σ,π Interaction in Halogen-Substituted Biadamantylidene Radical Cations

Stephen F. Nelsen,* Susan J. Klein, Dwight A. Trieber, II, Rustem F. Ismagilov, and Douglas R. Powell

S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1396

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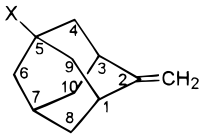
The order of $E^{o\prime}$ and vIP for 4-eq-halogenated-biadamantylidene is F > Cl ≅ Br, and the 5-F-substituted compound is harder to ozidize than the 4-eq-F-substituted one. The former result is most consistent with a detectable resonance contribution through the σ-framework, and the latter with σ-hyperconjugative destablilization proceeding through two pathways being more than double the same effect through one pathway (the Whiffen effect). AM1 calculations predict these results. The facial selectivity for epoxidation and diazetidine formation from 4-eq-halogenated **3** (**4(X)**) is in the order Cl > F > Br, and the 5-fluoro compound (**8**) is less selective than **4(F)** for both reactions. Steric as well as electronic factors might well contribute to these results, neither of which was expected from consideration of σ,π interaction. Cation radical catalyzed chain dioxetane formation from **4(F)** and **3(Cl)** is significantly more face selective than epoxidation or diazetidine formation, as expected on electronic grounds; σ,π interaction should be larger in the radical cation.

Introduction

The advantage of using 5-substituted adamant-2-yl derivatives (such as **1**) for study of substituent effects transmitted through σ-bonds has been pointed out by le Noble and co-workers.[1] Substituents at C(5) do not



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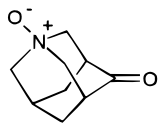

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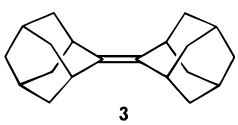
interact sterically with those at C(2) unless the substitutents are quite large,[1g] and any effect seen should be attributable entirely to the electronic differences caused by the substituent. They have shown that the π-bond face selectivity for addition reactions increases as more electron-withdrawing substituents are placed on 5-phenyl groups of **1** and related compounds and that the 5-F compounds give measurable face selectivity differences for a wide variety of reactions involving both additions and eliminations having cationic, anionic, and radical intermediates. The transition state is lower in energy for bond formation or breaking from the face *syn* to the 5-F group in all cases studied. The selectivities observed are relatively small for **1** derivatives but become much larger when the difference between donating ability of σ-bonds on opposite faces of the π-bond is larger, as for 5-azonium compounds such as **2**.[1m] These results were interpreted as unusually clear-cut examples of the Cieplak effect,[2] which predicts stabilization of a transition state for which a better electron-donating σ-bond is *anti* to the stretched bond. Cieplak emphasized stabilization from interaction of the filled σ_{anti} and empty $\sigma^{*\ddagger}$(stretched) bond as the rationalization for the face selectivity.[2] Electron-withdrawing C(5) groups make the 1,9 and 3,4 CC bonds poorer electron donors than the corresponding ones on the unsubstituted face. More recently, on the basis of calculations on nucleophiles adding to **2** and related compounds, Coxon, Houk, and Luibrand[3a] report that the $\sigma_{anti},\sigma^{*\ddagger}$ energy gap is in fact too large to have much of an effect and suggest that the majority of the face selectivity arises from smaller torsional destabilization between σ_{anti} and the filled $\sigma^{\ddagger}$ than when attack is *syn*. Gung and Wolf have emphasized the distortion present in **2** and suggest that steric effects might be principally responsible for the high facial selectivity observed for **2**.[3b]

Because orbital interactions increase as the energy gap between the orbitals decreases, larger σ,π mixing effects will occur when a p orbital at C(2) is more stabilized, and σ-framework, C=C π interactions are larger in alkene radical cations than in the neutral compounds. Biadamantylidene, **3**, gives a stable enough radical cation that its formal redox potential for oxidation, $E^{o\prime}$, can be



