Table I. Photoproduct Distribution from Irradiation of Triphenylsulfonium Triflate

solvent	sensitizer	λ, nm	concn, $\times 10^{-4}$ M 2	 3	 4	 5
CH_3CN	none	254	3.1	3.0	0.3	0.6
acetone	acetone	254	3.9	1.7	0.3	0.4
CH_3CN	none[a]	254	2.9	3.0	0.3	0.6
acetone	acetone	300	13.2	0	0	0
CH_3CN	none	300	0.2	0.2	trace	trace

sensitizer	rel ϕ[b]	E_T[c]	sensitizer	rel ϕ[b]	E_T[c]
acetone	81	79-82	xanthone	1.0	74.0
1-indanone	10.1	75.8	benzophenone	0.2	69.2
acetophenone	7.5 (0.80)[a]	74.1	none	0.95	

[a] O_2 saturated. [b] Reference 14. [c] Reference 15.

Scheme III. Photochemical Pathway for Product Formation

Direct Photolysis

$$\begin{aligned}
&\mathrm{Ph_3S^+\ X^-} \xrightarrow{h\nu} \left[\mathrm{Ph_3S^+\ X^-}\right]^1\\
&\left[\mathrm{Ph_3S^+\ X^-}\right]^1 \longrightarrow \left[\mathrm{Ph_2S^{+\cdot} + Ph^{\cdot} + X^{\cdot}}\right]^1\\
&\left[\mathrm{Ph_2S^{+\cdot} + Ph^{\cdot} + X^{\cdot}}\right]^1 \xrightarrow{\mathrm{RH}} (1) + (2) + (3) + (4)\\
&\qquad + (5) + \mathrm{Ph\text{-}H} + \mathrm{H^+}\\
&\left[\mathrm{Ph_3S^+\ X^-}\right]^1 \longrightarrow \left[\mathrm{Ph_2S\ + Ph^+ + X^-}\right]^1\\
&\left[\mathrm{Ph_2S\ + Ph^+ + X^-}\right]^1 \xrightarrow{\mathrm{RH}} (1) + (2) + (3) + (4)\\
&\qquad + (5) + \mathrm{Ph\text{-}R} + \mathrm{H^+}\\
&\left[\mathrm{Ph_3S^+\ X^-}\right]^1 \longrightarrow \left[\mathrm{Ph_3S^+\ X^-}\right]^3\\
&\left[\mathrm{Ph_3S^+\ X^-}\right]^3 \longrightarrow \left[\mathrm{Ph_2S^{+\cdot} + Ph^{\cdot} + X^{\cdot}}\right]^3\\
&\left[\mathrm{Ph_2S^{+\cdot} + Ph^{\cdot} + X^{\cdot}}\right]^3 \xrightarrow{\mathrm{RH}} (2) + \mathrm{H^+} + \mathrm{Ph\text{-}H}
\end{aligned}$$

Sensitized Photolysis

$$\begin{aligned}
&\mathrm{Sens} \xrightarrow{h\nu} \left[\mathrm{Sens}\right]^1 \longrightarrow \left[\mathrm{Sens}\right]^3\\
&\left[\mathrm{Sens}\right]^3 + \mathrm{Ph_3S^+\ X^{\cdot}} \longrightarrow \mathrm{Sens} + \left[\mathrm{Ph_3S^+\ X^-}\right]^3\\
&\left[\mathrm{Ph_3S^+\ X^-}\right]^3 \longrightarrow \left[\mathrm{Ph_2S^{+\cdot} + Ph^{\cdot} + X^{\cdot}}\right]^3\\
&\left[\mathrm{Ph_2S^{+\cdot} + Ph^{\cdot} + X^{\cdot}}\right]^3 \xrightarrow{\mathrm{RH}} (2) + \mathrm{H^+} + \mathrm{Ph\text{-}H}
\end{aligned}$$

solvent.[5a] Acetanilide is not observed in any of the triplet sensitized reactions in acetonitrile, which indicates that phenyl cation is not formed from the triplet excited state. The only other photoproduct is benzene, which is probably formed by reaction of phenyl radical with solvent. Furthermore, in our experiments no significant amount of biphenyl is formed at low conversion.[16]

