π-Facial Stereoselectivity: Rates and Stereoselectivities of Cycloadditions of Hexachlorocyclopentadiene to 7-Substituted Norbornadienes, and Photoelectron Spectral and Molecular Orbital Computational Investigations of Norbornadienes

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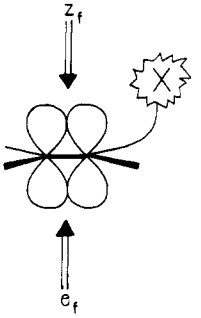
Abstract: The partial rate factors for the Diels–Alder cycloadditions of hexachlorocyclopentadiene to 7-substituted norbornadienes in the four possible modes were measured. Syn-endo and anti-endo rates are essentially identical and decrease slightly as the effective electronegativity of the 7-substituent increases. The rates of the anti-exo cycloadditions decrease more rapidly in the same direction. Only the 7-*tert*-butoxy substituent gives significant acceleration of syn-endo attack. Both the ionization potentials (from photoelectron spectroscopy) of the π orbitals of norbornadienes and the rates and stereoselectivities of the cycloadditions are related to the effective electronegativities of the 7-substituents. Ab initio STO-3G calculations indicate that 7-substituents cause moderate shifts of the HOMO onto one of the norbornadiene double bonds but that reorientation of the directions in which the π bonds point in space is also significantly influenced by these substituents. The ease of various distortions of the olefinic hydrogens out of plane, and perhaps alkene planarity itself, are influenced by the 7-substituents. A model for the influence of the 7-substituents on the π orbitals of norbornadiene, and the stereochemistry of attack, is proposed which differs significantly from previous models but only partially accounts for π-facial stereoselectivity in these systems.

Introduction

When the two faces of a π bond are nonequivalent, as in the generalized system shown below, attack of a reagent may occur on the same side as the perturbing substituent or away from this substituent. We define the former as z_f stereoselectivity (where z implies attack near the out-of-plane group of highest Cahn–Ingold–Prelog (C–I–P) priority and the subscript f denotes facial stereoselectivity)[2] and the latter as e_f stereoselectivity (where e denotes stereoselective attack on the face of the π bond away from the out-of-plane substituent of highest C–I–P priority).



Facial stereoselectivity is frequently observed. Recent examples include S_N2' reactions,[3] additions and cycloadditions to alkenes (see below) and electrophilic attack on unsymmetrical 7-methylenenorbornadienes.[4] Related π-facial stereoselectivity on carbonyl compounds is well documented.[7]

Several hypotheses have been advanced to explain specific examples of this type of facial stereoselectivity.[4-9] Most of these hypotheses either are too specific to be of general utility, or lack quantitative theoretical support. Frequently, there are insufficient data on both the rates and stereoselectivities of these types of reactions with which to test the theories.

In an attempt to remedy this situation for one class of molecules, we report here experimental data and stereoselectivity data for hexachlorocyclopentadiene cycloadditions to 7-substituted norbornadienes. Photoelectron spectra of the norbornadienes and ab initio molecular orbital calculations on model 7-substituted norbornadienes were also carried out in an attempt to confirm, or to develop, a viable electronic theory to explain the data. While we are unable to offer a complete explanation of variations observed in facial selectivity, it has been possible to understand the decrease in anti-exo attack with increased electronegativity of the 7-substituent. Furthermore, 7-*tert*-butoxynorbornadiene has been shown to be anomalous rather than the prototypical case.

Hexachlorocyclopentadiene Cycloadditions to Norbornadienes

The series of 7-substituted norbornadienes (**1a–j**) studied here can undergo cycloadditions with dienes to give four stereoisomeric adducts, arising from syn or anti attack on the exo or endo face of norbornadiene. While syn-exo attack is prevented in most cases by steric hindrance, the other three modes of attack should be influenced electronically but not sterically. Various cycloadditions

(1) (a) University of Maryland. (b) Louisiana State University. (c) On leave from the University of Pavia, Italy.

(2) Earlier, we have suggested the use of z and e to codify regioselectivity: Houk, K. N. In, "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E. Eds.; Academic Press: New York 1977; Vol. 2, pp 229–230. This suggestion now needs modification to the symbols, z_f and e_f, to denote regioselectivity and to differentiate these cases from facial stereoselectivity.

(3) Stork, G.; Kreft, A. F., III *J. Am. Chem. Soc.* **1977**, *99*, 3850, 3851. Overton, K. H.; Oritani, T. *J. Chem. Soc., Chem. Commun.* **1978**, 454. Magid, R. M.; Fruchey, O. S. *J. Am. Chem. Soc.* **1979**, *101*, 2107 and references therein.

(4) Okada, K.; Mukai, T. *J. Am. Chem. Soc.* **1978**, *100*, 6509. Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Böhm, M. *Ibid.* **1978**, *100*, 6510.

(5) Liotta, C. L. *Tetrahedron Lett.* **1975**, 519, 523. Liotta, C. L.; Burgess, E. M., unpublished results. See also: Klein, J. *Tetrahedron* **1974**, *30*, 3349; Eisenstein, O.; Lefour, J.-M.; Klein, J. *Ibid.* **1979**, *35*, 225.

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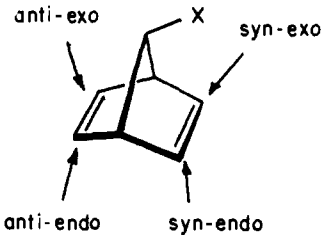

1a, X = H
b, X = *t*-BuO
c, X = $PhCO_2$
d, X = *p*-MeOPh
e, X = *p*-MePh
f, X = Ph
g, X = *p*-FPh
h, X = Cl
i, X = CH_3CO_2
j, X = Me

to 7-substituted norbornadienes have been reported in the literature, and some relevant cases are sumarized in Table I.[10-19] Electrophilic species prefer to attack exo on norbornadiene itself, but such species attack syn-endo on 7-oxygenated norbornadienes. Carbenes give both 1,2-endo and 1,4-endo cycloaddition.[18,19] Nucleophilic species, such as diazoalkanes, prefer anti-endo attack.

In spite of these many investigations of the stereochemistry of cycloadditions to 7-substituted norbornadienes, the only quantitative rate data were reported by Battiste and co-workers, who measured the overall rates and partial rate factors for hexachlorocyclopentadiene (HCCP) cycloadditions to norbornadiene (**1a**), 7-*tert*-butoxynorbornadiene (**1b**), and 7-(benzoyloxy)norbornadiene (**1c**).[10] These authors assumed that attack at all positions of 7-*tert*-butoxynorbornadiene would be slowed down to approximately the same extent by the inductive electron-withdrawing effects of these substituents and that once a correction for this effect was made, syn-endo and anti-endo attacks were accelerated 65–90-fold, and 30–45 fold, respectively.

This apparently dramatic kinetic effect spurred us to assess further the magnitude of these steric, inductive, and through-space electronic effects. Our approach was to synthesize a series of 7-arylnorbornadienes (**1d–g**) carrying para substituents. These compounds were attractive since steric effects in the transition states for syn-endo addition should be identical, and there should be little difference in inductive effects based on the similarity of the group electronegativities[20] for these substituents (Table II).

The overall rate constants for HCCP cycloadditions were measured by NMR or GC methods, and product ratios were determined in order to calculate partial rate factors (relative to the corresponding position in norbornadiene) for attack at the various positions. The details about product identifications and rate measurements are given in the Experimental Section, and the results are listed in Table II.