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measured by cyclic voltammetry.[4] **3** has about the same $E^{o\prime}$ value as tetraphenylethylene, implying that there must be significant charge delocalization into the alkyl groups of the radical cation, i.e., significant σ,π interaction. Large σ,π interaction in $\mathbf{3}^{\bullet+}$ is indicated spectro-

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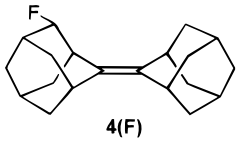
scopically by the unusually large long-range proton ESR splitting constants observed, 6.05 G at the δ position, H(5), and 3.27 G at the aligned γ position H(4-eq).[5] This paper concerns the changes induced by 4-equatorial and 5 substitution of halogen on **3** on the ease of electron removal and the face selectivity for epoxidation with MCPBA,[6] diazetidine formation upon reaction with *N*-methyltriazolinedione,[7] and cation radical chain catalyzed oxygenation to dioxetanes.[8]

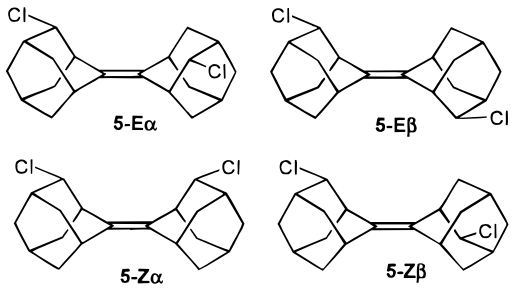
Results: Compound Preparation

The 4-equatorial fluoride, chloride, and bromide of **3**, **4(X)**, were prepared by known methods (see Experimental Section). Wynberg and co-workers[9] reported that chlorination of **3** with chlorine produces dichlorides **5** as well as **4(Cl)** but could not separate the isomers. Tol-

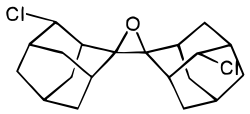


4(F)

stikov and co-workers[10] investigated the polychlorination of **3** using SCl_2 and reported that a single isomer of the dichloride, mp 123−5 °C, was obtained using silica gel chromatography. They identify this compound as the **E**β isomer shown below, but report only the ^{1}H NMR as support. We use α and β to designate isomers with



chlorines on carbons on the same and on opposite π-bond faces because *syn* and *anti* are used in a difference sense here. Neither ^{1}H nor ^{13}C NMR can distingish the **E**α, **E**β, **Z**α, and **Z**β isomers of **5**, each of which has 10 different carbons. Considering the Cieplak effect, it would be surprising for **4(Cl)** to react predominately on the face *anti* to chlorine, which is what obtaining **E**β requires, and our experiments do not support it as a major product. The mixture of dichlorides (mp 121-6 °C) we isolated from the chlorination of **3** by *N*-chlorosuccinimide shows only one vinyl carbon signal by ^{13}C NMR, but there are three *C*HCl peaks, with the major isomer representing about 70% of the mixture by integration. We were not able to separate this mixture. Epoxidation of the olefin mixture followed by silica gel chromatography produced an 85:15 mixture of two chloro epoxides, each of which has 10 different carbons, demonstrating that they are both derived from α dichloro compounds (the epoxides derived from a β dichloride have 20 different carbons). Repeated recrystallization of this mixture provided a crystal of the major dichloro epoxide, shown to be **6** by X-ray crystallography. We presume that the



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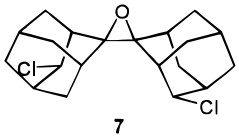

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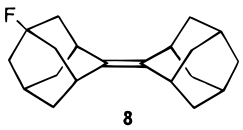
two epoxides are those obtained by oxygenation on the faces *syn* and *anti* to the chlorines of the major olefin present, **5-E**α, and that the 15% isomer is therefore **7**. Unfortunately, we were unable to find conditions which would deoxygenate biadamantylidene epoxides without dechlorination and were unable to use the epoxides to purify an isomer of **5** for further studies. We also tried to achieve a kinetic purification of the dichloro halide mixture by reaction with *N*-methyltriazolinedione, because the diazetidinones are easily cleaved back to olefins,[7] but also failed to achieve useful separation this way, and finally abandoned trying to obtain a pure 4,4′-dichloride.

