range 370–420–510 nm measured on an HP 8450 spectrometer as soon as possible after mixing and assuming an extinction coefficient of ca. 10^4 at 510 nm.

Acknowledgment. We are grateful to a reviewer for thoughtful comments. Support by the National Science Foundation (Organic Chemical Dynamics and International Program) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Awards of a NATO grant to F.O. and a CNPq grant to C.Z. are gratefully acknowledged.

Supplementary Material Available: Figure S1, ^{1}H NMR spectrum of 0.05 M 2,4-DNCB after addition of 0.13 M KOD in 80:20 (v/v) DMSO-d_6–D_2O and further addition of 0.15 M DCl after 2 min, and Figure S2, ^{1}H NMR spectrum of 0.04 M 2,6-DNCB on addition of 0.2 M KOD in 72:28 (v/v) DMSO-d_6–D_2O at 25 °C as a function of time, and with mesitoate ion as standard (2 pages). Ordering information is given on any current masthead page.

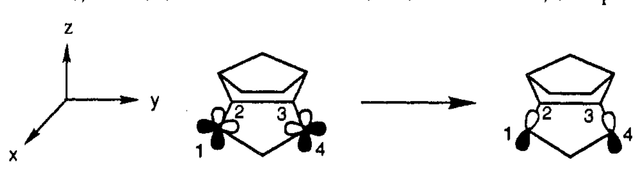
Remote Electronic Perturbation of π-Facial Stereoselectivity in [4+2] Cycloadditions to Isodicyclopentafulvenes. The Consequences of *p*-Phenyl Substitution[1]

Melinda Gugelchuk[2] and Leo A. Paquette*

Contribution from Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received July 2, 1990*

Abstract: Isodicyclopentafulvenes that carry an exocyclic para-substituted phenyl group as in **11** enter into Diels–Alder cycloaddition with highly reactive dienophiles exclusively from below the plane. The situation with the more sterically hindered and less reactive (*Z*)-1,2-bis(phenylsulfonyl)ethylene is one where addition occurs from both faces. The variation in the ratio **18**:**19** as a function of the group X adheres well to a linear free energy relationship involving σ_R^+ constants, especially when the NO_2 and CN examples are excluded. Photoelectron spectroscopic studies involving **11** provide insight into their orbital energies. A linear relationship was noted to exist between the **18**:**19** ratios and the fulvene HOMO–LUMO gaps. Competition experiments are also described, and theoretical studies are reported. The collective data provide the first evidence that long-range electronic effects can affect Diels–Alder stereoselection.

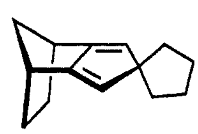
The extent of σ/π interaction within an isodicyclopentadiene is recognized to be dependent on the relative orbital energies of the interacting wave functions and on the size of the interaction matrix element $F_{\mu\nu}$. As $F_{\mu\nu}$ increases, interaction is enhanced and the terminal diene π lobes experience a remarkable, although modest, disrotation.[3] As seen in structures **1** and **2**, this phe-



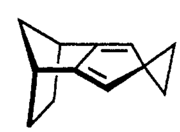
1 **2**

nomenon stems from superpositioning of the p_y component originating in the σ frame with the p_z component of the π network. The sense of disrotation is controlled by the sign of the p_y coefficient. If p_y and p_z are of the same sign, the lobes in question are rotated toward the methano bridge as in the illustration. The parent isodicyclopentadiene adopts this sense of twist.[4] When the signs of p_y and p_z are opposed, rotation occurs in the opposite sense.

Alteration in the extent and direction of disrotation has been held responsible for the π-facial stereoselectivity exhibited by dienes of this class in various cycloaddition reactions.[5,6] Indeed, we have earlier demonstrated that changes in the kinetically preferred direction of diene capture can be brought on by appropriate substitution of the cyclopentadiene methylene group or the apical methano bridge carbon.[7–9] In spirocyclopentane **3**, for



3



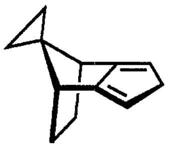
4

example, the terminal π lobes are outwardly splayed and an above-plane approach is favored by a dienophile.[9] The lower analogue **4** experiences π-bond rotation in the opposite sense in response to the proximal cyclopropane ring, and [4+2] cycloaddition occurs from the below-plane direction in order to minimize the four-electron destabilization energy.[9]

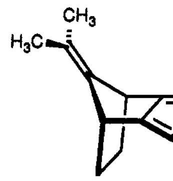
As concerns **5** and **6**, long-range through-bond interactions act to reduce the size of the p_y coefficient. This should translate into a diminished capacity to govern stereoselectivity. These hydrocarbons are in fact notable in that insignificant diastereoface discrimination is demonstrated in their Diels–Alder reactions.[7,8]

(1) Isodicyclopentadienes and Related Molecules. 54. Part 53: Moorhoff, C. M.; Paquette, L. A. *J. Org. Chem.*, in press. Part 52: Sivik, M. R.; Rogers, R. D.; Paquette, L. A. *J. Organomet. Chem.*, in press.
(2) Lubrizol Fellow, 1987.
(3) Gleiter, R.; Böhm, M. C. In *Stereochemistry and Reactivity of Pi Systems*: Watson, W. H., Ed.; Verlag Chemie International: Deerfield Beach, FL, 1983; pp 105–146.
(4) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 7218.
(5) Paquette, L. A. In *Stereochemistry and Reactivity of Pi Systems*; Watson, W. H., Ed.; Verlarg Chemie International: Deerfield Beach, FL, 1983; pp 41–73.
(6) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328.
(7) Paquette, L. A.; Kravetz, T. M.; Hsu, L.-Y. *J. Am. Chem. Soc.* **1985**, *107*, 6598.
(8) Paquette, L. A.; Green, K. E.; Gleiter, R.; Schäfer, W.; Gallucci, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 8232.
(9) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105*, 3136.

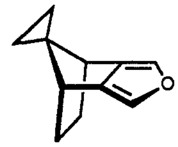
0002-7863/91/1513-246$02.50/0



5



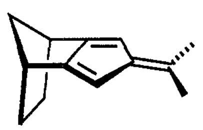
6



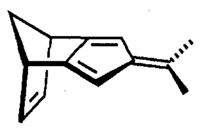
7

On the other hand, the structural modifications found in **7** cause disrotation to occur away from the methano bridge (as in **3**), resulting in preferential bonding to its upper surface.[8]

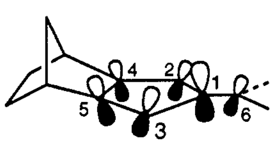
The overwhelming predilection of isodicyclopentafulvenes such as **8** and **9** for below-plane dienophile capture has been extensively documented.[10,11] These results conform to INDO and MINDO/3 calculations and to photoelectron spectroscopic determinations, which combine to suggest that the π-lobe deformation in these π-extended systems is as shown in **10**.



8



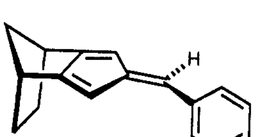
9



10

The close correspondence between theory and experiment documented above lends considerable support to the orbital tilting hypothesis.[3,6] Alternative rationalization of these results in terms of the Brown–Houk torsional control proposal[12] requires that this modulation of stereoselectivity be linked to changes in the dihedral angle relationship between the norbornyl (or norbornenyl) bridgehead C–H bonds and those central to the cyclopentadiene ring. However, X-ray analyses of several isodicyclopentafulvenes have turned up essentially no dihedral angle modification among them.[13] Nonetheless, their stereoselectivity responses vary widely. These findings are inconsistent with arguments based on torsional factors.

