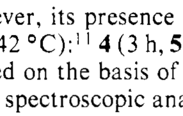
Scheme I

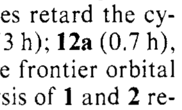


with a stoichiometric quantity of bromine,[6] and reductive debromination of **8a** to hydrocarbon **8b.** An authentic sample of **8b** was made available by hydrogenation of the well-known diene **9.**[7,8] Alternate possibility **11** was comparably prepared from **10**[7-9] and shown to differ notably from **8b** in its spectra.

The homogeneous products obtained by comparable reaction of **1** (42 °C, 11 h) and **2** (65 °C, 24 h) with methyl propiolate were shown to be **12a** (93%) and **12b** (83%) by partial or complete saturation of the latter to give **12a** and **6**, respectively, followed by epimerization of **6** to provide exo ester **4**. Clearly, the additional double bond in **2** does not perturb stereoselection.[10] However, its presence does retard the cycloaddition rate [$T_{1/2}$ (42 °C):[11] **4** (3 h, **5** (73 h); **12a** (0.7 h), **12b** (18 hr)] as expected on the basis of the frontier orbital energies. Photoelectron spectroscopic analysis of **1** and **2** revealed π_A and π_S to reside at 7.96 and 9.68, and 8.06 and 9.85 eV, respectively.


12a, saturated
b, unsaturated


13a, saturated
b, unsaturated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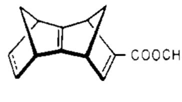
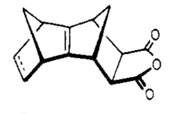
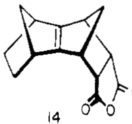

15a, saturated
b, unsaturated

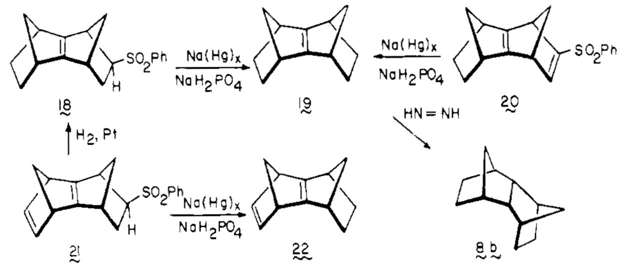

16a, saturated
b, unsaturated


17

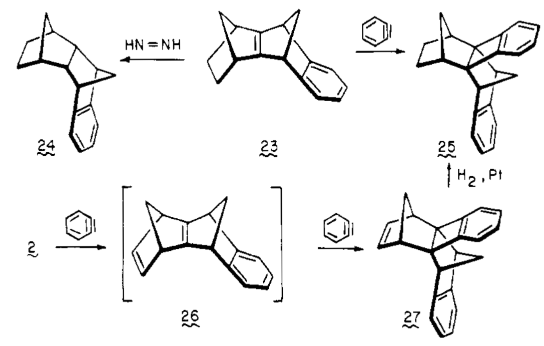
On standing with maleic anhydride in benzene at 25 °C, **1** was consumed to provide (90%) a 2:1 mixture of **13a** and **14.** In the case of **2**, only **13b** was formed. The differing product distributions appear contrary to steric approach control considerations and are therefore considered to arise from the higher reactivity of **1**. A similar effect is not encountered with *p*-benzoquinone which reacted to deliver only **15a** (94%) and **15b** (88%). Comparable factors are, of course, not revealed in the *N*-methyltriazolinedione adducts **16.** In all cases, the **a** and **b** adducts were interrelated by hydrogenation. The ^{1}H NMR data for **13b** and **15b** expectedly showed high levels of shielding for the pair of α-carbonyl protons thrust into the region of the π bond; these shifts are entirely normal in **13a** and **15a.** Final confirmatory proof of structure, at least for **13** and **14,** involved their conversion into **17** by sequential diimide reduction, hydrolysis, and oxidative decarboxylation;[12] the hydrogenation of **17** in turn afforded **8b.**

Phenyl vinyl sulfone[13] added smoothly to **1** and **2** to provide **18** (91%) and **21** (77%) exclusively. Isodicyclopentadiene (**1**) was also converted into **20** with ethynyl phenyl sulfone.[14] Reductive desulfonylation[15] of these adducts has delivered the topologically interesting hydrocarbons **19** and **22** whose structural assignments again rest upon relay with **8b** (Scheme II).

Scheme II

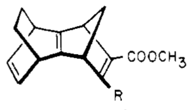


Scheme III

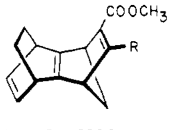


Benzyne, as traditionally generated from anthranilic acid, reacted with **1** to give **23** (71%) which was transformed to the known **24**[8,16] upon treatment with diimide (Scheme III). With **2**, only a 2:1 adduct was obtained without regard for the relative amounts of benzyne utilized. Evidently, the central double bond of initial adduct **26** 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 **27** were elucidated by treatment of **23** with excess benzyne to give **25** which proved to be identical with dihydro-**27.**