Figure 1 is a plot of the log of the partial rate factor for each of the three processes vs. the substituent group electronegativity.[20,42] There is a reasonable correlation of reactivity for each of the three addition processes with electronegativity of the 7-substituent. As the substituent electronegativity increases, the rate of anti-exo attack decreases rapidly, whereas the rates of syn or anti-endo attack are decreased very slightly. The total change in partial rate factors for anti-endo and syn-endo cycloaddition over the series **1a–h** is 3.6 and 5.2, respectively, whereas the anti-exo rates change

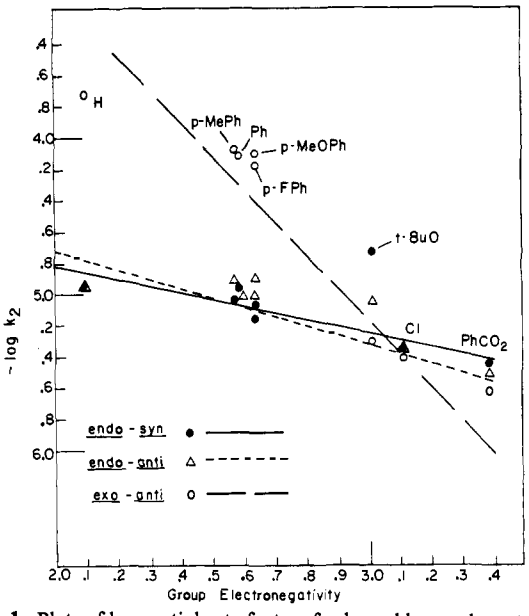

Figure 1. Plots of log partial rate factors for hexachlorocyclopentadiene cycloadditions vs. the Huheey group electronegativity[20] of the 7-substituent.

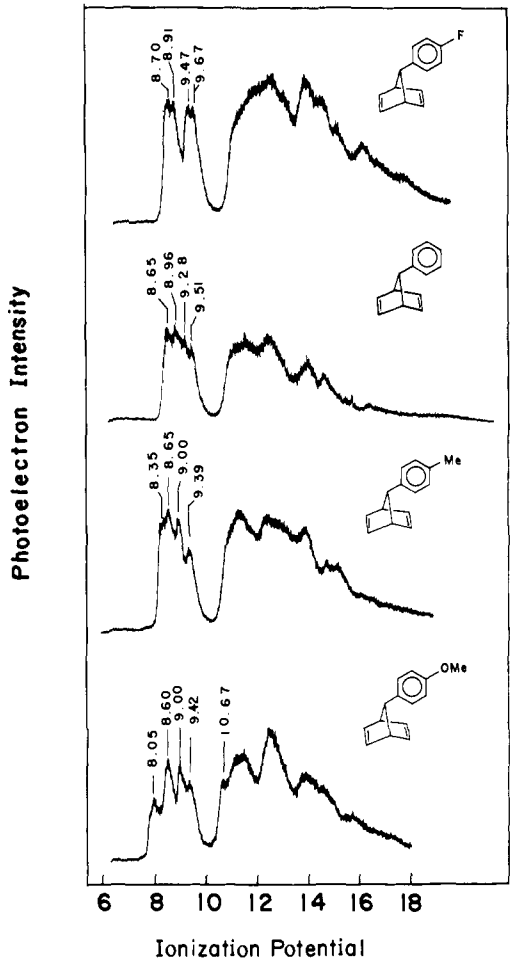

Figure 2. Photoelectron spectra and IPs (±0.06 eV) of 7-arylnorbornadienes.

by a factor of 84.5. Only the 7-*tert*-butoxy derivative (**1b**) significantly deviates from this correlation. For this compound, these deviations correspond to a 3.4-fold acceleration of syn-endo addition, a 1.6-fold acceleration for anti-endo addition and deceleration by a factor of 2 for anti-exo addition. Although there is a small activation of the syn double bond by the *tert*-butoxy

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(20) Huheey, J. E. *J. Org. Chem.* **1966**, *31*, 2365. Watts, J. C. Ph.D. Thesis, University of Maryland, 1971.

Table I. Product Ratios (Relative to Anti-Exo) Reported for Cycloadditions to Norbornadiene and 7-Substituted Norbornadienes

X	cycloaddend	anti-exo	anti-endo	1,4-endo	syn-endo	syn-exo	ref
H	C_5Cl_6[a]	1.0	0.06		0.06	1.0	10
Me	C_5Cl_6	1.0	0.10		0.05 (?)		10
$OCOCH_3$	C_5Cl_6	1.0	1.1		1.9		11
OCOPh	C_5Cl_6	1.0	1.5		1.7		10
O-*t*-Bu	C_5Cl_6	1.0 (1.0)	1.4 (1.8)		3.8 (3.9)		12 (11)
O-*t*-Bu	$C_5Cl_4(OMe)_2$[b]	1.0	1.8		3.2		12
O-*t*-Bu	$C_5Cl_4(OCH_2CH_2O)$[c]	1.0	2.0		3.4		12
O-*t*-Bu	phencyclone[d]	1.0	3.5		10.3		12
H	PhN_3	1.0	0.1		0.1	1.0	13
H	Ph_2CN_2	1.0				1.0	14
O-*t*-Bu	Ph_2CN_2	1.0	0.9		1.0	0.07	15
Cl	Ph_2CN_2	1.0	2.2		0.6		16
Cl	CH_2N_2		1.0				17
Cl	CH_3CHN_2		1.0				17
H	CF_2	1.0	0.1–0.2	1.2	0.1–0.2	1.0	18
Me	CF_2	1.0	0.1	1.9	0.1		18
H	CFCl	1.0	0.3	0.7	0.3	1.0	18
H	CCl_2	1.0	0.1	0.3	0.1	1.0	19[a]
O-*t*-Bu	CCl_2	1.0	0.3	1.2	1.5		19[a]
O-*t*-Bu	CBr_2	1.0	0.5–0.6		0.5–0.6	1.0	19[a]
H	CBr_2	1.0		0.5	2.5		19[a]
H	PhCNO	1.0	1.0		0.1	0.1	19[b]

[a] Hexachlorocyclopentadiene. [b] 5,5-Dimethoxytetrachlorocyclopentadiene. [c] Tetrachlorocyclopentadienone ethylene ketal. [d] The structure for phencyclone is

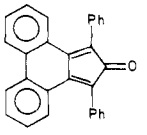

Table II. Rates and Partial Rate Factors for Hexachlorocyclopentadiene Cycloadditions to Norbornadienes

norbornadiene	overall rate 10^5k_2, s^{-1}	partial rate factors: anti-endo (2)	partial rate factors: syn-endo (3)	partial rate factors: anti-exo (4)	substituent group electronegativity[b]
1a	39.8[a]	1[a] (1.11×10^{-5} s^{-1})	1[a]	16.9[a] (1.89×10^{-4} s^{-1})	2.1
1b	3.17[a]	0.78[a]	1.67[a]	0.42[a]	3.02
1c	0.88[a]	0.28[a]	0.32[a]	0.20[a]	3.39
1d	10.1	1.13	0.74	7.23	2.64
1e	10.3	1.09	0.83	7.37	2.58
1f	9.85	0.85	0.97	7.05	2.59
1g	8.26	0.86	0.63	5.95	2.64
1h	1.32	0.40	0.40	0.35	3.11

[a] Data taken from Battiste et al.[10] [b] Pauling electronegativities (Huheey, J. E. *J. Org. Chem.* 1966, *31*, 2365; Watts, J. C. Ph.D. Thesis, University of Maryland, 1971).

substituent, this is not a general phenomenon and is, moreover, a small kinetic effect rather than the striking effect previously suggested.[10]

Photoelectron Spectra of 7-Substituted Norbornadienes

The photoelectron spectra of eight 7-substituted norbornadienes are shown in Figures 2 and 3; the assignments and correlations between IPs of these compounds are given in Figures 4 and 5. The photoelectron spectrum of norbornadiene represents a classic case of through-space coupling.[21] Two π-ionization potentials (IPs) at 8.69 and 9.55 eV arise from the antibonding combination of the π orbitals, π_-, and the bonding combination, π_+, respectively.[21]

Each of the 7-arylnorbornadienes has four resolved IPs in the 8–10-eV region, corresponding to the two norbornadiene and the two high-lying aromatic IPs. Because there are no distinguishing vibrational characteristics in the various bands, assignments are based on correlations with IPs of model compounds. These correlations are shown in Figure 4. The photoelectron spectra of cumene, *p*-methylcumene, and *p*-methoxycumene were measured here,[22] while the IPs of *p*-fluorocumene were estimated from