Both 5-fluoro-**3** (**8**) and 5,5′-difluoro-**3** (**9**) were prepared using the Barton method,[11a] reacting the 2-adaman-



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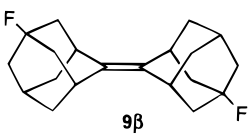

9β

tanone ketazine derivatives with H_2S to give bis-adamantyl substituted thiazolidines, oxidizing to the thiazolines,[11b] and decomposing them in the presence of triphenylphosphine as a thiophile, which has proven successful for preparation of several adamantyl-substituted olefins.[11c−e] The α and β isomers of **9** were separated by silica gel chromatography. The more polar isomer is expected to be α, and it gives two epoxides, each having 10 different carbons, proving the point. An X-ray crystallographic structure of the the less polar isomer proved that it is **9**β. The epoxides,[6] diazetidenes,[7] and dioxetanes[8] were prepared from the halogenated compounds by standard methods.

Results and Discussion: Ease of Electron Removal

Table 1 shows that electron removal from **4(X)** becomes more difficult in the order F < Cl ≅ Br. The accuracy of our $E^{\circ\prime}$ measurements is about 0.005 V, and the Cl and Br compounds have the same $E^{\circ\prime}$ within experimental error. Both field and resonance effects for the halogen substituents might be involved in determining the change in $E^{\circ\prime}$. Extensive studies of substituent parameters have not produced very consistent estimates of the field effect on equilibria and spectroscopic properties for changing halogens. The only parameter often considered relevant for species with saturated carbons intervening between the substituent and the probe center has been the field/inductive parameter σ_I, which depending upon how it was evaluated either decreased in the order F, Cl, Br (Taft,[12]

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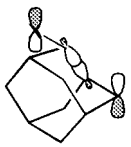
Table 1. Solution Phase $E^{o\prime}$, Gas Phase vIP, and AM1 Calculations of aIP and vIP for 3 and Halogenated Derivatives

compd	$E^{o\prime}$,[a] V vs SCE	rel $\Delta\Delta G°$,[b] kcal/mol	sym	rel aIP [AM1], kcal/mol[c]	vIP (rel $\Delta\Delta H$), eV (kcal/mol)[d]	vIP [AM1] (rel $\Delta\Delta H_f$),[e] eV (kcal/mol)
3 = **4(H)**	1.59_0(0.08)	≡ 0	D_{2h}	≡ 0	7.76 (≡ 0)	8.21 (≡ 0)
4(F)	1.67_7(0.12)	$+2.0_1$	C_1	+4.51	8.01 (+5.8)	8.40 (+4.38)
4(Cl)	1.69_6(0.14)	$+2.4_4$	C_1	+4.69	8.03 (+6.2)	8.42 (+4.84)
4(Br)	1.70_0(0.15)	$+2.5_4$	C_1	+4.71	8.04 (+6.5)	8.41 (+4.61)
8	1.69_3(0.13)	$+2.3_8$	C_s	+4.80	8.08 (+7.4)	8.42 (+4.84)
5-Cl-**3**			C_s	+4.38		
9α	1.88_8(0.15)	$+6.8_7$	C_{2v}	+9.38	8.34 (+13.4)	8.62 (+9.45)
9β	ir 1.94[f]		C_{2h}	+9.49		

[a] $E^{o\prime}$ in CH_2Cl_2 containing CF_3CO_2H and $(CF_3CO)_2O$, vs saturated calomel electrode reference, at −78 °C, 200 mV/s scan rate, calculated as $(E_p^{ox} + E_p^{red})/2$. The numbers in parentheses are $(E_p^{ox} - E_p^{red})$ values in V. [b] Values of formal potential for oxidation relative to **3**, i.e., $23.06(E^{o\prime} - 1.59)$. [c] AM1-UHF calculation on the radical cation and AM1 calculation on the neutral compound, both constrained to planarity of the olefin and bridgehead carbons. Differences in values of ΔH_f(cation) − ΔH_f(neutral) relative to the value for **3**, $\Delta\Delta H_f$ − 184.372, are quoted. [d] Photoelectron spectroscopic vIP, error estimated at ± 0.03 eV. [e] AM1-UHF calculation of vertical ionization potential. [f] No reduction wave observed, even at 1000 mV/s scan rate. E_p^{ox} at 500 mV/s scan rate is reported.