Since no assessment had yet been made of possible long-range electronic effects on stereoselection in Diels–Alder cycloadditions to isodicyclopentafulvenes, we have set out to examine the π-facial consequences of dienophile capture by **11** as a function of variations in X. It can reasonably be assumed that those torsional



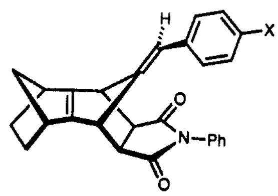
11

factors extant in the norbornyl moiety will remain essentially invariant through the series. Certainly, the phenyl ring in **11** will be twisted from coplanarity with the fulvene system for steric reasons.[14-17] Notwithstanding the rather uniform steric environment presented to the incoming reagent, the stereochemical course of [4+2] reactions involving **11** will be shown to be intimately linked to the nature of the para substituent X, provided that the dienophile possesses only modest reactivity.[18]

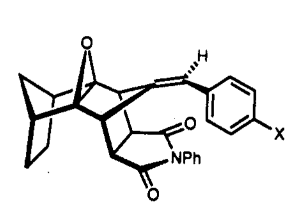
Results

Isodicyclopentafulvene Synthesis. The substrates where X = H, Me, OMe, Cl, and NMe_2 were prepared by condensation of the appropriate 4-substituted benzaldehyde with isodicyclopentadiene at room temperature in the presence of alcoholic potassium hydroxide according to Pines and Rabinovitz.[14] The fulvenes were obtained as highly colored solids in moderate yields. The same conditions were not conducive to the satisfactory preparation of analogues carrying the powerful electron-withdrawing substituents F, CF_3, NO_2, and CN. In these cases, satisfactory yields were realized when recourse was made instead to sodium methoxide in hot methanol as the condensing agent.

Cycloaddition Studies Involving *N*-Phenylmaleimide, Dimethyl Acetylenedicarboxylate, and Benzyne. Since the isodicyclopentafulvenes are sluggish in their capacity as 4π donors,[19] elevated temperatures or high-pressure conditions were necessary to achieve reasonable rates. When heated with *N*-phenylmaleimide in benzene to 60–70 °C, all examples proceeded exclusively to give **12** by below-plane anti-Alder capture. The stereochemical features



12

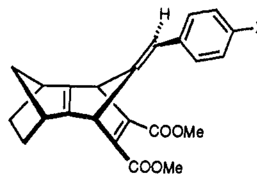


13

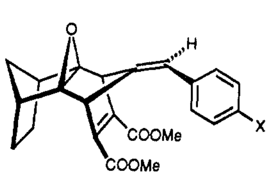
of these adducts are convincingly revealed by the high-field position (δ 0.41–0.46) of their endo ethano protons,[8,20,21] the absence of spin–spin coupling between the vicinal α-carbonyl and bridgehead protons,[22] and the characteristic shielding of their apical methano and methylidene carbons following epoxidation of the central double bond as in **13**.[7,23] This trend is exemplified for the OMe derivative. Thus, the two carbon atoms in question appear in **13**-OMe at 37.51 and 137.69 ppm, respectively, reflecting an upfield shift of 12.1 and 9.0 ppm relative to **12**-OMe (49.56 and 146.65 ppm). Additional confirmation of *syn*-sesquinorbornene geometry can be gleaned from the benzylic trigonal carbon, which exhibits a downfield shift when progressing from **12**-OMe (114.05 ppm) to **13**-OMe (119.82 ppm) in line with observations in similar systems.[10]

When **11** was warmed with dimethyl acetylenedicarboxylate in benzene, the air-sensitive *syn*-sesquinorbornadienes **14** were uniformly produced. The diagnostic properties of these adducts were their marked propensity for autoxidation,[24] the appreciable shielding experienced by the endo ethano protons (δ 0.56–0.60),[8,20,21] and the strong anisotropy contributions of the oxirane ring in **15** to the ^{13}C shifts of the nearby apical carbons[7,23] (consult the Experimental Section). A recalcitrance on the part

(10) Paquette, L. A.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Org. Chem.* **1983**, *48*, 1250.
(11) (a) Paquette, L. A.; Shen, C.-C. *Tetrahedron Lett.* **1988**, *29*, 4069. (b) Paquette, L. A.; Waykole, L.; Shen, C.-C.; Racherla, U. S.; Gleiter, R.; Litterst, E. *Ibid.* **1988**, *29*, 4213. (c) Paquette, L. A.; Shen, C.-C.; Engel, P. *J. Org. Chem.* **1989**, *54*, 3329.
(12) Brown, F. K.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 1971.
(13) Gallucci, J. C.; Kravetz, T. M.; Green, K. E.; Paquette, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 6592.
(14) Pines, A.; Rabinovitz, M. *J. Chem. Soc. B* **1971**, 385.
(15) Bünzli, P.; Otter, A.; Neuenschwander, M.; Huber, H.; Kellerhals, H. P. *Helv. Chim. Acta* **1986**, *69*, 1052.
(16) Sardella, D. J.; Keane, C. M.; Lemonias, P. *J. Am. Chem. Soc.* **1984**, *106*, 4962.
(17) Gugelchuk, M.; Paquette, L. A. *Isr. J. Chem.* **1989**, *29*, 165.
(18) Preliminary communication: Paquette, L. A.; Gugelchuk, M. *J. Org. Chem.* **1988**, *53*, 1835.
(19) No reaction was observed with *N*-methyltriazolinedione (CH_2Cl_2, −78 °C → room temperature), *p*-benzoquinone (C_6H_6, room temperature to reflux), or (methoxyvinylcarbene)pentacarbonyltungsten (C_6H_6, room temperature to reflux) under the conditions specified.
(20) Paquette, L. A.; Hayes, P. C.; Charmulind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3148.
(21) Paquette, L. A.; Künzer, H.; Green, K. E.; DeLucchi, O.; Licini, G.; Pasquato, L.; Valle, G. *J. Am. Chem. Soc.* **1986**, *108*, 3453.
(22) (a) Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1986**, *90*, 3724. (b) Marchand, A. P. *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*; Verlag Chemie International: Deerfield Beach, FL, 1982.
(23) Paquette, L. A.; Carr, R. V. C.; Arnold, E.; Clardy, J. *J. Org. Chem.* **1980**, *45*, 4907.
(24) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1965**, *102*, 7553.



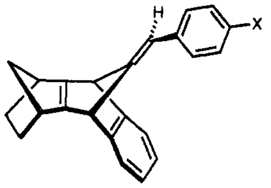
14



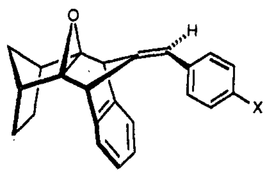
15

of 14-NMe_2 to undergo autoxidation upon exposure to air was noted. Epoxide formation was not observed with this adduct, even after long periods of exposure to air.