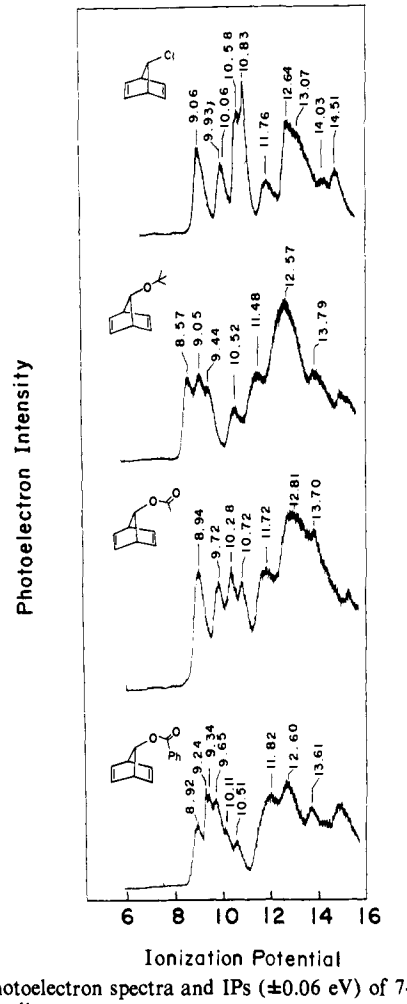

Figure 3. Photoelectron spectra and IPs (±0.06 eV) of 7-chloro- and 7-oxynorbornadienes.

(21) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745. Hoffmann, R.; Heilbronner, E.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 706.

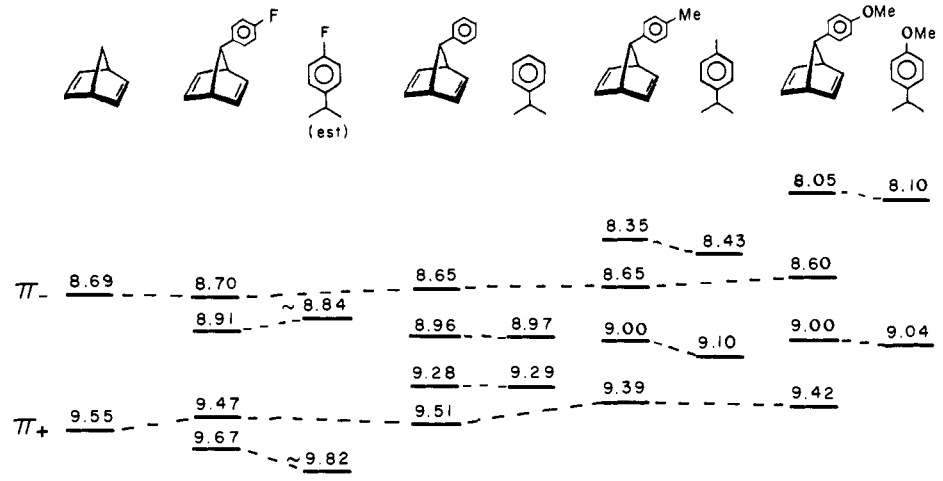

Figure 4. Assignments of, and correlations between, IPs of 7-arylnorbornadienes and models.

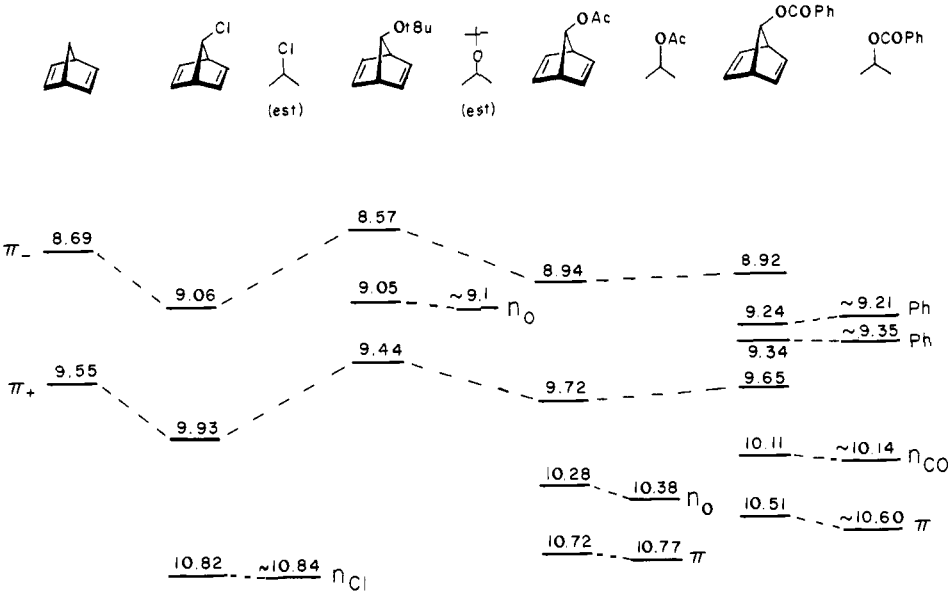

Figure 5. Assignments of, and correlations between, IPs of 7-chloro- and 7-oxynorbornadienes and models.

the IPs of fluorobenzene (9.11 and 9.82 eV),[23] assuming that a para isopropyl substituent lowers the first IP by 0.27 eV, as it does in benzene. Except for the para fluoro compound, there is almost no difference between the IPs of the 7-arylnorbornadienes and the IPs of the models. The apparent discrepancy with the fluoro compound is probably due to the broadness of the bands in fluorobenzene,[23] which makes assignments of vertical IPs difficult.

The spectra of the chloro, alkoxy, or acyloxy substituted compounds are shown in Figure 3. Assignments were made by using appropriate model compounds shown in Figure 5. Ethyl chloride and propyl chloride have chlorine spin–orbit split lone-pair IPs centered at 10.88 and 11.01 eV, respectively.[24] For isopropyl chloride we estimate the slightly lower IP of about 10.84 eV. Photoionization values of 10.98, 10.82, and 10.78 eV have been measured for ethyl, propyl, and isopropyl chlorides.[25] In 7-chloronorbornadiene, the chlorine lone-pair IP is unchanged from the estimated value for isopropyl chloride, while the norbornadiene π orbitals have both been stabilized by about 0.4 eV.

The photoelectron spectrum of 7-*tert*-butoxynorbornadiene was reported earlier at 8.55, 9.03, and 9.40 eV,[12] in good agreement with the values reported here. The first and third bands are shifted by about 0.1 eV to lower IP than the π IPs of norbornadiene. The second IP (9.05 eV) is very close to that (8.94 or 9.16 eV)[26] measured for di-*tert*-butyl ether. We have estimated the IP of isopropyl *tert*-butyl ether as about 9.1 eV on the basis of the somewhat higher IPs of isopropyl compounds than *tert*-butyl analogues.[26]

Isopropyl acetate has IPs due to the carbonyl lone pair and the highest occupied π orbital of 10.38 and 10.77 eV,[27] very close to the third and fourth IPs of 7-acetoxynorbornadiene. The alkene π IPs of this compound are both raised by about 0.2 eV from their positions in norbornadiene.

Although the PES of isopropyl benzoate is unavailable, methyl benzoate has IPs of 9.31 and 9.4–9.5 eV for the aromatic π orbitals and 10.24 eV for the carbonyl lone pair.[28] In other esters the CO π orbitals are at about 10.6–10.8 eV.[28] We assume that the isopropyl analogue will have IPs about 0.1 eV lower than these. Using these values to locate the benzoate IPs in the norbornadiene derivative, we can assign the 8.92 and 9.65-eV IPs to the norbornadiene π orbital IPs. These are essentially identical with those of 7-acetoxynorbornadiene.

The differences in energy between the π_+ and π_- IPs are remarkably constant in this whole series, ranging from 0.73 to 0.87 eV. The difference of 0.14 eV between the largest and smallest splits is close to the experimental error (~0.08 eV) in measurement of this split. Thus, both π_+ and π_- IPs are changed to the

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(28) Meeks, J.; McGlynn, S. P., unpublished results.