0.50, 0.46, 0.44; Charton,[13] 0.54, 0.47, 0.47), increased (Adcock,[14] 0.39, 0.43, 0.44 [in CCl_4], 0.41, 0.43, 0.44 [in MeOH]), or was irregular (Grob,[15] converted to a similar scale by Adcock,[14] 0.47, 0.46, 0.48). Any difference in field effect between these halogens is clearly quite small, which presumably makes other small effects able to change the order. More recently, Taft and Topsom[16] have replaced σ_I by field (σ_F) and electronegativity (σ_x) parameters but suggest that the electronegativity effect is negligible even for attachment at the second atom from the probe center, so it can be ignored for our compounds. This is clearly consistent with our data; F is the most electronegative halogen, but 4-F-**3** is the easiest to oxidize. They quote σ_F values for F and Cl of 0.44 and 0.45 but do not consider Br,[16] presumably because careful evaluation of σ_F using chemical shift correlations by Reynold and co-workers[17] produced the same σ_F for all three within the statistical error they quote: (F, Cl, Br: 0.454 ± 0.030, 0.454 ± 0.013, 0.450 ± 0.022). F < Cl ≅ Br is the $E^{o\prime}$ order observed for *p*-substituted diarylamines (0.94, 1.02, 1.06 V, respectively)[18a] and triarylamines (0.95, 1.04, 1.05 V, respectively),[18b] which have five σ-bonds between the halogen and the nitrogen which is the site of highest formal charge density, but also clearly have significant π-resonance effects. It appears to us that a detectable resonance effect (σ-conjugation of the halogen lone pair with the C(2) p orbital through the aligned C_3-C_4 bond as indicated in **A** below), so that the



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better resonance electron-donating ability of the F lone pair is able to make oxidation easier, is most consistent with the F < Cl ≅ Br $E^{o\prime}$ order we observed for **4(X)**, although the difference is small. AM1 calculations of the adiabatic ionization potential aIP, the gas phase enthalpy analogue of formal oxidation potential, are also included in Table 1. Although these calculations show $\Delta\Delta H_f$ to be about twice as large as the solution $\Delta\Delta G°$ values, they predict the 4-F compound to be slightly easier to oxidize than the 4-Cl and 4-Br compounds, as observed. AM1 calculations do a surprisingly good job of predicting the effect of halogen substitution on the thermodynamics for electron removal, suggesting that differences in solvation energies are not very significant for F-, Cl-, and Br-substituted compounds.

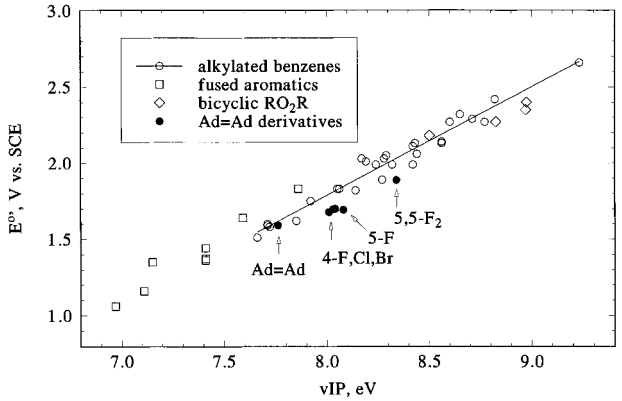

Figure 1. Plot of $E^{o\prime}$ vs vIP for alkylated benzenes (correlation line shown),[20a] fused aromatic compounds,[20b] and bicyclic peroxides,[20c] along with those for **3** derivatives (filled circles).