Benzyne, as generated from anthranilic acid and isoamyl nitrite in hot 1,2-dimethoxyethane,[25] added smoothyl to **11** to give **16**. Once again, purification was hampered due to extremely facile autoxidation.[24] Proton NMR spectra were recorded at 300 MHz



16

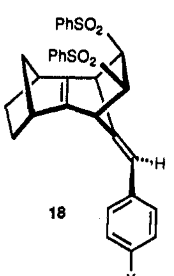


17

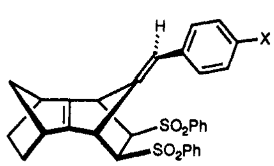
for each adduct immediately after filtration of the reaction mixture through a small plug of silica gel. ^{13}C NMR spectra were also recorded for certain of the less susceptible products prior to conversion to the corresponding epoxides **17** by treatment with *m*-chloroperbenzoic acid (MCPBA). Again, the dimethylamino derivative proved stable to both autoxidation and epoxidation.

As before, product homogeneity was established by $^1H/^{13}C$ NMR spectroscopy and TLC analysis. Stereochemistry was defined by comparative analysis of the spectra of **16** and **17**. A striking feature of the ^1H NMR data for **16** is the extreme upfield shift of the endo ethano protons (δ −0.02 to −0.05). Long-range shielding of this magnitude could only arise from benzyne addition to the endo surface of **11**. The situation in **16**-Me and **17**-Me reflects the standard chemical shift changes that materialize in this series upon introduction of the oxiranyl oxygen; the methano (33.44 → 47.20 ppm) and methylidene carbons (154.89 → 164.21 ppm) show strong anisotropic shielding while the benzylidene carbons move in the opposite direction (110.13 → 104.22 ppm).

Cycloadditions Involving (*Z*)-1,2-Bis(phenylsulfonyl)ethylene. The results described above disclose that the response of **11** to highly reactive dienophiles is overwhelmingly dictated by the flanking norbornane ring. The less reactive (*Z*)-1,2-bis(phenylsulfonyl)ethylene reagent[26] does not, however, adhere to this trend. When pressurized with **11** at 90 000 psi and 20 °C for 5–7 days, two adducts were produced, chromatographically separated, and identified as **18** and **19**. These disulfones exhibit individually



18



19

characteristic ^1H NMR spectra (Table I). Their relative ratios were reproduced in duplicate and triplicate experiments and quantified by MPLC analysis of the unpurified reaction mixtures.

The ^1H NMR spectra of the major adducts **18** show endo ethano proton resonances at δ 1.03–1.07, whereas in **19** they are

(25) Fieser, L. M.; Haddadin, M. J. *Can. J. Chem.* **1965**, *43*, 1599.
(26) De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596.

Table I. Comparative ^1H NMR Data for **18** and **19** (300 MHz, $CDCl_3$ Solution, δ Values)

compound	H_{endo}	$H_{\sigma\text{-sulfonyl}}$[a]	H_{syn}
18-H	1.06	4.25	2.25
19-H	0.74	3.33	1.07
18-Me	1.03	4.25	2.23
19-Me	0.74	3.32	1.07
18-OMe	1.05	4.23	2.24
19-OMe	0.73	3.37	1.06
18-NMe_2	1.06	4.24	2.23
19-NMe_2	0.75	3.34	1.07
18-Cl	1.07	4.24	2.24
19-Cl	0.65	3.25	1.03
18-NO_2	1.04	4.17	2.26
19-NO_2	0.73	3.33	1.09
18-F	1.05	4.23	2.24
19-F	0.73	3.30	1.07
18-CF_3	1.05	4.24	2.25
19-CF_3	0.73	3.32	1.08
18-CN	1.04	4.23	2.25
19-CN	0.72	3.31	1.08

[a] The chemical shifts for the two nonequivalent protons have been averaged to simplify matters.

Table II. Comparison of Experimentally Determined **18**:**19** Product Ratios with Those Predicted on the Basis of Several σ Constants

X	obsd[a]	pred-1[b]	pred-2[c]	pred-3[d]
NMe_2	1.8	2.1	1.9	1.8
OCH_3	2.4	2.5	2.5	2.6
F	3.3	3.1	3.1	3.2
Cl	3.6	3.3	3.4	3.4
CH_2	3.3	3.1	3.2	3.2
NO_2	2.9	4.5	4.3	4.0
CF_3	3.7	4.1	4.0	3.9
CN	2.3	4.4	4.2	4.0
H	3.5	3.4	3.4	3.5

[a] Average values derived from experiments performed at least in duplicate except for the chloro example (accuracy level ±0.2). [b] Calculated from correlation with $\sigma_R{}^0$ values but with NO_2 and CN omitted. [c] As in *a*, $\sigma_{R(BA)}$ values. [d] As in *a*, $\sigma_R{}^+$ values.

shifted upfield (δ 0.73–0.74). The σ-sulfonyl protons in **18** are seen to couple to the vicinal bridgehead protons (J = 3 Hz), thereby confirming Alder-like stereochemistry. On the other hand, these same protons in **19** are not coupled and are shielded by 0.92 ppm relative to their counterparts in **18** as required of anti-Alder stereochemical features. Possibly the single most revealing feature stems from the syn proton on the methano bridge in **18**, which is deshielded to the extent of 1.18 ppm with respect to its position in **19**. Such a large difference conforms nicely to the indicated stereochemical assignments. In **18**, projection of the phenylsulfonyl groups in the vicinity of this proton would be expected to have deshielding consequences.[27] In **19**, this proton is projected into the shielding cone of the apical double bond.

The preference for above-plane cycloaddition is attributed to steric factors arising from the relatively large steric bulk of the phenylsulfonyl groups.[21] However, this contribution can reasonably be expected to be consistent throughout the series. Strikingly, the variation in the **18**:**19** ratio as a function of X (Table II) adheres well to a linear free energy relationship (Figure 1), the NO_2 and CN examples excepted. Maverick reactivity has been encountered frequently[28-30] for *p*-NO_2- and *p*-CN-substituted systems. On the assumption that the **18**:**19** ratios reflect kinetic differences, the mean value (3.3) provides an estimate of the difference in activation energy[31] between top-face/endo and bottom-face/exo bonding of 0.69 kcal/mol.

(27) Paquette, L. A.; Gugelchuk, M.; McLaughlin, M. L. *J. Org. Chem.* **1987**, *52*, 4733.
(28) Hammett, L. P. *Physical Organic Chemistry*; McGraw-Hill: New York, NY, 1940.
(29) Taft, R. W., Jr. *J. Phys. Chem.* **1960**, *64*, 1805.
(30) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.
(31) Mok, K.-L.; Nye, M. J. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1810.

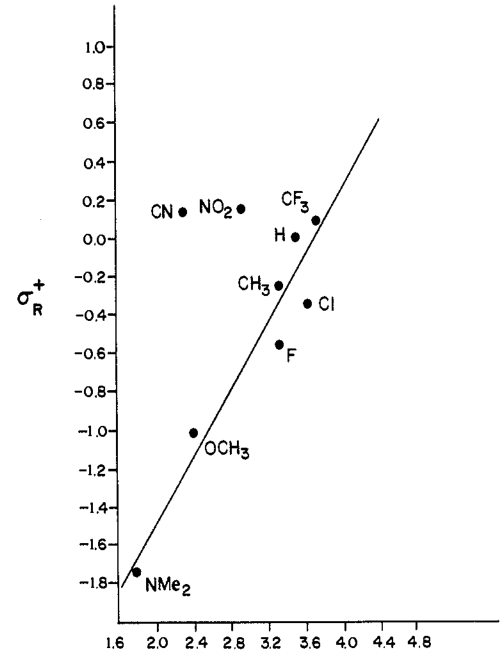


Figure 1. σ_R^+ values of X versus the experimental **18**:**19** product ratios.