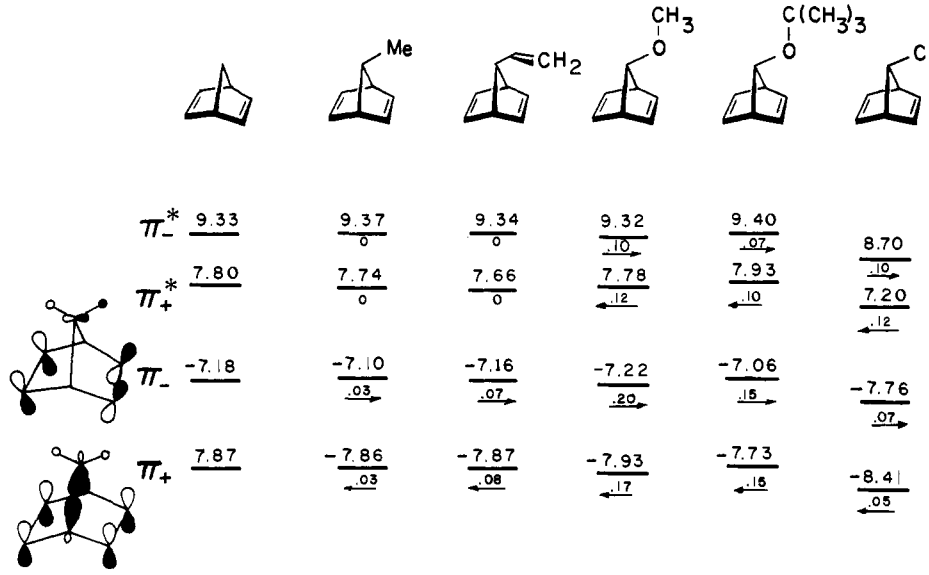

Figure 6. Summary of π orbitals from STO-3G calculations on substituted norbornadienes. Orbital energies are in eV. The numbers and arrows represent the shift in orbital density.

same extent by the 7-substituent. None of the aryl substituents have any significant influence on the norbornadiene IPs, while the electronegative chlorine, *tert*-butoxy, and acetoxy substituents cause an appreciable increase in π-ionization potentials. The two norbornadiene IPs stay essentially constant along the aryl-substituted series; while the aromatic π ionizations vary considerably across the series of molecules, there is little or no effect on the norbornadiene π IPs.

There is not a good correlation of increasing IP with increasing group electronegativity of the substituent. That is, all of the 7-aryl compounds have essentially the same IP as the parent, in spite of the greater electronegativity of aryl than H. Chloro and benzoyloxy have the largest group electronegativities and also the highest IPs, but the *tert*-butoxy, which has an electronegativity nearly the same as that of Cl, has the lowest IP in the series.

Molecular Orbital Calculations on Norbornadienes

Astin and MacKenzie have reported MINDO/2 calculations on 7-methoxynorbornadiene as a model for 7-*tert*-butoxynorbornadiene.[12] These calculations indicated a very small split between the two π orbitals, with the HOMO essentially localized on the syn double bond. This appeared to offer a rationale for the preferred attack of electron-deficient dienes on this double bond. Unfortunately, this is an artifact of MINDO calculations, which underestimate through-space interactions.[29] Indeed, MINDO/3 also indicates that the π_+ and π_- orbitals of norbornadiene and derivatives are nearly degenerate.

Because MINDO/3[30] calculations do not correctly predict IPs of norbornadienes or other homoconjugated systems,[31] we used ab initio calculations using the STO-3G basis set[32] for calculations of orbital energies and shapes of suitable models. The results are summarized in Figure 6. In each case, the MINDO/3 optimized geometry for norbornadiene was used, and standard substituents were attached without further changes in geometry. The only exception to this was for the 7-*tert*-butoxy derivative, which was reoptimized by MINDO/3. Figure 6 shows the filled orbitals for the parent system, but since the vacant orbitals are essentially localized π_+* and π_-* orbitals with little σ contributions, these are not drawn.

Because we were interested in the possible drift of electron density in the π orbitals away from the equal distribution in norbornadiene, an index to measure this was devised. The numbers under each level represent the change in density distribution away from a symmetrical one measured as: $\sum C_a^2 - \sum C_b^2$, where C_a's are all the coefficients on double bond a and C_b's are all the coefficients on double bond b.

In every case, the polarization alternates in direction upon progressing from the lowest to the highest π orbital. Perhaps surprisingly, the *tert*-butoxy compound is not unusual in its polarizing effect, with the magnitude of polarization here being essentially the same as that due to several other substituents. The same polarization is observed, if only weakly, even when there is essentially no change in IP, in contrast to previous explanations of polarization by substituent oxygen lone pairs.[8,12]

There are several mechanisms by which a 7-substituent might influence the norbornadiene π orbitals. First, a 7-substituent might distort the geometry of the norbornadiene skeleton away from C_{2v} and might interact directly through-space with the neighboring double bond. This interaction could involve either orbital overlap[5] or a field effect. The substituent might act as an electron-donor substituent, due to overlap of lone pair or π orbitals on the substituent with the neighboring π bond, or as an acceptor, if low-lying vacant orbitals such as σ^*_{CX} orbitals overlap with the syn, or with the anti,[17] π bond. A substituent may also act as an electron-donor through a field effect, since substitution of any group for hydrogen should cause a region of negative charge to be introduced over the syn π bond. Such a negatively charged region would have qualitatively the same influence on the π orbitals as overlap of a filled orbital of the substituent.[34] Finally, the substituent orbitals could interact with the π orbitals through bonds rather than through space. For example, the ability of the C_1–C_7–C_4 bridge of norbornadiene to hyperconjugate with the two π orbitals could be altered by a 7-substituent. Alternatively, the 7-substituent could interact differently with the bonds connecting the bridgehead to the sp^2 carbons, and this could modify the potential at one π bond differently from that of the other.

Returning to the calculated polarizations shown in Figure 6, these are in the direction expected to be caused by a donor orbital, or a partial negative charge, on the syn side or by an acceptor orbital, or a partial positive charge, on the anti side of the norbornadiene. That is, a donor or a negative charge causes high-lying orbitals to be mixed into lower lying orbitals in a minus fashion at the site of perturbation and vice versa, while an acceptor or a positive charge has an opposite effect.[3,33,34] Inspection of the

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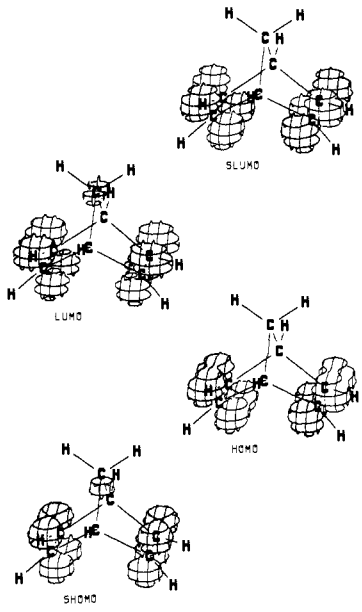

Figure 7. Orbital contour plots for π orbitals of norbornadiene.[35]

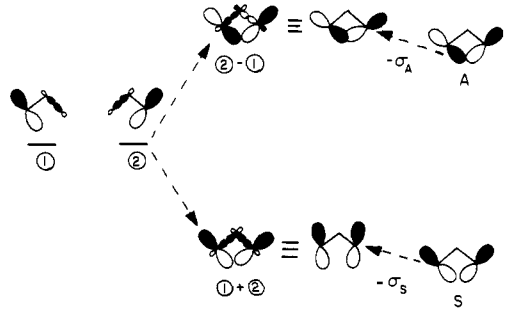

Figure 8. Derivation of the norbornadiene π-orbital "tilting".

orbitals obtained from the STO-3G calculations suggests no clear pattern of substituent mixing, particularly in the LUMOs which remain almost purely localized on carbons 2, 3, 5, and 6. This suggests that the observed polarization occurs through a Coulombic interaction between the partial negative charge on the substituent (as compared to H) and the syn double bond. This mechanism of polarization seems most plausible, since it requires no orbital mixing at all, only a modification of the potential field on the two sides of norbornadiene. The polarization of the π_+ and π_- orbitals thus appears to be a "field effect" rather than an orbital mixing effect.

