oxidizer[20]) to be endothermic.[26] It is likely that the endothermic oxidations of many azoalkanes are driven to nitrogen evolution by the instability of $R{-}N{=}N{-}R^{\bullet+}$.[7] These cation radicals become less stable when the hydrocarbon cation radicals formed by deazatation are more heavily substituted. In the bridgehead dimethyl derivative of DBO, for example, we find that reaction with 2 equiv of $TBPA^{\bullet+}$ causes quantitative nitrogen evolution and no formation of red material.

The pattern of behavior of azoalkanes which begins to emerge from this and other studies may, perhaps, be fitted to the general concept of nucleophile/cation radical reactions popularized by Parker.[20] If an initial encounter between an azoalkane and a cation radical leads to a complex, one can imagine that this complex either breaks up to produce the azoalkane cation radical or undergoes further oxidation by the reactant cation radical. In the case of DBO, further oxidation would end in covalent bonding as shown in products **1** and **2**.

In summary, we find that DBO oxidatively forms an adduct with stable cation radical salts, in contrast to previously studied azoalkanes that undergo oxidative deazatation.

Acknowledgment. We thank the National Science Foundation (Grants No. CHE 86-12031 and CHE 86-04364) and the Robert A. Welch Foundation (Grants No. D-028 and C-499) for financial support.

Supplementary Material Available: ORTEP diagram and stick diagram of **1**, listing of positional and thermal parameters, bond distances, bond and torsion angles, and method for determining stoichiometry shown in Tables I and II (14 pages). Ordering information is given on any current masthead page.

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[26] We use ionization potentials because unpublished work from our laboratory and that of Prof. S. F. Nelsen has shown that electrochemical oxidation of azoalkanes is irreversible.

Hyperconjugation as a Factor in Face Selectivity during Cycloaddition

Wen-Sheng Chung,[†] N. J. Turro,*[,†] Sushil Srivastava,[‡]
Haifang Li,[‡] and W. J. le Noble*[,‡]

Departments of Chemistry, Columbia University
New York, New York 10027
State University of New York (SUNY)
Stony Brook, New York 11794

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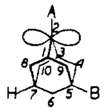
Several instances have been published in which 2,5-disubstituted adamantane derivatives were used as probes in research aimed at stereoselection in additions to trigonal carbon; these have included the capture of nucleophiles by carbocations,[1] carbenes,[2] and ketones[3] and of electrophiles by olefins.[4] The principal merit of these probes is that they are essentially free from steric bias, yet they direct facial stereoselection by virtue of electronic induction by substituent B. The results to date demonstrate that



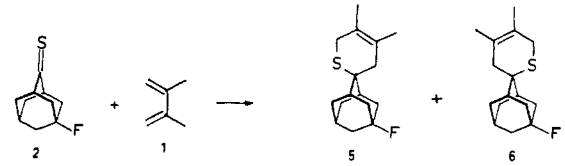
an electron-withdrawing substituent at C_5 causes syn approach by *both* nucleophiles and electrophiles. We have interpreted these results in terms of a model proposed by Cieplak[5] to explain the well-known axial approach observed in the reduction of cyclohexanones; this model holds that hyperconjugation of antiperiplanar σ bonds with the incipient σ^* orbital is responsible for the selectivity. Extending the model to adamantanones and to electrophiles, we correctly predicted that syn approach is favored with an electron-withdrawing substituent B, because the C_1–C_8 and C_3–C_{10} bonds are the better donors for hyperconjugative σ assistance. Recent X-ray[6] and NMR[7] results are consistent with an influence of hyperconjugation even on the ground-state structures of such electronically perturbed cations and adamantanone complexes. The corollary of this work has been the general rule that the approach during addition to trigonal carbon is always anti to the electron richest bond,[4] sometimes even when steric effects oppose such selectivity.[8] We report here that both thermal and photocycloadditions are accommodated by this prediction.

Table I. Stereochemical Course of Photocycloaddition of 5-Substituted Adamantan-2-ones with Fumaronitrile[a] in Acetonitrile at Room Temperature

5-substituent X	%[b] 7-X	8-X	analysis
F	57	43	VPC, NMR, X-ray
Cl	58	42	VPC, NMR
Br	59	41	VPC, NMR
OH	53	47	VPC, NMR

[a] Comparable results were obtained in those cases in which measurable amounts of adducts were obtainable from the maleonitrile formed by photoisomerization (*cis*-oxetanes *E*:*Z* = 60:40 for X = Cl and Br). [b] Errors ca. ±2%.

We have tested the rule in the Diels–Alder reaction of 2,3-dimethylbuta-1,3-diene (**1**) with 5-fluoroadamantane-2-thione (**2**) (eq 1) and in the photocycloadditions of fumaronitrile (**3**) to several 5-substituted adamantan-2-ones **4**-X (eq 2); we find that the favored approach is indeed syn as predicted, in all instances.



(1)

Treatment of 2 mmol of **2**[9] with 0.1 mmol of hydroquinone and 20 mmol of **1** in 15 mL of toluene at reflux for 3 days[10] gives 80% of a mixture consisting of **5** and **6** in a 2:1 ratio (GC). The isomers were separated and converted into sulfones by means of K_2SO_5 oxidation. The sulfone of the major product was indeed (*E*)-**5**-O_2 as shown by the effect of the shift reagent $Eu(fod)_3$; carbons 8 and 10 were affected more than twice as strongly as carbons 4 and 9 (identified by their ^{19}F coupling), and even C_5 is shifted downfield one third more than C_7. Application of the ^{13}C NMR additivity scheme[11] with the sulfides furthermore leads to carbon resonances correctly predicted to within ±0.3 ppm if the major product is assumed to have the *E*-configuration, whereas the deviations are several ppm if the opposite assumption is used. When **5** and **6** are separately subjected to the exact reaction conditions that gave rise to them, each can be recovered unchanged with no trace of the other: both products are formed in kinetically controlled processes.