The vertical ionization potentials (vIP) measured by photoelectron spectroscopy also appear in Table 1. All show vibrational fine structure in the first (π) ionization band, with the most intense band (whose maximum is reported as vIP) the 0 → 1 feature, as observed for a wide variety of tetraalkyl olefins.[19] We found a 0.16 eV (1290 cm^{-1}) separation between the first and second vibrational bands of **3**, consistent with the 1320 ± 50 cm^{-1} reported by Mollere and co-workers,[19] although the vIP we report is 80 meV lower than theirs. The same order with halogen change was obtained for vIP as for $E^{o\prime}$, although the differences are also small compared to the experimental error, which we estimate to be on the order of 0.03 eV. Figure 1 shows a plot of $E^{o\prime}$ vs vIP for these compounds with literature data for alkylated benzenes,[20a] fused aromatics,[20b] and bicyclic peroxides,[20c] all systems which are known not to relax in geometry very much upon electron removal. Unsubstituted **3** lies close to the alkylated benzene correlation line shown, and **4(X)**

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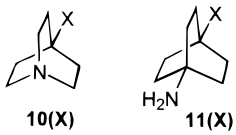
Table 2. Halogen Atom Effect on Proton Transfer Equilibria and Vertical Ionization Potential of 4-Halogenated Quinuclidines (10(X)), in kcal/mol

substit	$\Delta\Delta G°$(prot)	$\Delta\Delta G°$(prot) gas[b]	ΔvIP gas[c]
F	3.51	7.1	
Cl	3.42	7.8	11.3
Br	3.67		9.2

[a]Reference 15. [b]Reference 21. [c]Reference 22.

derivatives have a small (ca. 2.3 kcal/mol) lowering of $E°'$ relative to hydrocarbons of similar ionization potential. There appears to be very little difference in solvation energies between different **4(X)**$^{\bullet+}$ examples because the order as halogen is changed is the same for vIP and $E°'$.

There is well-documented evidence for σ-resonance being detectable in one δ-substituted system, 4-X-quinuclidine, **10(X)**, for which pK_a in water,[15] gas phase



10(X) **11(X)**

acidity,[21] and vIP[22] measurements have been reported for a wide range of subsitutents (see Table 2 for the F, Cl, and Br data only); **10**$^{\bullet+}$ is too unstable in solution to allow measurement of $E°'$ values. Adcock, Grob, and Taft et. al.[21] point out that considering all substitutents, there is an "apparent dependence" upon the resonance parameter for both the solution and gas phase acidity data, although data for the halogenated compounds appears rather irregular. A regression analysis gives a significant ρ_R when resonance substituent constants σ_R are employed as well as σ_F values in a $\sum\sigma_i\rho_i$ regression ($|\rho_F/\rho_R| = 5.4$ for solution, 5.6 for the gas phase data). The same halogen order, **10(F)** being easier to protonate than **10(Cl)**, was found in the gas phase as we find for **3** derivatives and interpreted (along with data for other substitutents) as **10** being a σ-conjugated system showing a resonance effect. The observed ease of protonation order is different in water (Cl < F < Br), where the differences are significantly smaller, which would tend to make even small solvation energy differences more apparent. As might be expected, the ρ_R term drops out for acidities of the ϵ-substituted system, 4-amino-1-substituted bicyclo[2.2.2]octanes **11(X)**, where an additional σ-bond separates the substituent and the probe and the probe lone pair is also not aligned with the σ framework.[21] Because the σ-conjugation effect suggestion for **10(X)** seems reasonable from the protonation data, it seems odd that the vertical ionization potentials measured by photoelectron spectroscopy[22] show no hint of a resonance effect.[23] It may be noted that although **10** has an additional σ-bond between the substitutent and the probe center than 4X-substituted-**3**, there are three equivalent σ-pathways for interaction of a symmetrical X group with the probe center of **10(X)** but only one for **4(X)**.