The proposed photochemical pathway for decomposition of 1 is shown in Scheme III. The triplet excited state of 1 can be formed by intersystem crossing from the singlet excited state upon direct irradiation or by energy transfer from the excited triplet state ($E_T > 74$ kcal/mol) of the sensitizer. The triplet excited state yields only diphenyl sulfide, presumably from the triplet diphenylsulfinyl radical cation-phenyl radical pair. The triplet radical pair would require spin inversion prior to recombination to yield the (phenylthio)biphenyl species (3-5) and starting material (1); instead, escape from the solvent cage to yield diphenyl sulfide is favored. The singlet excited state does not require spin inversion for recombination, and the cage reaction to yield 1 and 3-5 becomes the predominant process, accompanied by some escape to give 2.

John L. Dektar, Nigel P. Hacker*
IBM Almaden Research Center
San Jose, California 95120
Received October 23, 1987

Modulation of π-Facial Selectivity in Diels-Alder Cycloaddition to Isodicyclopentafulvenes by Remote Para Substitution of an Exocyclic Phenyl Group

Summary: Isodicyclopentafulvenes that carry an exocyclic para-substituted phenyl group as in **3** enter into Diels-Alder cycloaddition with highly reactive dienophiles exclusively from below-plane. The situation with the more sterically hindered and less reactive reagent (*Z*)-1,2-bis(phenylsulfonyl)ethylene is one where addition occurs from both faces.

Sir: No assessment has heretofore been made of the potential for modulating the π-facial selectivity of a [4 + 2] cycloaddition by means of remote electronic perturbation. Studies of the effects of substituents on rate, stereochemistry, and orientation abound,[2] and correlations based upon the Hammett equation are extant.[3] In the case of a system such as isodicyclopentadiene (**1**), dienophiles can in principle bond to either face. However, there exists a strong preference for below-plane capture,[4] except where steric factors become dominant in either reaction partner.[5] This single fact has been the source of considerable mechanistic

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[16] At higher conversions, biphenyl concentration markedly increases upon direct photolysis. This suggests that much of the biphenyl observed is a secondary photoproduct, probably formed from the (phenylthio)biphenyls 3-5.

(1) Lubrizol Fellow, 1987.

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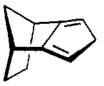
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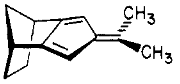

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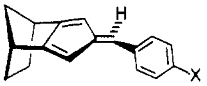

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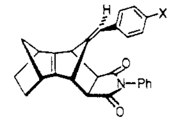

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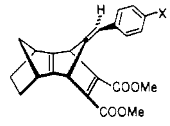

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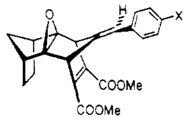

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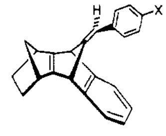

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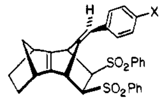

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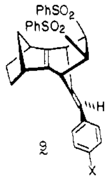

9

contention.[6] The identical predilection of planar fulvenes such as **2** to capture dienophiles from below[7] has been interpreted as substantiation of the Gleiter–Paquette orbital tilting theory,[8] especially in light of the stereochemistry crossover observed upon modest structural alteration of the apical methano bridge.[9]

In the present paper, we show that the stereochemical course of Diels–Alder cycloaddition to **3** is intrinsically related to the nature of para substituent X, provided that the dienophile is only modestly reactive. We disclose further that very good correlatibility exists between the top/bottom ratio and the appropriate σ_R^+ values except for the NO_2 and CN substituents which exhibit corresponding unexalted effects.[10] The regression analyses to be described demonstrate that subtle long-range electronic effects can indeed control the extent to which one or the other π-surface in **3** is utilized during [4 + 2] bonding.