Table III. Statistical Analysis of Substituent Effects on the **18**:**19** Product Ratios by the DSP Method According to the Four Established Scale Parameters

scale parameter	data utilized	ρ_I	ρ_R	λ	R^2
σ_R^-	all points	0.110	0.152	1.382	0.010
	omit CN	0.375	0.591	1.576	0.126
	omit NO_2, CN	1.471	2.264	1.539	0.604
σ_R^0	all points	-0.234	1.145	-4.893	0.167
	omit CN	0.143	1.703	11.909	0.431
	omit NO_2, CN	1.116	2.662	2.385	0.842
$\sigma_{R(BA)}$	all points	-0.349	1.074	-3.077	0.280
	omit CN	0.061	1.413	23.164	0.570
	omit NO_2, CN	0.961	1.897	1.974	0.923
σ_R^+	all points	-0.574	0.753	-1.312	0.430
	omit CN	-0.161	0.887	-5.509	0.717
	omit NO_2, CN	0.579	1.025	1.770	0.959

From the outset, the varied nature of X was purposefully selected to be broadly representative of polar (σ_I) and resonance effects (σ_R). This has permitted statistical evaluation of the data by means of the dual substituent parameter (DSP) method,[30,32] which considers the electronic effect of a remote substituent to derive from these two factors. The resultant multiple linear regression analyses provided values of R^2 ranging from 0 to 1, the larger numerical value corresponding to a better fit. The term ($\lambda = \rho_R/\rho_I$) is an indicator of the relative importance of resonance and inductive effects. As reflected in Table III, the model that best predicts the experimentally determined **18**:**19** ratios correlates with σ_R^+ values, particularly if NO_2 and CN are omitted from the regression analysis.

Equally informative was a similar DSP analysis of the effects of the same parasubstituents on the chemical shifts of H_{cis} and H_α.[14-16,33] Once again, the best linear corrlation materialized

(32) Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 1.
(33) The locations of these protons are defined as follows:

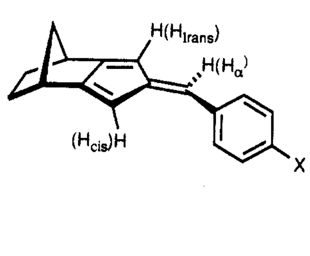


Table IV. DSP Analysis of the Proton Chemical Shifts of **11** (80 MHz, C_6D_6 Solution, δ Values) against σ_R^+ Constants

A. Chemical Shifts

X	H_{cis}	H_{trans}	H_α
NMe_2	6.55	5.94	7.03
OMe	6.34	5.84	6.86
Me	6.33	5.82	6.88
H	6.24	5.78	6.84
F	6.10	5.75	6.67
Cl	6.06	5.73	6.61
CF_3	6.01	5.70	6.60
CN	6.07	5.81	6.64
NO_2	5.90	5.64	6.47

B. DSP Analysis

proton	ρ_I	ρ_R	λ	R^2
H_{cis}	-0.467	-0.180	0.39	0.955
H_{trans}	-0.141	-0.082	0.58	0.742
H_α	-0.479	-0.125	0.26	0.950

when σ_R^+ values were utilized (Table IV). H_{trans} responds less well to this treatment.

One might inquire whether high-pressure conditions have any bearing on the outcome of these stereoselective processes. High pressure is known to strongly accelerate Diels–Alder reactions due to their large negative activation volumes (typically −31.5 to −42 cm^3/mol).[34] The use of pressure also avoids retro-Diels–Alder complications since activation volumes are positive.

It has been determined that, for an increase in selectivity to occur by application of high pressure, the difference in activation volumes for the respective orientations need to exceed ± 1 cm^3/mol.[35] Typical $\Delta\Delta V^\ddagger$ values for endo/exo orientations of Diels–Alder addition to cyclopentadiene are between +1.0 and −0.5 cm^3/mol.[36] Therefore, stereoselectivity would not be expected to increase as a result of high pressure. In the case of hetero-Diels–Alder reactions where the $\Delta\Delta V^\ddagger$ values are much larger (5.8 cm^3/mol), diastereoselectivity has been enhanced by applying high pressure.[35]

Pressure effects on the facial selectivity of bonding to **11** can be dismissed since it would require that the difference in activation volumes be dependent upon the electronic nature of the substituent. It has been demonstrated that activation volumes for Diels–Alder reactions are indepedent of the substituent within a given series of substrates.[37]

The nonexistence of pressure effects on facial selection was supported by subjecting a mixture of isodicyclopentadiene and (*Z*)-1,2-bis(phenylsulfonyl)ethylene to high-pressure conditions. By ^{1}H NMR analysis of the crude reacton mixture, the same product ratio of top- to bottom-face adducts (1.2:1) was realized as was previously observed at atmospheric pressure.[21]

That the observed stereoselection is a result of kinetically controlled dienophile capture was demonstrated by subjection of individual disulfone adducts admixed with isodicyclopentadiene to the high-pressure reaction conditions. After 24 h, HPLC analysis of the mixtures showed no indication of retro-Diels–Alder fragmentation of the cycloadduct that was initially introduced.

Discussion

The stereochemical course of Diels-Alder additions to **11** is herein shown to be related intrinsically to the nature of the para substituent X in those circumstances where the dienophile is only modestly reactive. The ratios of above-plane to below-plane cycloadditions are seen to correlate well with σ_R^+ values, except for the NO_2 and CN substituents, which exhibit correspondingly unexalted effects. Furthermore, multiple linear regression analyses

(34) Jenner, G. *Angew*, Chem., *Int. Ed. Engl.* **1975**, *14*, 137.
(35) Tietze, L. F.; Hubsch, T.; Voss, E.; Bubach, M.; Trost, W. *J. Am. Chem. Soc.* **1988**, *110*, 4065.
(36) Seguchi, K.; Sera, A.; Marayuma, K. *Tetrahedron Lett.* **1973**, *17*, 1585.
(37) Vasil'vitskaya, E. M.; El'yanov, B. S. *Izv. Akad. Nauk SSSR* **1981**, *31*, 2679.

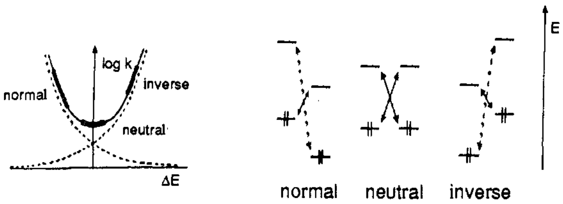


Figure 2. Electronic distinction of three types of Diels–Alder reactions.

demonstrate that subtle long-range electronic effects can indeed control the extent to which one or the other π surface in **11** is utilized during [4+2] bonding.

When considering the mechanism(s) by which substituent effects can be transmitted through conjugated π systems, several options become available.[38] The first of these consists of *through-space transmission* and may involve either direct electrostatic interaction or a mesomeric field effect (a secondary electrostatic interaction in which changes are produced by polarization of a π system). Alternatively, the impact of the substituent could be felt as a consequence of *through-bond transmission*. Three options now exist. These are the following: (a) resonance (charge transfer between the substituent and π-electron system), (b) π-inductive or π-polarization effect (redistribution of electron density due to the electronegativity of the substituent), and (c) σ-inductive contributions (redistribution of electron density via the σ frameworks).