There is an additional effect which arises from $\pi-\sigma$ mixing in these compounds. As shown in Figure 7,[35] the HOMO and SHOMO of norbornadiene are not merely antibonding and bonding combinations of pure π orbitals, but the p orbitals in the HOMO are tilted in a direction which formally maximizes the antibonding interaction between the π bonds, while the SHOMO is tilted to minimize bonding! This effect is also manifested in the shapes of the two low-lying vacant π^* orbitals, but to a lesser extent.

There are two equivalent ways of rationalizing the opposite "tilting" of the π_+ and π_- orbitals of norbornadiene. Starting from the isolated orbitals before overlap, each of these π orbitals overlaps with a lower energy σ_{CC} orbital situated across the ring. Figure 8 shows the side view of these orbitals, labeled 1 and 2. Each of these is a π orbital mixed in an antibonding fashion with a lower lying σ_{CC} orbital which is situated across the ring. 1 and 2 combine to form a bonding combination, 1 + 2, and an antibonding combination, 2 − 1, shown in Figure 8. These are also drawn in Figure 8 in a representation equivalent to the "Jørgensen plots"[35] given in Figure 7.

(35) Jorgensen, W. L.; Salem, L. "The Organic Chemists' Book of Orbitals"; Academic Press: New York, 1973. We thank Professor Jorgensen for the program used to draw these orbitals.

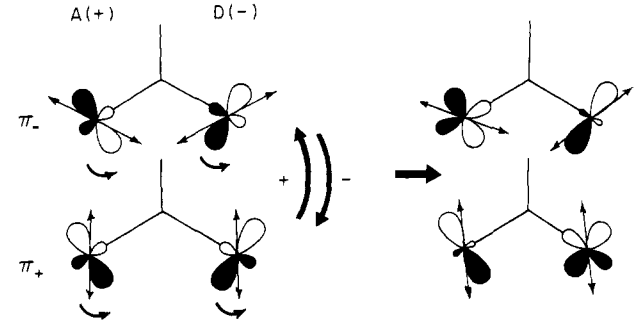

Figure 9. Alteration of "tilt" by mixing of π_+ and π_- orbitals. The arrows indicate the orientation of the resultant p orbitals.

Alternatively, the tilt can be derived, starting with the delocalized π_+ symmetric (S) bonding orbital and the π_- antisymmetric (A) combinations, shown at the far right of Figure 8. The symmetric orbital, S, will mix with a lower lying skeletal σ_S orbital in an antibonding fashion to give the orbital 1 + 2, while the antibonding combination will mix in a lower lying antisymmetric orbital, σ_A, to give 2 − 1. The tilting occurs because each π orbital interacts across the ring with the appropriate σ orbital to a greater extent than it interacts with the adjacent σ orbital.

There is a second type of orbital tilting which barely can be discerned in Figure 7. In the HOMO, the exo lobes of the p orbitals on C_2 and C_3 (and on C_5 and C_6) are tilted toward each other while the endo lobes are tilted away from each other. Exactly the opposite occurs in the SHOMO. This effect is smaller than the previously described tilting, and arises from the same type of $\pi-\sigma$ mixing shown in Figure 8.

These tilting effects should have some influence on the relative rates of attack of reagents on the exo and endo faces of norbornadiene. For example, electrophilic attack should be accompanied by somewhat greater interaction of the electrophile LUMO with the norbornadiene HOMO than with the norbornadiene SHOMO. The overlap of the electrophile LUMO with the norbornadiene will be greatest on the exo face of the molecule, because of this tilting and the unfavorable antibonding interaction on the endo side of norbornadiene.

The polarization of the norbornadiene orbitals by substituents at the 7-position is accompanied by a change in the "tilt" of these orbitals. Figure 9 shows how this occurs. A donor, or negative charge, on the "right-hand side" and/or acceptor, or positive charge, on the "left-hand side" of norbornadiene causes π_+ to mix into π_- in a plus fashion on the right-hand side and π_- into π_+ in a negative fashion on the right side. The resulting "tilt" alteration caused by substituents is shown in Figure 9.

Relationships between Electronic Structures and Rates of Cycloadditions of Norbornadienes

At this stage, it would be satisfying to claim that the partial rate factors for cycloaddition correlated well with the ionization potentials of the 7-substituted norbornadienes. Unfortunately, as shown in Figure 10, this is not the case. There may be a fundamental reason for the lack of good correlation, or the difficulty may lie in the accurate determination of ionization potentials for such molecules where changes in IPs are very small. Generally, ionization potentials are quoted to ±0.05 eV, but for broad bands, difficulties in obtaining a reproducible maximum may make vertical IPs uncertain to ±0.1 eV. Since the entire range of IPs is only 0.5 eV in this series, the lack of correlation may well simply be a reflection of uncertainty in the experimental data.

For that reason, we return to the plot of reactivities vs. group electronegativities (Figure 1), which provides a consistent pattern of reactivity, except for the 7-*tert*-butoxy compound.

Starting with norbornadiene, exo attack will be favored upon interaction of the HOMO with the electrophilic (e.g., C_5Cl_6) LUMO because of the extension of the π orbitals away from the

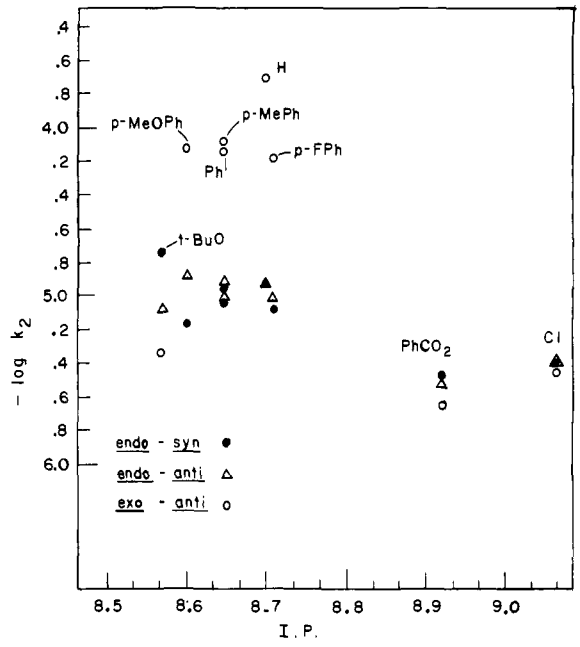

Figure 10. Plot of the log of the partial rate factors for hexachlorocyclopentadiene cycloadditions to 7-substituted norbornadienes vs. the vertical IP of the π_- orbital. Symbols have the same meaning as in Figure 1.

CH_2 group. Attachment of an electronegative substituent at C-7 makes the entire system less electron-rich and decreases the rate of attack at any position. The polarization of the HOMO away from the anti double bond diminishes the rate of anti attack faster than syn attack, as is clearly observed for anti–exo attack and nicely explains this major kinetic effect. However, experimentally, the rates of anti-endo and syn-endo attack remain essentially constant, whereas both the polarization of the HOMO toward the syn double bond and the HOMO "tilting" in a direction such as to decrease the accessibility of the anti-endo p orbitals and increase the accessibility of the syn-endo p orbitals would suggest that anti-endo attack should become less favorable and syn-endo more favorable. In fact, both decrease in rate to essentially the same extent, which we cannot readily rationalize.

The only molecule which does fit the expectation based on changes in orbital shapes is the 7-*tert*-butoxy compound. That is, the polarization trends deduced before should eventually cause activation of the syn double bond. Since syn-exo attack is sterically blocked towards hexachlorocyclopentadiene, only endo attack is observed. However, smaller electrophilic reagents do attack syn-exo[36] as would be expected by the polarization occurring in this system. If a stronger polarizer than *tert*-butoxy could be found, the syn-endo addition should be additionally favored over anti attack.