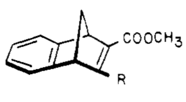
Given the preceding unambiguous proof of kinetically favored stereospecific capture of **1** and **2** from the endo direction, the contrasting behavior of **3** now to be demonstrated must be viewed as suggestive that diagnostically important electronic alterations, which bear directly on product development, are being manifested. Thus, admixture of **3** with dimethyl acetylenedicarboxylate at 25 °C resulted in production of **28a** and **29a** in a 14:86 ratio. Heating **3** at 42 °C with methyl propiolate gave rise to a comparable distribution of **28b** and **29b** (21:79). The crossover in stereoselection is not restricted to α,β-unsaturated ester dienophiles, as evidenced by the response of **3** to benzyne (**31**:**32**, 19:81). Owing to the isolation of pairs of stereoisomers in these examples, structural assignments can be deduced readily from the ^{1}H NMR spectra. For example, the proximity of the carbomethoxy substituted double bond



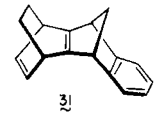
28a, R = COOCH3
b, R = H

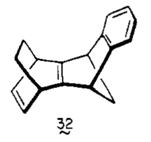


29a, R = COOCH3
b, R = H



30a, R = COOCH3
b, R = H


31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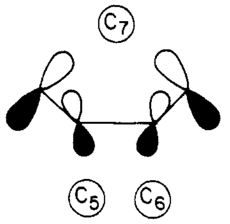

Figure 1. Schematic representation of the π_S orbital as obtained using the STO 3G method.

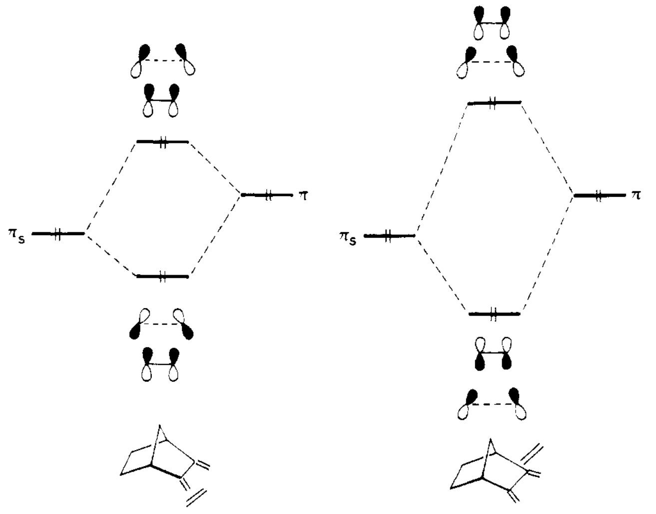

Figure 2. Qualitative diagram of the interaction between π_S of the diene unit and a π bond: left, approach from the direction anti to the methano bridge; right, corresponding syn approach.

to the ethano bridge in **29a** causes the proximal and distal methylene protons to be characterized by disparate chemical shifts (m at δ 1.61–0.60, 4 H). In **28a,** where such shielding does not operate, the four protons of the ethano bridge appear as a pseudosinglet at δ 1.62. Additionally, independent heating of **28a** and **29a** at 50 °C promoted the loss of ethylene with aromatization to provide diester **30a.** Likewise, **28b–29b** cleanly gave **30b** and **31–32** were transformed to dibenzonorbornadiene.[17]

The stereoselectivity observed above cannot be attributed to steric factors because C_1 and C_4 of each cyclopentadiene unit are too remote from either bridge.[18] Were such a working hypothesis adopted, the behavior of **1** and **3** would necessarily be contrasteric, an implausible premise. Steric attraction[2] and π-orbital hybridization arguments[2] are also considered by us to be inapplicable. Rather, rationalization of the observed stereoselectivity has presently been approached by performing extensive semiempirical (MINDO/3, SPINDO, EHT, modified INDO) and ab initio (STO 3G) calculations on 2,3-dimethylenenorbornane (**33**) and 2,3-dimethylenenorbornene (**34**) as simpler prototypes. These calculations, in combination with appropriate PE data, clearly indicate the π MO's in both compounds to reside above the σ MO's. More importantly, while the HOMO (π_A) of **33** and **34** is seen not to interact significantly with the σ framework, the π_S butadiene orbital admixes substantially, with the result that the terminal π lobes experience a disrotatory tilt which enhances electron density syn to the methano bridge ($S \neq 0$). Also, the π orbital associated with the central atoms of the butadiene unit rotate in the opposite direction as shown in Figure 1. As a direct result of this rotation, addition of a dienophile anti to the methano bridge can be predicted since the antibonding interaction between π_S of the butadiene moiety and the dienophile HOMO is considerably smaller for endo attack. This feature is indicated schematically in Figure 2.

The notable rotation of the π lobes, which arises because of a strong interaction between the semilocalized pure π_S orbital and a precanonical σ orbital[19] of the same symmetry, has also been observed computationally for **1** and **2**. Theory predicts a substantial reduction in stereoselectivity for **3**. These points will be elaborated upon in the full paper.[20]

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(20) The authors are grateful to the National Cancer Institute (CA-12115), Deutsche Forschungsgemeinschaft, and Fonds der Chemischen Industrie for financial support.

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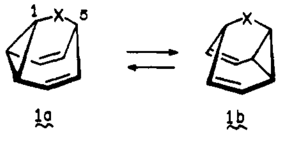
Optical Activity Associated with a Highly Fluxional Molecule. Absolute Configuration and Chiroptical Properties of 2(4)-Methylsemibullvalene

Sir:

Rigid constraint of a *cis*-divinylcyclopropane system into a folded conformation as in **1** results in appreciable canting of



1a **1b**

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