Numerous attempts have been made at separating through-space effects from those transmitted through-bond. As a result, a large variety of substituent constant scales has been developed. The substituent constants adopted here for the DSP analyses were chosen because they are well-established measures of polar and resonance effects. Alternative scales such as the Swain–Lupton F/R values[39] and Dewar's FFMF constants[38a] were scrutinized with similar results. This is fully as expected, since neither of these treatments take into consideration the ability and mode of transmitting the substituent effects.

The somewhat exceptional nature of NO_2 and CN can be understood in conformational and π-polarization terms. Under normal circumstances, the phenyl ring in **11** is forced out of planarity with the fulvene ring for steric reasons.[14-16] Electron-releasing groups X increase the overlap of the phenyl and fulvene subsystems and significantly reduce the dihedral angle between the two rings. This expenditure of energy due to the unfavorable conformation is compensated by conjugation of the substituent with the fulvene system. When X is characterized instead by an elevated σ_R^+ value, not only is the resonance effect strongly curtailed but π electronic transmission is additionally attenuated because of the twist in existence about the bond interconnecting the two networks. The maximum deviation from coplanarity would be expected in the case of NO_2.[40]

On the basis of studies conducted on 4-substituted styrenes, resonance effects can be anticipated to drop off by $\cos^2 \phi$ whereas π-polarization effects decrease by $0.7 \cos^2 \phi$. This is due to a direct, independent polarization mechanism that exists at $\phi = 90°$ and accounts for 30% of the π-polarization effect.[38b] In coplanar systems, an "extended π-polarization" effect also operates.

On the other hand, the irregular behavior of NO_2 and CN may reflect the fact that a linear correlation does not exist. Usually, deviations from a linear free energy relationship are attributed to a change in the mechanism of the reaction. However, these same observations, when viewed in terms of PMO theory, have been construed in some cases to be the result of a crossover in the preferred orbital interactions without a change in mechanism.[41]

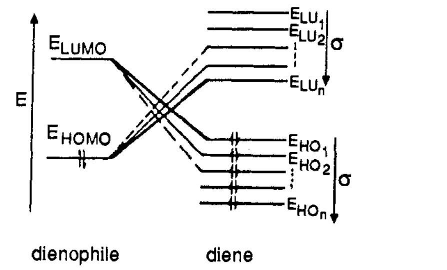
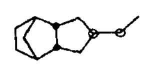
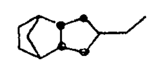


Figure 3. Change in favored FMO interaction with increasing σ value.



b$_1$



a$_2$

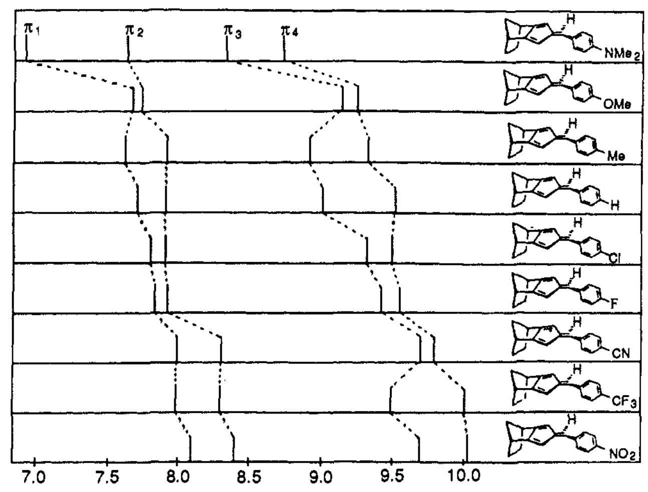


Figure 4. Orbital assignments and orbital energies for the ionization energies of **11**.[46]

For the reaction of a series of dienes with the same dienophile, the greatest part of the interaction energy depends on the frontier orbital separation of the addends:

$$\Delta E = A\gamma^2[(\mathrm{HO_{diene}} - \mathrm{LU_{dienophile}})^{-1} + (\mathrm{HO_{dienophile}} - \mathrm{LU_{diene}})^{-1}]$$

The pattern of this function is represented by two branches of hyperbola. When both terms are important, superimposition of the two curves gives a U-shaped function.[42-44] From this, three types of Diels–Alder reactions can be distinguished on the basis of relative frontier orbital separations as illustrated in Figure 2.

Substituent effects on all three reaction types have been investigated,[44b,45] and excellent correlations between HOMO energies versus σ^+, log k versus σ^+, and HOMO energies versus log k exist for the normal and inverse types. Therefore, the HOMO–LUMO energies of a diene must be a function of the substituents in order that the Hammett substituent constants can be taken as a quantitative measure of the substituent effect on the HOMO–LUMO energies. As the σ value increases, the HOMO–LUMO energies are lowered.

However, when both frontier molecular interactions are similar as in neutral-type reactions, a deviation from linearity in a Hammett plot could signal an inversion in preferred interactions as seen in Figure 3.

(38) (a) Dewar, M. J. S.; Golden, R.; Harris, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 4187. (b) Hamer, G. K.; Peat, I. R.; Reynolds, W. F. *Can. J. Chem.* **1973**, *51*, 897, 915. (c) Reynolds, W. F.; Gomes, A.; Maron, A.; MacIntyre, D. W.; Tanin, A.; Hamer, G. K.; Peat, I. R. *Ibid.* **1983**, *61*, 2376.

(39) Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492.

(40) Orlov, V. D.; Grigorov, P. A.; Klinsenko, L. B. *Zh. Org. Khim.* **1981**, *51*, 457.

(41) Henri-Rousseau, D.; Texier, F. *J. Chem. Educ.* **1978**, *55*, 437.

(42) Herndon, W. C. *Chem. Rev.* **1972**, *72*, 157.

(43) Sustmann, R.; Trill, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 838.

(44) (a) Sustmann, R. *Tetrahedron Lett.* **1972**, 2721. (b) Sustmann, R.; Schubert, R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 840.

(45) (a) Konovalov, A. I.; Samuilov, Ya. D.; Slepova, L. F.; Breus, V. A. *Zh. Org. Khim.* **1973**, *9*, 2086, 2519. (b) Alston, P. V.; Ortenbrite, R. M. *J. Org. Chem.* **1974**, *39*, 1584. (c) Desimoni, G.; Gamba, A.; Monticelli, M.; Nicola, M.; Tacconi, G. *J. Am. Chem. Soc.* **1976**, *98*, 2947.