The polarization effects described here are very small, indeed. However, in model calculations, we have found that the 7-substituent not only influences the polarization of the orbitals in the isolated species but also affects the ease of various distortions. For example, in unsubstituted norbornadiene, the energy required to bend both H_2 and H_3 upward away from planarity by 10° is 2.5 kcal/mol by STO-3G; the energy required for a 10° downward bend is 1.0 kcal/mol. In fact, these calculations suggest that the alkene carbons and four attached substituents are nonplanar. Whether this is indeed the case will require full optimization of the norbornadiene skeleton. The easier downward bending is compatible with the easier attack of electrophilic reagents from an exo direction, since the pyramidalization of C_2 and C_3 is easier upon attack from the exo direction. In 7-fluoro- or 7-hydroxynorbornadiene, the downward H bending (and thus attack of a reagent from the exo direction) is more difficult, while the upward H bending is easier than in norbornadiene. This should cause the preference for exo attack to diminish. The influence of the 7-fluoro or 7-hydroxy upon bending is greater for the hydrogens attached to the anti double bond than for the hydrogens attached to the syn double bond. For example, in 7-fluoronorbornadiene, the energy for bending away from planarity is as follows: syn-up, 2.3 kcal/mol; syn-down, 1.2 kcal/mol; anti-up, 2.2 kcal/mol; anti-down, 1.3 kcal/mol.

We hypothesize that effects of this kind, which alter the ease of reactant distortion and thus the ease of reaching a particular transition state, will prove to be of greater significance than polarization of undistorted reactant orbitals in influencing π-facial stereoselectivity. A fuller exploration of these effects and a determination of the source of them are the subjects of continuing investigations.

Comparisons to Previous Hypotheses of Facial Stereoselectivity

We have suggested here that substituents at the 7-position of norbornadiene influence the shapes of the π orbitals primarily by a through-space electrostatic or field effect and that the ease of attack of reagents in various positions is most likely influenced more by the ease of various distortions than by the polarization of isolated norbornadiene orbitals. Both of these hypotheses differ substantially from previous suggestions.

Alston and Ottenbrite reported CNDO/2 calculations on a number of 7-substituted norbornadienes[8] and found that 7-F, -Cl, -OH, and $-O_2CH$ caused the same type of polarization found here. However, the model used to explain this polarization involves mixing of donor orbitals of the substituents with the norbornadiene orbital, an effect which should raise the HOMO energy. Our photoelectron spectra and calculations indicate that these types of substituents lower the HOMO energies. Astin and MacKenzie[12] and Paddon-Row et al.[9] have invoked similar orbital mixing effects to explain related phenomena.

Franck-Neumann and Sedrati suggested that the highly preferred anti-endo attack of diazoalkanes on 7-halonorbornadienes arises from the interaction of the anti π-bond with the σ^*_{CX} bond, which lowers the LUMO of the anti orbital.[17] While our calculations do indicate polarization of the LUMO toward the anti double bond and "tilting" of this orbital in such a way so as to make attack on the anti-endo orbital more accessible, the mixing of σ^*_{CCl} into the norbornadiene LUMO is not evident in the STO-3G calculations.

Byrne et al.[11] proposed that 7-substituents force C_7 and its substituents away from the syn double bond, causing steric hindrance to anti-exo attack. Unfortunately, our calculations do not have any direct bearing on this suggestion, although the MINDO/3 optimized 7-*tert*-butoxynorbornadiene geometry does have C_7 0.06 Å closer to the anti carbons than the syn carbons. It is not clear, however, how this would influence the relative rates of syn-endo and anti-endo attack. Other cases of facial stereoselectivity in cycloadditions have been rationalized by considerations of secondary orbital interactions between the cycloaddend and substituent orbitals.[37] This is not directly relevant to the case at hand, since no direct secondary orbital interactions between HCCP and the 7-substituents are possible for anti or syn-endo attack.

On a more general level, Liotta considered the direction of addition of nucleophiles and electrophiles to facially unsymmetrical cyclohexene derivatives.[5] He postulated that the π frontier molecular orbitals of a molecule distort by admixture of s orbital character in such a fashion as to maximize bonding and minimize antibonding.[5] For norbornadiene itself, however, STO-3G calculations indicate that s orbital contributions to the HOMO and LUMO are miniscule and the "tilt" of the HOMO and LUMO, which arises from π–σ mixing, maximizes antibonding in the HOMO and minimizes bonding in the LUMO. Nevertheless, the

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(37) Franck-Neumann, M. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 210. Bianchi, G.; DeMicheli, C.; Gamba, A.; Gandolfi, R. *J. Chem. Soc., Perkin Trans. 1* **1974**, 137. DeMicheli, C.; Gamba-Invernizzi, A.; Gandolfi, R. *Tetrahedron Lett.* **1975**, 2493. DeMicheli, C.; Gamba-Invernizzi, A.; Gandolfi, R.; Scevola, L. *J. Chem. Soc., Chem. Commun.* **1976**, 246.

Liotta "orbital distortion" may well be parallel to the direction of easiest distortion of the molecules.

Inagaki and Fukui explicitly treated the preference for exo attack shown by electrophiles in reactions with norbornene and related hydrocarbons.[6] Electron density plots show that the electron density due to the π orbital is greater on the exo face than on the endo face. This behavior was rationalized by involving the donor character of the C_1–C_7–C_4 bridge σ orbitals. A donor orbital will cause a lower energy orbital (in this case the C_2–C_3 σ orbital) to mix into a higher energy orbital in a positive fashion at the site of perturbation (here the exo face of norbornene). However, the STO-3G calculations we have performed on norbornadiene suggest no significant s orbital contribution to the π orbitals for norbornadiene; for this molecule at least, the greater exo electron density must arise from the tilting described earlier, which arises from p–σ contributions to the HOMO.

Conclusion

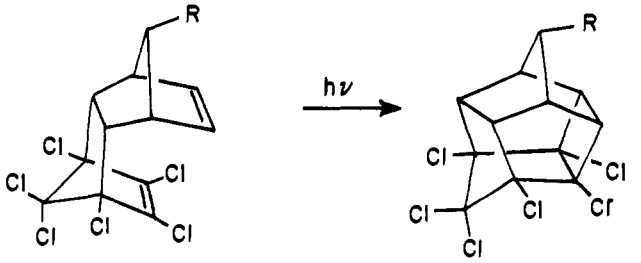
The patterns of substituent polarization of the π orbitals of 7-substituted norbornadienes agree with those of Alston and Ottenbrite. The origin of these polarizations and "tilting" is suggested to be predominantly a field effect rather than the more usually invoked through-space orbital mixing effect. The many hypotheses used to rationalize these and related phenomena are all deficient in one or another respect, and a comprehensive theory of facial stereoselectivity is still to be found. In the present case, the deactivation of the exo-anti attack by electronegative substituents has been satisfactorily rationalized, but the more subtle rate effects of syn-endo and anti-endo attack are not fully understood. Studies in progress on the influence of substituents on the ease of various molecular distortions should provide further understanding of cycloadditions to norbornadienes.[38]

Experimental Section

Elemental analyses were carried out by Dr. Franz Kasler. Acceptable analyses, within 0.4% of calculated, were obtained on all new adducts. NMR spectra were obtained on Varian XL-100 or EM-360 spectrometer and IR spectra on either Beckman IR-8 or Perkin-Elmer 281 spectrometer.

Photoelectron spectra were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer, using xenon and argon as calibrants. Resolution was 20–25 meV. The vertical ionization potentials are taken, for simplicity, as the maxima of each band. Reported IPs are each the average of at least five determinations and are accurate to ±0.05 eV.

Adduct Structure Proofs. Structure proofs were based on the NMR spectra of the adducts, by using criteria previously developed for the HCCP adducts of 7-acetoxynorbornadiene (**1c**)[11] and norbornadiene,[39] which show a long-range coupling between the olefinic protons and the *anti*-7-methine proton. Thus the olefinic protons in the compounds assigned the exo-anti (**4**) and endo-anti (**2**) structures appear as multiplets (apparent sextuplets) whereas the olefinic protons in the endo-syn (**3**) adduct appear as a triplet since the long-range coupling with the anti-7-proton is absent in this case. The endo-anti and exo-anti adducts are easily differentiated in that the 5,6-protons appear as a sharp singlet in the latter compound. Furthermore, irradiation of the endo-anti adducts resulted in formation of the cage products shown below, whose NMR spectra were characterized by a broad absorption from δ 2.8–3.8 and the absence of any olefinic proton resonances. NMR spectra are summarized in Table IV.