We shall now consider compound **8**. The δ-fluoro compound **8** is detectably harder to oxidize than is the γ-fluoro **4(F)**, despite the fluorine being one bond further away from C(2). This result cannot reasonably be attributed to experimental error because it occurs both experimentally and in the calculations for both adiabatic and vertical ionization. $E°'$ is 0.3_7 kcal/mol higher for **8** than for **4(F)**, calculated aIP is 0.29 kcal/mol higher, and the experimental vIP is 1.6 kcal/mol higher and is calculated to be 0.46 kcal/mol higher. Grob and coworkers found a corresponding anomaly for the solvolysis rates of 4-eq and 5-substituted 2-adamantyl *p*-nitrobenzenesulfonates.[24] They determined $\rho_I = -0.80$ for the 4-eq-substituted compounds, which is significantly smaller than the -1.02 found for the 5-substituted ones and noted that this was not expected because field effects drop-off significantly when an additional saturated carbon is introduced between a probe and a substituent. As already pointed out by le Noble,[25] a factor which should increase the effectiveness of a 5-F substituent is that there are two equal length σ-bond pathways for 5-F but only one for 4-F. This does not, however, really remove the problem in explaining 5-substituents having a larger effect than 4-substituents, because the drop-off in field effect for introducing another saturated carbon is expected to be larger even with the factor of two. Using the Taft rule-of-thumb that introducing a saturated carbon between a charge-bearing center and a probe decreases the inductive effect by a factor of 0.45,[26] the inductive effect for 4-F should be $(0.45)^2 = 0.20$ times that for a directly attached fluorine, and that for 5-F $2 \times (0.45)^3$, or 0.18.[26b] We suggest that the reason for the turnaround is revealed in the ESR spectrum of **3**$^{\bullet+}$. A spectroscopic measurement which is clearly related to the effectiveness of through-bond and through-space interactions between C(2) and substituents at the 5- and 4-eq positions is the size of the hydrogen ESR splitting constants, and $a(H_\delta[5])$ is 1.85 times as large as $a(H_\gamma$[4-eq]).[4] Whiffen first pointed out[27a] that when a compound having $C_\beta H$ has a SOMO with amplitudes on spin-bearing C_α atoms i and j having coefficients c_i and c_j, the splitting constant will be given by $a(H_\beta) = (c_i + c_j)^2 Q$, where Q is a proportionality constant which converts α

(20) (a) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasimo, L.; Wrightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968. Data from Table 3, with the NHE $E°'$ values converted to the SCE scale by subtracting 0.24 V. (b) Parker, V. D.; *J. Am. Chem. Soc.* **1976**, *98*, 98. Clar, E.; Schmidt, W. *Tetrahedron* **1975**, *33*, 2093; **1977**, *35*, 1027. Schmidt, W. *J. Phys. Chem.* **1966**, *66*, 828. (c) Nelsen, S. F.; Teasley, M. F.; Bloodworth, A. J.; Eggelte, H. J. *J. Org. Chem.* **1985**, *50*, 3299.

(21) Adcock, W.; Anvia, F.; Butt, G.; Cook, A.; Duggan, P.; Grob, C. A.; Marriott, S.; Rowe, J.; Taagepera, M.; Taft, R. W.; Topsom, R. W. *J. Phys. Org. Chem.* **1991**, *4*, 353.

(22) Bieri, G.; Heilbronner, E. *Helv. Chim. Acta* **1974**, *57*, 546.

(23) (a) Topsom[23b] points out that there is an excellent correlation with σ_F. Using Charton's σ_I values[13] (which are equivalent to σ_F, p 291, ref 8b, and include all the substituents used) the average deviation for all 15 vIP values is 0.05 eV, and **10(OH)**, which has the most powerful resonance group, is 0.07 eV harder to ionize than the regression predicts, instead of being easier. The worst deviator is **10(I)**, 0.14 eV easier to ionize, and **10(Br)** is 0.06 eV easier to ionize than the regression predicts. As shown in Table 2, **10(Br)** is 2.1 kcal/mol easier to oxidize than **10(Cl)**, which is also the wrong direction for a resonance effect. (b) Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 193 (p 209 for the plot, p 227 for discussion).