Table V. Tabulation of Orbital Energies (eV) for **11** and Results of Their Linear-Regression Analysis According to Hammett σ Values

A. Orbital Energies

X	$I_{v,1}$	$I_{v,2}$	$I_{v,3}$	$I_{v,4}$	$-E_{LUMO}$
NMe_2	6.90	7.60	8.30	8.70	0.61
OMe	7.65	7.71	9.12	9.22	
Me	7.60	7.90	8.90	9.30	
H	7.70	7.90	9.00	9.50	0.84
Cl	7.80	7.90	9.32	9.48	
F	7.80	7.92	9.42	9.54	1.08
CN	8.00	8.30	9.70	9.78	1.30
CF_3	8.00	8.30	9.50	10.00	1.41
NO_2	8.10	8.40	9.70	10.02	1.71

B. Regression Analysis

parameter	ρ	r
$I_{v,1}$	1.35	0.943
$I_{v,2}$	1.74	0.952
$I_{v,3}$	1.08	0.949
$I_{v,4}$	1.20	0.970
$-E_{LUMO}$	1.28	0.944

To gain some appreciation of the state of affairs in **11**, photoelectron spectroscopic (PE) and theoretical studies were undertaken.[46] The orbital assignments and correlation diagram are shown in Figure 4. The first two PE bands are due to ionization from the fulvene-type a_2 and b_1 orbitals. The third and fourth bands arise from the two highest occupied π MO's of the benzene ring. In contrast to the usual fulvene sequence, viz., a_2 above b_1,[47] MINDO/3 calculations predict a switch in this splitting pattern for **11**.

As can be deduced from Table V, very good correlations are realized when Hammett σ_p values are employed in conjunction with the experimental ionization potentials and calculated LUMO energies.

In the most fundamental sense, stereoselectivity in the Diels–Alder reactions of **11** with (*Z*)-1,2-bis(phenylsulfonyl)ethylene is the result of existing kinetic inequities between top-face and bottom-face addition. The linear relationship observed between the energy of the fulvene HOMO and the corresponding substituent constants demonstrates that the relative rates of reaction with this dienophile follow the same trend. If the assumption is made that the substituent effect within this series influences the relative rates of top-face and bottom-face attack by comparable magnitudes, then a linear relationship between product ratios and HOMO energies or substituent constants should be found. This relationship explicitly assumes a normal Diels–Alder reaction.

If, on the other hand, the energy difference between the HOMO of the fulvene and the LUMO of the dienophile is similar to the energy difference between the dienophile HOMO and fulvene LUMO, a neutral cycloaddition would be in hand for which perturbation theory predicts a parabolic relationship due to the importance of both frontier orbital interactions. Since knowledge of the HOMO–LUMO energies of the disulfone is lacking, an indication of the reaction type involved was obtained indirectly. Plots of the **18**:**19** product ratios versus the fulvene HOMOs as well as the fulvene LUMOs proved *not* to be linear. Least-squares regression analyses of these data gave correlation coefficients of −0.566 and −0.337, respectively. A linear relationship was noted, however, with the **18**:**19** ratios and the fulvene HOMO–LUMO energy differences (correlation coefficient 0.862).

We sought further corroboration by carrying out competition studies with various pairs of isodicyclopentafulvenes. Dichloromethane solutions containing equimolar amounts of the two dienes and 0.5 equiv of (*Z*)-1,2-bis(phenylsulfonyl)ethylene were pressurized to 6000 atm for periods of time ranging from 1 to 4 h. HPLC analyses of the reaction mixtures gave the results summarized in Table VI. Exact correspondence to either a normal or neutral Diels–Alder reaction type was not seen, the approximate order followed being Cl < NO_2, F, NMe_2 < Me, OMe < H. Perhaps a more painstaking kinetic analysis might clarify the situation.

(46) Gleiter, R. Private communication.

(47) Houk, K. N.; George, J. K.; Duke, R. E., Jr. *Tetrahedron* **1974**, *30*, 523.

Table VI. Relative Reactivities Determined for the Cycloaddition of **11** with (*Z*)-1,2-Bis(phenylsulfonyl)ethylene

X_1:X_2	product ratio[a]	relative rate
NO_2:H	1.3:1	H > NO_2
NO_2:Cl	2.2:1	NO_2 > Cl
OMe:Me	1.1:1	OMe > Me
NO_2:Me	1.9:1	Me > NO_2
NMe_2:OMe	1.5:1	OMe > NMe_2
Me:F	2.2:1	Me > F
H:OMe	1.5:1	H > OMe
F:NO_2	1.1:1	F > NO_2

[a] Product ratio determined for top-face adducts.

In any event, it is intriguing to inquire at this point if the observed π-facial preferences can be rationalized in terms of σ/π interactions. If one accepts the orbital tilting hypothesis and sets **11**-H as the standard, the heightened production of **19** when X is, for example, NMe_2 or OMe signals that electron-releasing groups provide an influence synergistic to the norbornane contribution, much as in the isodicyclopentadienyl anion.[48,49] Electron release into the fulvene ring may thus cause the π_p lobes at the reaction sites to experience disrotatory tilting toward the methano bridge[3,6] and/or deformation along the longitudinal axis in the direction of the ethano bridge.[13]

While the latter working premise has not been proven, the correlation observed here provides striking confirmation for the first time that remote electronic influences can indeed directly affect Diels–Alder stereoselection.

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz. ^{13}C NMR were recorded at 20 and 75 MHz as indicated. Elemental analyses were obtained from the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Exact mass determinations were obtained at The Ohio State University Chemical Instrument Center by use of a Kratos MS-30 mass spectrometer. Capillary GC analyses were carried out on a 0.25-m DB-5 Durabond column at a flow rate of 2 mL/min calibrated at 100 °C and a split ratio of 30:1 on injection. Solvents were reagent grade and were dried prior to use.

4,5,6,7-Tetrahydro-2-[(4-nitrophenyl)methylene]-4,7-methano-2*H*-indene (11-NO_2). To a stirred suspension of sodium methoxide (1.6 g, 0.03 mol) in anhydrous methanol (25 mL) was added isodicyclopentadiene (1.0 g, 8.0 mmol). After a few minutes, 4-nitrobenzaldehyde (1.12 g, 7.0 mmol) in methanol was added dropwise. The reaction mixture was heated to 60 °C and stirred for 4 h at this temperature. The mixture was diluted with water (100 mL) and extracted with dichloromethane (3 × 100 mL). The extracts were washed with brine, dried, and concentrated to give a dark red oil. The oil was purified by chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) to give 0.749 g (38%) of **11**-NO_2 as dark red-orange flakes after recrystallization from ethanol: mp 123–124 °C; IR ($CHCl_3$, cm^{-1}) 3030, 2970, 2950, 2920, 2880, 1590, 1510, 1340, 1315, 1110, 1100, 950, 910, 890, 865, 840, 820, 695, 640; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 8.8 Hz, 2 H), 7.63 (d, J = 8.8 Hz, 2 H), 6.91 (s, H), 5.99 (s, 1 H), 5.68 (s, 1 H), 3.13 (s, 2 H), 1.90 (d, J = 7.9 Hz, 2 H), 1.77 (s, 2 H), 1.48 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$ ppm) 162.45, 157.24, 154.26, 146.81, 144.11, 130.36, 129.34, 123.66, 110.88, 104.28, 44.12, 38.91, 38.48, 28.74, 28.68; MS m/z (M^+) calcd 265.1103, obsd 265.1090.

2-[(4-Fluorophenyl)methylene]-4,5,6,7-tetrahydro-4,7-methano-2*H*-indene (11-F). Condensation of isodicyclopentadiene (1.5 g, 0.011 mol) with 4-fluorobenzaldehyde (1.4 g, 0.011 mol) and sodium methoxide (2.5 g, 0.046 mol) in anhydrous methanol (25 mL) at reflux for 24 h gave an oily residue that was purified by chromatography on silica gel (elution with petroleum ether) to afford 0.355 g (13%) of **11**-F as a yellow-orange powder: mp 59–60 °C; IR (cm^{-1}) 3000, 2970, 2950, 2920, 2870, 1599, 1505, 1315, 1295, 1230, 1210, 1160, 1150, 1115, 1100, 945, 905, 885, 870, 830, 820, 635; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.46 (m, 2 H),

(48) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1983**, *105*, 3126.