Product distributions were determined by integration of the olefinic region of the NMR spectra of the original reaction mixtures. Although the olefinic proton signals of the three isomers were not completely resolved in $CDCl_3$ solution, spectra obtained in cyclohexane gave sufficient separation to allow integration. The results are shown in Tables II and III.

Table III. Product Distributions[a] from HCCP Additions (%)

starting material	% of adduct formed: endo-anti (2)	endo-syn (3)	exo-anti (4)
1a[b]	2.8[c]	2.8[c]	47.2[c]
1b[b]	27.4	57.7	14.9
1c[b]	35.4	40.3	24.4
1d	12.4	8.1	79.5
1e	11.7	8.9	79.4
1f	9.6	10.9	79.5
1g	11.6	8.4	80.0
1h	33.6	36.9	29.5
1i[b]	28	47	25
1j[b]	9	4	87

[a] Product distributions determined by NMR on reaction mixtures. [b] Results from ref 10. [c] Results statistically corrected for number of equivalent positions available.

Determination of Reaction Rates. NMR Method. In each of nine NMR tubes, 400 μL of a 20:1 stock solution of HCCP/norbornadiene was placed. The tubes were immersed in a 120 ± 0.1° oil bath, the tubes were sequentially removed and cooled, and an NMR spectrum was obtained for each time. Essentially identical results were obtained by using a single NMR tube and obtaining a spectrum at regular intervals.

GLC Method. Stock solutions were prepared, consisting of 20:2:1 volume ratios of HCCP/norbornadiene/standard. Heptadecane was used as standard for **1d** runs and 2-methoxynaphthalene was used for **1e** runs. A 10-μL portion of the stock solution was sealed in each of several capillary tubes which were then immersed in a 120 ± 0.1 °C oil bath. Tubes were removed at various times and cooled in a dry ice/acetone bath. Samples were analyzed on a Varian Aerograph, Series 1200, flame ionization detector gas chromatograph using a 5-ft, 3% SE-30, on Varaport 30 column. Column temperatures were 107 °C for **1e** runs and 140 °C for **1d** runs. Average integrations from two injections were used in calculations.

Pseudo-first-order rate constants were calculated by using a standard regression analysis. Correlation coefficients were 0.99 for all runs, and NMR and GLC determinations gave essentially identical results.

Preparations of 7-Arylnorbornadienes. The syntheses were essentially identical with that previously reported for 7-phenylbicyclo[2.2.1]heptadiene.[40,41] Thus, the Grignard reagent prepared from 8.3 g (0.044 mol) of *p*-bromoanisole and 1.1 g (0.044 mol) of magnesium was treated, in benzene, with 4.0 g (0.22 mol) of 7-*tert*-butoxybicyclo[2.2.1]heptadiene (**1b**). After reflux for 3 days, workup of the reaction afforded 2.0 g (55%) of 7-(4-methoxyphenyl)bicyclo[2.2.1]heptadiene (**1d**): bp 119–120 °C (2mm); IR (CCl_4) 3070, 2990, 2910, 2840, 1600, 1510, 1250, 1180, 1045, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0–6.3 (m, 8 H), 3.6 (broad s, 6 H). Anal. Calcd: C, H.

Treatment of the Grignard reagent from 3.0 g (0.12 mol) of magnesium and 20.9 g (0.12 mol) of *p*-bromotoluene with 10.0 g (0.61 mol) of **1b** gave 6.4 g (62%) of 7-(4-methylphenyl)bicyclo[2.2.1]heptadiene (**1e**): bp 104–106 °C (1.7mm); IR ($CDCl_3$) 3080, 3040, 3000, 2990, 1550, 1515, 1330, 1310 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.9 (m, 6H), 6.5 (m, 2 H), 3.8 (m, 3 H), 2.3 (s, 3 H). Anal. Calcd: C, H.

Treatment of the Grignard reagent from 6.0 g (0.25 mol) of magnesium and 40.4 g (0.25 mol) of *p*-bromofluorobenzene with 20.0 g (0.122 mol) of **1b** gave 12.6 g (56%) of 7-(4-fluorophenyl)bicyclo[2.2.1]heptadiene (**1g**): bp 85–88 °C (1.8mm): IR ($CDCl_3$) 3060, 2980, 1600, 1508, 1305, 1230, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.9 (m, 6 H), 6.5 (m, 2 H), 3.7 (m, 3 H). Anal. Calcd: C, H.

HCCP Cycloaddition of 7-(4-Methoxyphenyl)bicyclo[2.2.1]heptadiene (1d). A mixture of 8.0 g (0.040 mol) of **1d** and 15.26 g (0.055 mol) of freshly distilled HCCP was heated at 118–122 °C in a nitrogen atmosphere for 36 h. The reaction mixture was treated with 100 mL of petroleum ether (bp 60–110 °C), and crude product was recrystallized five times from petroleum ether (bp 60–110 °C) to give 2.1 g of pure exo-anti isomer **4d**: mp 98–100 °C; IR (CCl_4) 3020, 2980, 2920, 1600, 1515, 1250, 1185, 1040, 840 cm^{-1}. Anal. Calcd: C, H.

In this and subsequent cases, the mother liquors from the initial crystallizations were chromatographed on 300 g of neutral alumina in a 2.5 × 90-cm column. The column was eluted with ethyl ether/petro-

(38) For an additional phenomenon involving norbornadiene, see: Jean, Y. *Tetrahedron Lett.* **1977**, 2689.
(39) Snyder, E. I.; Franzus, B. *J. Am. Chem. Soc.* **1964**, *86*, 1166.
(40) Story, P. R.; Fahrenholtz, S. R. *J. Org. Chem.* **1963**, *28*, 1716.
(41) Normant, A. *Bull. Soc. Chim. Fr.* **1940**, *7*, 371.

Table IV. NMR Data on HCCP Adducts[a]

compd	proton chemical shifts (δ)				
	1(4)	2(3)	5(6)		other
2d	3.5 (m, 2)	5.8 (m, 2)	~3.3[b]	~3.3[b]	6.8 (m, 4),[c] 3.8 (s, 3)[d]
3d	3.5 (m, 2)	6.15 (m, 2)	~3.3[b]	~3.3[b]	6.9 (m, 4),[c] 3.8 (s, 3)[d]
4d	3.2 (m, 2)	6.10 (m, 2)	2.9 (s, 2)	3.40 (m, 1)	6.8 (m, 4),[c] 3.7 (s, 3)[d]
2e	3.55 (m, 2)	5.85 (m, 2)	~3.35[b]	~3.35[b]	6.9 (m, 4),[c] 2.27 (s, 3)[d]
3e	3.40 (m, 2)	6.15 (m, 2)	~3.23[b]	~3.23[b]	7.1 (m, 4),[c] 2.30 (s, 3)[d]
4e	3.26 (m, 2)	6.10 (m, 2)	2.87 (s, 2)	3.45 (m, 1)	6.9 (m, 4),[c] 2.27 (s, 3)[d]
2f	3.60 (m, 2)	5.9 (m, 2)	~3.4[b]	~3.4[b]	7.1 (m, 5)[c]
3f	3.32 (m, 2)	6.15 (m, 2)	~3.1[b]	~3.1[b]	7.0–7.4 (m, 5)[c,e]
4f	3.30 (m, 2)	6.10 (m, 2)	2.9 (s, 2)	3.50 (m, 1)	7.1 (m, 5)[c]
2g	3.57 (m, 2)	5.86 (m, 2)	~3.35[b]	~3.35[b]	6.9 (m, 4)[c]
3g	3.38 (m, 2)	6.16 (m, 2)	3.18 (m, 2)	3.26 (m, 1)	7.05 (m, 4)[c]
4g	3.25 (m, 2)	6.12 (m, 2)	2.90 (s, 2)	3.44 (m, 1)	6.9 (m, 4)[c]
2h	3.36 (m, 2)	6.02 (m, 2)	3.24 (m, 2)	4.04 (m, 1)	
3h	3.57 (m, 2)	5.91 (m, 2)	2.84 (m, 2)	3.38 (m, 1)	
4h	3.22 (m, 2)	6.34 (m, 2)	2.92 (s, 2)	4.36 (m, 1)	