Since **3**[11] is sluggish in its capacity as a 4π donor, elevated temperatures or high-pressure conditions were required to achieve reasonable rates. The situation with *N*-phenylmaleimide (60–70 °C, C_6H_6) involved exclusive formation of **4** by below-plane anti-Alder capture. The telltale stereochemical features of these adducts are (i) the high-field position (δ 0.41–0.46) of their endo ethano protons,[5b,12] (ii) the lack of coupling between the vicinal α-carbonyl and bridgehead protons,[13] and (iii) the characteristic shielding of their apical methano and methylidene carbons following epoxidation of the central double bond.[14] Exposure of **3** to dimethyl acetylenedicarboxylate in warm benzene afforded the air-sensitive adducts **5** of related stereochemistry.[15] The facility of autoxidation,[16] the strong shielding of the endo ethano protons (δ 0.56–0.60), and the comparative ^{13}C data of **5** and **6** reflecting the strong shielding contributions of the oxirane ring proved particularly diagnostic in this series. Benzyne, as generated from anthranilic acid and isoamyl nitrite,[17] reacted with **3** in hot 1,2-dimethoxyethane to give **7**. As before, the product homogeneity was established by $^1H/^{13}C$ NMR, and epoxidation was subsequently utilized to define stereochemistry.

The above results disclose that the response of **3** to highly reactive dienophiles is dictated overwhelmingly by the adjacent norbornane ring. This is, however, not the case with (*Z*)-1,2-bis(phenylsulfonyl)ethylene.[18] Following pressurization with **3** at 90 000 psi and 20 °C for 5–7 days, two adducts were isolated, chromatographically separated, and identified as **8** and **9**. These sulfones exhibit highly characteristic ^1H NMR spectra[19] and their relative ratios were, as before, reproduced in duplicate and triplicate experiments. The preference for above-plane cycloaddition[20] 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 **9**/**8** ratio as a function of X (Table I) adheres well to a linear free-energy relationship (Figure 1), the NO_2 and CN examples excepted.

Evaluation of these data was accomplished statistically by means of the dual substituent parameter (DSP) method.[10c,21] The DSP analysis considers the electronic effect of a remote substituent to derive from two factors, its polar nature (σ_I) and its resonance contribution (σ_R). The range of X was purposefully chosen to be broadly representative of σ_I and σ_R. Multiple linear regression analyses provided fits expressed as R^2, the values of which can range from 0 to 1. The larger the value, the better the fit. The term λ ($=\rho_R/\rho_I$) is an indicator of the relative importance of resonance and inductive effects. The results, summarized in Table II, indicate the model that best *predicts* the **9**:**8**

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(19) For example, **8**-OCH_3: ^1H NMR (300 MHz, $CDCl_3$) δ 8.12–8.09 (m, 2 H), 7.71–7.37 (series of m, 8 H), 7.15 (d, J = 9 Hz, 2 H), 6.89 (d, J = 9 Hz, 2 H), 5.82 (s, 1 H), 3.98 (s, 1 H), 3.85 (s, 3 H), 3.84 (s, 1 H), 3.37 ($^1/_2$AB q, J = 9 Hz, 1 H), 3.28 ($^1/_2$AB q, J = 9 Hz, 1 H), 3.02 (s, 1 H), 3.97 (s, 1 H), 1.67 (d, J = 8 Hz, 2 H), 1.35 (d, J = 8 Hz, 1 H), 1.06 (d, J = 8 Hz, 1 H), 0.73 (dd, J = 2.8 Hz, 2 H). **9**-OCH_3: ^1H NMR (300 MHz, $CDCl_3$) δ 8.07–8.02 (m, 4 H), 7.67–7.54 (m, 6 H), 6.84 (d, J = 9 Hz, 2 H), 6.75 (d, J = 9 Hz, 2 H), 5.28 (s, 1 H), 4.27 (dd, J = 3, 9 Hz, 1 H), 4.19 (dd, J = 3, 9 Hz, 1 H), 4.09 (d, J = 3 Hz, 1 H), 3.76 (s, 3 H), 3.35 (d, J = 3 Hz, 1 H), 3.27 (s, 1 H), 3.25 (s, 1 H), 2.24 (d, J = 9 Hz, 1 H), 1.79 (d, J = 8 Hz, 2 H), 1.42 (d, J = 8 Hz, 1 H), 1.05 (dd, J = 2, 8 Hz, 2 H).

(20) A preponderance of the above-plane adduct is also observed in the case of 1.[5b] The ratio (1.2:1) remains constant irrespective of whether the reaction is conducted at atmospheric pressure or at 90 000 psi.