(49) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; von R. Schleyer, P. *J. Am. Chem. Soc.* **1990**, *112*, in press.

Table VII. Selected Physical and Spectral Data for the Adducts

compd	yield, %	mp, °C	MS m/z (M^+) calcd	MS m/z (M^+) obsd	anal. calcd (found) C	anal. calcd (found) H
12-H	65	187–188	393.1729	393.1721	82.42 (82.09)	5.89 (5.98)
12-CH_3	89	183.5–184	407.1885	407.1885		
12-OCH_3	72	184.5–185.5	423.1834	423.1861	79.41 (79.30)	5.95 (5.94)
12-NMe_2	47	185–186	436.2151	436.2148		
12-Cl	53	172–173	427.1339	427.1312	75.78 (75.76)	5.18 (5.22)
12-NO_2	52	181–182	438.1579	438.1597		
12-F	58	174–175	411.1634	411.1650		
13-Cl	89	230–231	443.1288	443.1299		
14-H	29	oil	362.1518	362.1518		
14-CH_3	49	oil	376.1674	376.1714		
14-OCH_3	42	oil	392.1624	392.1610		
14-NMe_2	56	oil	405.1940	405.1966		
14-Cl	32	oil	396.1128	396.1151		
14-NO_2	49	oil	407.1369	407.1343		
14-F	62	oil	380.1424	380.1438		
15-H	23	oil	378.1467	378.1508		
15-CH_3	17	oil	392.1624	392.1577		
15-OCH_3	10	oil	408.1573	408.1604		
15-Cl	29	147–148	412.1077	412.1069	67.01 (66.66)	5.13 (5.12)
15-NO_2	16	oil	423.1318	423.1256		
15-F	7	145.0–145.5	396.1373	396.1361	69.69 (69.56)	5.34 (5.49)
17-H	57	oil	312.1514	312.1539		
17-CH_3	51	139.5–141	326.1671	326.1680		
17-OCH_3	49	164.5–166	342.1620	342.1630	84.18 (84.35)	6.48 (6.61)
17-Cl	76	oil	346.1124	346.1174		
17-NO_2	76	185–186	357.1365	357.1332		
17-F	58	154–155	330.1420	330.1455	83.61 (83.20)	5.80 (5.90)
18-H	41	157.0–157.5	528.10[a]	528.00	70.43 (70.02)	5.34 (5.32)
18-CH_3	35	148.5–150	542.16[a]	542.19		
18-OCH_3	23	oil	250.1346[b]	250.1357		
18-NMe_2	37	oil	571.19[a]	571.21		
18-Cl	21	148.5–150	256.0832[b]	256.0809		
18–NO_2	51	176–177	265.1096[b]	265.1102		
18-F	51	157.5–158	238.1158[b]	238.1156		
18-CF_3	43	177–178	288.1126[b]	288.1149	64.41 (64.04)	4.56 (4.72)
18-CN	21	180–181	245.1204[b]	245.1253		
19-H	12	174.5–175.5	528.10[a]	528.01	70.43 (70.37)	5.34 (5.71)
19–CH_3	11	173.5–174	542.20[a]	542.10		
19-OCH_3	23	169.5–170.5	558.20[a]	558.20		
19-NMe_2	31	165–166	571.19[a]	571.07		
19–Cl	6	170.5–171	254.0862[b]	254.0929		
19–NO_2	9	171.5–172	573.10[a]	573.10		
19-F	7	173–174	238.1158[b]	238.1180	63.11 (67.73)	5.98 (5.06)
19-CF_3	9	185 dec	288.1126[b]	288.1153		
19-CN	12	170 dec	245.1204[b]	245.1250		

[a] Derived from an FAB measurement. [b] m/z ion resulting from retro-Diels–Alder cleavage.

7.08–7.02 (m, 2 H), 6.88 (s, 1 H), 6.05 (s, 1 H), 5.68 (s, 1 H), 3.12 (s, 2 H), 1.91–1.45 (series of m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 162.55 (d, $^1J_{CF}$ = 242 Hz), 160.94, 155.60, 150.76, 133.79 (d, $^4J_{CF}$ = 3 Hz), 131.68, 131.53 (d, $^3J_{CF}$ = 8 Hz), 115.44 (d, $^2J_{CF}$ = 21 Hz), 110.00 104.47, 44.75, 39.98, 38.54, 28.88, 28.82; MS m/z (M^+) calcd 238.1158, obsd 238.1155.

4,5,6,7-Tetrahydro-2-[[4-(trifluoromethyl)phenyl]methylene]-4,7-methano-2*H*-indene (11-CF_3). Reaction was performed on an 8.0-mmol scale and gave the fulvene as an orange oil: 822 mg, 38%; IR ($CHCl_3$, cm^{-1}) 3000, 2960, 2920, 2860, 1610, 1445, 1410, 1320, 12950, 1250, 1185, 1170, 1130, 1065, 1015, 950, 910, 885, 830, 820, 645; ^1H NMR (300 MHz, $CDCl_3$) δ 7.59 (s, 4 H), 6.91 (s, 1 H), 6.01 (s, 1 H), 5.68 (s, 1 H), 3.11 (s, 2 H), 1.92–1.85 (m, 2 H), 1.76 (s, 2 H), 1.47 (d, J = 7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 161.64, 156.60, 152.87, 141.08, 137.61 (q, J_{CF} = 272 Hz), 130.60, 130.02, 125.26, 110.83, 104.50, 44.83, 38.93, 38.51, 38.51, 28.75; MS m/z (M^+) calcd 288.1126, obsd 288.1130.

4-[(4,5,6,7-Tetrahydro-4,7-methano-2*H*-inden-2-ylidene)methyl]-benzonitrile (11-CN). Reaction was performed on a 7.0-mmol scale and furnished the fulvene as an orange solid: 427 mg, 23%; mp 82–84 °C (from ethanol); IR ($CHCl_3$, cm^{-1}) 3000, 2980, 2940, 2860, 2220, 1600, 1495, 1410, 1315, 1250, 1190, 1175, 1100, 1080, 1060, 1020, 950, 910, 885, 830, 820; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (J = 8 Hz, 2 H), 7.57 (d, J = 8 Hz, 2 H), 6.86 (s, 1 H), 5.98 (s, 1 H), 5.66 (s, 1 H), 3.11 (br s, 2 H), 1.93–1.87 (m, 2 H), 1.76 (s, 2 H), 1.47 (d, J = 8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 162.18, 157.00, 153.70, 142.14, 132.10, 130.27, 129.89, 118.84, 110.84, 104.29, 44.23, 38.91, 38.49, 28.71; MS m/z (M^+) calcd 245.1204, obsd 245.1208.