[a] $CDCl_3$ solution. [b] These peaks overlap. [c] Aromatic proton multiplet. [d] Methyl signal. [e] Spectrum taken on a mixture of 3f and 4f.

leum ether mixtures containing from 1–15% ethyl ether. Middle fractions gave the endo-syn adduct **3d** mixed with exo-anti adduct. Repeated recrystallization of this mixture gave the pure endo-syn isomer **3d**: mp 169–170 °C; IR ($CDCl_3$) 1610, 1513, 1304, 1250, 1180, 1040 cm^{-1}. Anal. Calcd: C, H. Irradiation of an NMR sample with a 254-nm source resulted in the disappearance of the δ 6.15 multiplet.

Late column fractions contained only the endo-anti isomer. Recrystallization gave pure **2d**: mp 160–161 °C; IR ($CDCl_3$) 3020, 2980, 2900, 1600, 1510, 1300, 1180, 1040, 880 cm^{-1}. Anal. Calcd: C, H.

The endo-anti adduct **4d** was irradiated for 3 h with a 254-nm source in 50 mL of 2-propanol. The yield of pure cage product **6d** was 0.090 g (33%): mp 151–153 °C after recrystallization from petroleum ether. Anal. Calcd: C, H.

HCCP Cycloaddition to 7-(4-Methylphenyl)bicyclo[2.2.1]heptadiene (1e). A mixture of 6.6 g (0.031 mol) of **1e** and 11.8 g (0.043 mol) of HCCP was heated at 118–122 °C for 36 h. The reaction mixture was heated at 118–122 °C for 36 h. The reaction mixture was treated with 75 mL of petroleum ether to precipitate the exo-anti product. Five recrystallizations of the solid obtained gave the pure exo-anti adduct **4e**: mp 134–136 °C; IR ($CDCl_3$) 3020, 2980, 2940, 1600, 1520, 1320, 1210, 1180, 1040, 910, 830 cm^{-1}. Anal. Calcd: C, H.

Chromatography and subsequent recrystallization gave the endo-anti adduct **2e**: mp 190–191 °C; IR ($CDCl_3$) 3020, 2980, 2900, 1605, 1510, 1300, 1180, 1065, 1040, 1020, 905, 885 cm^{-1}. Anal. Calcd: C, H.

Irradiation of **2e** (0.157 g) in 30 mL of 2-propanol for 3 h gave 0.085 g (54%) of pure product **6e**, mp 193–196 °C. Anal. Calcd: C, H.

Recrystallization of late column fractions gave the pure endo-syn adduct **3e**: mp 169–170 °C; IR ($CDCl_3$) 2890, 2860, 1610, 1520, 1310, 1190, 1050, 1010 cm^{-1}. Anal. Calcd: C, H.

Irradiation of the NMR sample at 254 nm resulted in the disappearance of the olefinic proton signal at δ 6.15.

HCCP Cycloaddition of 7-Phenylbicyclo[2.2.1]heptadiene (1f). A mixture of 12.2 g (0.073 mol) of **1f** and 27.7 g (0.102 mol) of HCCP was heated at 118–120 °C for 36 h. The reaction mixture was treated with 75 mL of petroleum ether (60–110 °C), and the resulting solid was recrystallized seven times from petroleum ether (60–100 °C) to give 3.4 g of the exo-anti product **4f**: mp 122–124 °C; IR ($CDCl_3$) 3040, 2990, 1600, 1500, 1320, 1210, 1180, 1050, 1040, 1010, 910, 830 cm^{-1}. Anal. Calcd: C, H.

Middle fractions from the chromatography of the mother liquors from recrystallization gave mixtures of exo-anti and endo-syn adducts **4f** and **3f** which resisted further purification. NMR data in Table IV were obtained on a ca. 50:50 mixture of **4f** and **3f**.

Recrystallization of late chromatographic fractions gave the endo-anti adduct **2f**: mp 195–196 °C; IR ($CDCl_3$) 3020, 2990, 1600, 1500, 1305, 1180, 1040, 880 cm^{-1}. Anal. Calcd: C, H.

The endo-anti adduct **2f** (0.112 g) was irradiated for 3 h in 30 mL of 2-propanol. The yield of pure cage product **6f** was 70 mg (62%); mp 195–200 °C. Anal. Calcd: C, H.

HCCP Cycloaddition to 7-(4-Fluorophenyl)-bicyclo[2.2.1]heptadiene (1g). A mixture of 10.4 g (0.056 mol) of **1g** and 21.4 g (0.078 mol) of HCCP was heated at 118–122 °C for 36 h, 100 mL of petroleum ether was added, and the crystals were removed by filtration. Six recrystallizations of this material from petroleum ether gave pure exo-anti adduct **4g**: mp 136–137 °C; IR ($CDCl_3$) 3030, 2980, 1600, 1510, 1315, 1225, 1035, 910, 830 cm^{-1}. Anal. Calcd: C, H.

Column chromatography followed by preparative TLC (silica gel, petroleum ether eluant) gave the endo-anti adduct **2g**: mp 157–159 °C; IR (KBr) 3000, 2950, 1615, 1515, 1240, 1225, 1045, 890, 750, 675 cm^{-1}. Anal. Calcd: C, H.

The endo-anti product (0.040 g) was irradiated in 10 mL of acetonitrile for 2 h to give 0.005 g (13%) of pure cage product **6g**, mp 224–226 °C.

Similar workup of later fractions gave the endo-syn adduct **3g**: mp 215–216 °C; IR ($CDCl_3$) 2889, 1608, 1309, 1240, 1165, 1050, 1008 cm^{-1}. Anal. Calcd: C, H. Irradiation of the NMR sample of this material resulted in the disappearance of δ 6.16 signal.

HCCP Cycloaddition to 7-Chlorobicyclo[2.2.1]heptadiene (1h). A mixture of 16.5 g (0.082 mol) of **1h** and 31.2 g (0.114 mol) of HCCP was heated at 118–122 °C for 7 days. Half of the reaction was chromatographed on 300 g of alumina in a 2.5 × 90 cm column, using petroleum ether as eluant. Seventy 150-mL fractions were taken, and then the column was washed with ethyl ether. Early column fractions contained mostly the exo-anti adduct, and two recrystallizations from petroleum ether gave 3.6 g of pure exo-anti adduct **4h**: mp 124–126 °C; IR ($CDCl_3$) 300, 1600, 1320, 1255, 1065, 1040, 830 cm^{-1}. Anal. Calcd: C, H.

Middle fractions were recrystallized to yield pure endo-anti adduct **2h**: mp 212–213 °C; IR ($CDCl_3$) 300, 1605, 1310, 1190, 1040 cm^{-1}. Anal. Calcd: C, H.

The endo-anti adduct **1h** (0.372 g) was irradiated in 40 mL of chloroform for 2 h to give 0.178 g (48%) of cage product **6h**, mp 169–170 °C. Anal. Calcd: C, H.

The ether fractions were recrystallized to give pure endo-syn adduct **3h**: mp 238–240 °C; IR ($CHCl_3$) 2930, 1608, 1309, 1190, 1085, 1050, 1010, 845 cm^{-1}. Anal. Calcd: C, H.

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(42) **Note Added in Proof**: Professor G. W. Klumpp recently informed us of his work with P. M. Kwantes on CCl_2 additions to 7-substituted norbornadienes. Plots similar to Figure 1 are obtained by using Taft σ_1 values rather than group electronegativities. We obtain similar plots by using σ_1 values, but these had to be estimated for five of the substituents used in this work.