This result is noteworthy not only because it agrees with what we anticipate but also because it is opposite to the prediction made on the basis of another model recently proposed to account for Diels–Alder face selectivity.[12]

[†] Columbia University.
[‡] SUNY.

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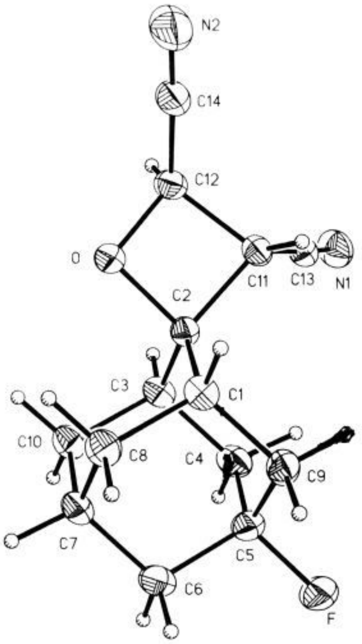
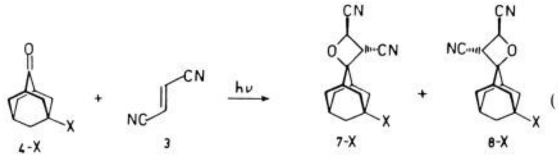


Figure 1. ORTEP structure of **7**-X.

Irradiation at 313 nm of a solution of 1 g of **3** and 0.5 g of **4**-X in 50 mL of spectrograde acetonitrile for 48 h leads[13] to the formation of *trans*- and *cis*-oxetanes and to the cis–trans isomerization of **3**. At low conversions only *trans*-oxetanes were formed (eq 2). After workup the solution gave residues that could be separated by column chromatography to give **7**-X and **8**-X (≥80% chemical yield by means of either VPC or NMR integration). In all instances examined (X = F, Cl, Br, OH), the major isomer (~60:40) was **7**-X (see Table I).



4-X 3 7-X 8-X (2)

The structural assignments were determined by means of ^{13}C NMR; the chemical shifts of both isomers could be calculated on the basis of those of **7**-H and those of adamantane itself in the manner described above. The question of *cis*- or *trans*-nitrile group configuration was determined from the magnitudes of the coupling constants for the oxetane ring protons: they fall within the range 5.5–5.8 Hz, consistent with trans configurations.[14] Finally, the configuration of **7**-F was established independently by means of an X-ray diffraction study (see Figure 1).[15]

In the Diels–Alder reaction, the diene functions as the donor; in the photocycloadditions, the carbonyl π^* state is the nucleophile. Although the mechanisms of the two cycloadditions are different, one being a concerted thermal process and the other involving an exciplex, we believe that bond formation in both cases is assisted by σ delocalization of the electron richer bonds anti to the 5-substituent into the incipient σ^* orbital and that these reactions constitute further evidence for the generality of the rule stated above. We note that several other cycloadditions already in the literature exhibit stereoselectivities explicable on the same basis: these include the Diels–Alder reactions of **9**,[16] the contra-steric axial [2 + 2] cycloaddition of dichloroketene to methylenecyclohexane to give **10** and **11** in 4:1 ratio,[17,18] and the contrasting stereochemistry of [1,3]-dipolar cycloaddition of diazomethane to **12** (100% syn) and **13** (100% anti).[19] The explanations offered or discussed were in all instances different from our own.

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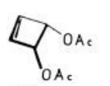

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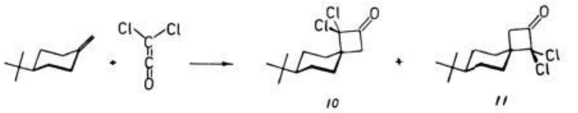

10 11

While we do not wish to assert the hyperconjugation has no rivals as the basis of these effects, it is noteworthy that the rule serves as a simple heuristic device that correctly anticipates the stereochemistry in both thermal and photochemical reactions: bond formation occurs at the face anti to the most electron rich σ bond. This rule can be readily employed to make predictions for the whole, rich variety of pericyclic reactions, and we shall report our results of studies aimed at determining their stereoselectivities in due time.

Acknowledgment. This work was supported at Columbia by the NSF and the AFOSR and at Stony Brook by the NSF and the Petroleum Research Fund; we thank the donors of this fund.

Supplementary Material Available: Tables of ^{13}C and ^{1}H NMR data of all compounds mentioned in this paper and X-ray data for compound **7**-X (21 pages). Ordering information is given on any current masthead page.

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Specific Deuterium Isotope Effects on the Rates of Electron Transfer within Geminate Radical-Ion Pairs

Ian R. Gould* and Samir Farid*

Eastman Kodak Company, Corporate
Research Laboratories, 1999 Lake Avenue
Rochester, New York 14650-2109

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Recent theories of electron-transfer reactions treat the rearranged high-frequency ($h\omega > kT$) internal vibrational modes quantum mechanically, whereas the low-frequency solvent modes are treated classically.[1] The role of quantum effects in the internal reorganization can, in principle, be investigated by the study of isotope effects. The Franck–Condon factors for electron transfer depend upon vibrational overlap and are proportional to the frequencies of the vibrational modes involved in the transition. Thus, isotopic substitution, which modifies these frequencies, should affect the reaction rate. Several examples of isotope effects

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