Prototypical Cycloaddition of (*p*-X-Phenyl)isodicyclopentafulvenes (11) with *N*-Phenylmaleimide. A solution of **11** (0.8 mmol) and *N*-phenylmaleimide (0.20 g, 1.1 mmol) in dry benzene (6–8 mL) was stirred for 24–30 h at 60–68 °C under a nitrogen atmosphere. The solvent was removed, and the resulting solid residue was purified by chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) to give the cycloadduct **12** in yields ranging from 47% to 89%. For selected physical and spectral data of the adducts, see Table VII.

Epoxidation of the *N*-Phenylmaleimide Adducts. (3aα,4α,5α,8α,8aα,9α,9aα)-3a,4,5,6,7,8,9,9a-Octahydro-10-[(4-methoxyphenyl)methylene]-2-phenyl-4a,8a-epoxy-4,9:5,8-dimethano-1*H*-benz[*f*]isoindole-1,3(2*H*)-dione (13-OMe). To a solution of **12**-OMe (50 mg, 0.1 mmol) in dry dichloromethane (10 mL) at 0 °C was added MCPBA (0.039 g) in dry dichloromethane (10 mL). The reaction mixture was stirred at 0 °C for 4 h and washed with 5% sodium thiosulfate solution (3 × 25 mL), saturated sodium bicarbonate solution (4 × 25 mL), and water (25 mL). The organic layer was dried, filtered, and concentrated to give a pale yellow residue. Purification by radial chromatography (silica gel, 1-mm plate, 30% ethyl acetate in petroleum ether) gave 0.052 g (99%) of the epoxide as a white powder: mp 245–246 °C; IR ($CHCl_3$, cm^{-1}) 3030, 3000, 2990, 2940, 1770, 1710, 1605, 1510, 1385, 1295, 1250, 1190, 1035, 885, 830, 690, 660; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38–7.32 (m, 3 H), 7.15 (d, J = 9 Hz, 2 H), 6.99–6.96 (m, 2 H), 6.81 (d, J = 9 Hz, 2 H), 6.10 (s, 1 H), 4.29 (s, 1 H), 3.78 (s, 3 H), 3.62 (s, 3 H), 2.94 (s, 2 H), 1.90 (d, J = 9 Hz, 1 H), 1.81–1.70 (m, 3 H), 0.84 (d, J = 9 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 176.34, 176.04, 158.76, 137.69, 131.55, 129.10, 129.05, 128.71, 126.46, 119.82, 113.94, 57.59, 57.38, 55.20, 51.77, 46.66, 46.53, 46.15, 40.78, 40.68, 37.51, 26.58, 26.44; MS m/z (M^+) calcd 439.1783, obsd 439.1819.

Prototypical Cycloaddition of 11 with Dimethyl Acetylenedicarboxylate. A solution of **11** (0.4 mmol) and dimethyl acetylenedicarboxylate (74 μL, 0.6 mmol) in dry benzene (10 mL) was evacuated and flushed with nitrogen several times. The reaction mixture was warmed to 60–65 °C and stirred for 1–3 days under nitrogen. Evaporation of the solvent provided oily residues, which were purified by MPLC on silica gel (elution with 20–25% ethyl acetate in petroleum ether) to afford cycloadducts **14** along with the corresponding epoxides **15**. Yields range from 52% to 69%.

Prototypical Cycloaddition of 11 with Benzyne. A solution of **11** (0.4 mmol) in dry dimethoxyethane (5 mL) was warmed to reflux under a nitrogen atmosphere. Solutions of anthranilic acid (66 mg, 0.5 mmol) in dimethoxyethane (5 mL) and isoamyl nitrite (90 μL, 0.7 mmol) in dimethoxyethane (5 mL) were added dropwise, simultaneously from separate addition funnels. After addition was complete, the reaction mixture was stirred at reflux for 1–3 h. Removal of the solvent followed by chromatography on silica gel (elution with 1–2% ethyl acetate in petroleum ether) gave cycloadducts **16** in yields of 27–78% overall.

Prototypical Epoxidation of 16. To a cold (0 °C) bicarbonate-buffered solution of **16** (0.06–0.27 mmol) in dichloromethane (5–10 mL) was added 1.5 equiv of MCPBA in a single portion. The reaction mixture was stirred at this temperature for 4 h, washed with 5% sodium thiosulfate (4 × 25 mL) and saturated sodium bicarbonate solutions (3 × 25 mL), dried, filtered, and concentrated to give nearly pure epoxides. Column chromatography on silica gel (elution with 2–5% ethyl acetate in petroleum ether) gave pure samples of **17**. Yields ranged from 41% to 76%.

Prototypical Cycloaddition of 11 with (*Z*)-1,2-Bis(phenylsulfonyl)ethylene. A solution of **11** (0.20 mmol) and the disulfone (300 mg, 1.0 mmol) in dry dichloromethane (2 mL) was pressurized to 90 000 psi for 3–7 days. Removal of the solvent followed by MPLC purification on silica gel (elution with 35–40% ethyl acetate in petroleum ether) gave adducts **18** and **19**. Small amounts of adducts arising from the *trans*-disulfone isomer were detected but were not characterized.

Acknowledgment. Financial support from the National Cancer Institute (Grant CA-12115) is gratefully acknowledged. We thank Professor Rolf Gleiter (Heidelberg) for his eager willingness to record the PE data and carry out the associated molecular orbital calculations.

Supplementary Material Available: Spectral and analytical data for compounds of type **12–15** and **17–19** (21 pages). Ordering information is given on any current masthead page.

Studies of the Antenna Effect in Polymer Molecules. 23. Photosensitized Dechlorination of 2,2′,3,3′,6,6′-Hexachlorobiphenyl Solubilized in an Aqueous Solution of Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene)

M. Nowakowska,[†] E. Sustar, and J. E. Guillet*

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1. *Received June 5, 1990*

Abstract: Photodechlorination of 2,2′,3,3′,6,6′-hexachlorobiphenyl (HCB) solubilized in an aqueous solution of poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) was studied with use of solar-simulated radiation. The reaction was found to be photosensitized by the naphthalene antenna units present in the copolymer. Studies performed in a low molecular weight model system have shown that dechlorination of HCB may occur via an exciplex intermediate. Exciplex formation in the system is efficient because of the high local concentration of HCB in proximity to the naphthalene polymeric units.

Introduction

In previous papers in this series, it has been shown that novel antenna polyelectrolytes commonly referred to as "photozymes" behave as efficient photocatalysts.[1-9] In aqueous solutions these polymers adopt a pseudomicellar conformation that results in the formation of hydrophobic microdomains that are capable of solubilizing sparingly water-soluble organic compounds. Aromatic chromophores such as naphthalene, anthracene, phenanthrene, or carbazole incorporated in the polymer chain absorb light from the near-UV–visible spectral region. Excitation energy may then be used to induce photochemical reactions involving molecules solubilized within the polymer. It has been shown that the

[†] On leave from the Faculty of Chemistry, Jagiellonian University, Krakow, Poland.

(1) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1988**, *21*, 3430.
(2) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1989**, *22*, 2317.
(3) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1989**, *22*, 3903.
(4) Nowakowska, M.; Guillet, J. E. *Zesz. Nauk. Uniw. Jagiellon. Pr. Chem.*, in press.
(5) White, B.; Nowakoska, M.; Guillet, J. E. *J. Photochem. Photobiol.* **1989**, *50*, 147.
(6) Sustar, E.; Nowakowska, M.; Guillet, J. E. *J. Photochem. Photobiol. A* **1990**, *53*, 233.