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Table I. Comparison of Experimentally Determined 9:8 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_3	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 using $\sigma_R{}^0$ values but omitting NO_2 and CN. [c] As in $a - \sigma_{R(BA)}$ values. [d] As in $a - \sigma_R{}^+$ values.

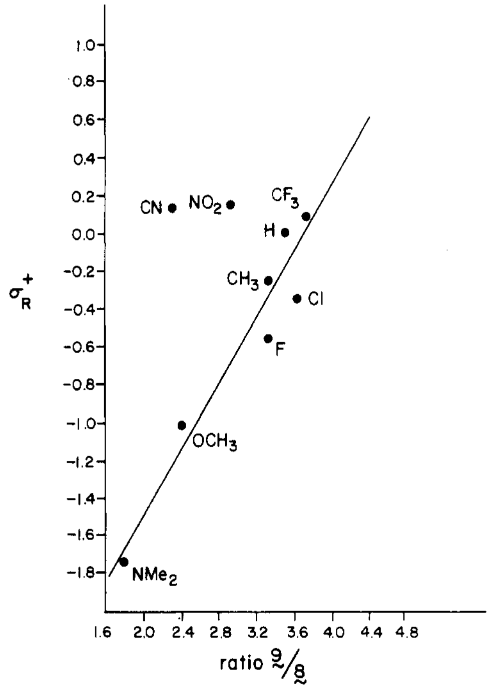

Figure 1. Plot of the $\sigma_R{}^+$ values of X versus the experimental 9:8 product ratios.

Table II. Statistical Analysis by the DSP Method According to the Four Established Scale Parameters

scale parameter	data utilized	ρ_I	ρ_R	λ	R^2
$\sigma_R{}^-$	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
$\sigma_R{}^0$	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
$\sigma_R{}^+$	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

ratios to depend on $\sigma_R{}^+$ values, particularly if NO_2 and CN are omitted from the regression analysis.

Para-substituent effects on the chemical shifts of H_{cis} and H_α[11,22,25] in **3**, when analyzed by the DSP method, were also found to provide the best linear correlation when evaluated against $\sigma_R{}^+$ values. 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 **3** is forced out of coplanarity with the fulvene ring for steric reasons.[11,22,23] Electron-releasing groups X increase the π overlap of the phenyl and fulvene part structures and significantly reduce the dihedral angle between the two rings. When X is characterized instead by an elevated $\sigma_R{}^+$ 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 π networks.

At this point, it becomes intriguing to inquire what leads to the observed π-facial preferences. If one accepts the orbital tilting hypothesis[8] and sets 3-H as the standard, the heightened production of **8** when X is, for example, NMe_2 or OCH_3 signals that electron-releasing groups provide an influence synergistic to the norbornane contribution, much as in the isodicyclopentadienyl anion.[24] Electron release into the fulvene ring may thus cause the pπ lobes at the reaction sites to experience disrotatory tilting toward the methano bridge[8] and/or deformation along the longitudinal axis in the direction of the ethano bridge.[9] Tandem photoelectron spectroscopic/theoretical studies of **3** are expected to clarify which phenomenon is the more dominant. Nonetheless, the correlation observed here provides striking confirmation that remote electronic influences can indeed directly affect Diels–Alder stereoselection.

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Leo A. Paquette,* Melinda Gugelchuk[1]
Evans Chemical Laboratories
The Ohio State University
Columbus, Ohio 43210

Received February 9, 1988

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Contrasting Behaviors in the Cleavage of Aryl Alkanoates by α- and β-Cyclodextrins in Basic Aqueous Solution

Summary: The kinetics of ester cleavage of 4-carboxy-2-nitrophenyl alkanoates (C2, C4, C6, C7, C8) in aqueous base containing α- or β-cyclodextrin (α- or β-CD) indicate that for the three longer esters there are processes involving *two* CD molecules which are quite distinct: with α-CD a 2:1 binding leads to *inhibition*; with β-CD a second-order process provides *catalysis*.

Sir: In aqueous base cyclodextrins (CDs)[1] cleave phenyl acetates via ester·CD complexes in which the aryloxy group is included in the hydrophobic cavity of the CD.[1-3] Longer

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