(24) Grob, C. A.; Wang, G.; Yang, X. *Tetrahedron Lett.* **1987**, *28*, 1247.

(25) Reference 1c, footnote 15.

(26) (a) Taft, R. W., Jr. *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; p 594. (b) In the light of more recent work, the 0.45 drop-off appears to be too high. Using the most extensive data set available, Charton's,[13] there are 19 cases for which $\sigma_I(CH_2Y)/\sigma_I(Y)$ are available. The ratios range from 0.18 (for Y = CH=CH_2) to 0.50 (for Y = C≡CH and OAc) are 0.36−0.43 for the halogens, and average to 0.36. The ratio does not correlate well with σ_X.[12b] The point that using any reasonable drop-off does not make an additive two-pathway δ-substituted system have a larger effect than a γ-substituted system is not changed.

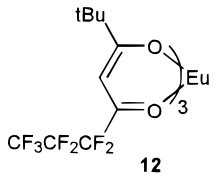
(27) (a) Whiffen, D. H. *Mol. Phys.* **1963**, *6*, 223. (b) Dixon, W. T. *J. Chem. Soc., Chem. Commun.* **1969**, 559. (c) For recent application in fullerene radical spectra, see Percivcal, P. W.; Wlodek, S, *Chem. Phys. Lett.* **1992**, *196*, 317. Borghi, R.; Lunazzi, V.; Placucci, G.; Krusic, P. J.; Dixon, D. A.; Matsuzawa, N.; Masafumi, A. *J. Am. Chem. Soc.* **1996**, *118*, 7608. (d) Roth recently argued that there was a logical error in deriving the Whiffen effect [Roth, H. D.; Lakkaraju, P. S. *J. Phys. Chem.* **1993**, *97*, 13403], but as Williams has pointed out, these arguments are not correct [Williams, F. *J. Phys. Chem.* **1994**, *98*, 8258].

spin density to $a(H_\beta)$. This makes the splitting constant observed twice as high as an additive effect if $c_i = c_j$: an additive effect would be proportional to $2c_i^2$, while the Whiffen expression gives $4c_i^2$. The Whiffen effect has been used repeatedly for rationalizing ESR splitting constants, but Dixon pointed out[27b] (without mentioning Whiffen) that the effect relates to the nodal properties of orbitals and will affect chemical as well as spectroscopic properties. Both the experiments and the AM1 calculations indicate that the Whiffen effect applies to ionizations, although it is not trivial to think about it applying quantitatively to **3** because there are several σ-orbitals having different symmetry properties, through which effects are in principle transmitted between C_2 and C_5. The AM1 calculations do successfully predict the perhaps unexpected experimental result that having two σ-pathways for δ interaction in these adamantane derivatives causes a larger δ-F than γ-F effect.

Both isomers of **9** show unexpected effects in their cyclic voltammograms. It is anomalous that $\Delta\Delta G°$ for the *syn* isomer, **9**α, was determined to be larger than twice that for **8**; the number reported is 2.9 times larger. AM1 calculations give ratios slightly under 2 for ΔaIP, and both experiment and calculation give similar results for vIP of these two compounds. It is also anomalous that the *anti* isomer **9**β appears from its irreversibility in the CV experiment to be significantly shorter-lived than the *syn* isomer. We suspect that $E°'$ has been determined inaccurately for **9**α, which is probably too short-lived to measure an accurate $E°'$.

Results and Discussion: Facial Selectivity

Although the differences in NMR chemical shift between *syn* and *anti* adducts to C(2) double bonds of 2-unsaturated adamantyl systems are rather small, the rigidity of these systems makes the identification of such diastereomeric pairs by NMR quite reliable.[1] The 4-eq-substituted adducts were identified by ^{1}H NMR of the C*H*X signals. The *syn* dichloro epoxide **6** (identified by X-ray crystallography) has its C*H*Cl signal at δ 4.47, while that of **7** occurs at δ 4.30, and the epoxides from **4(X)** also showed the major isomer (assigned as *syn*) signal downfield of that of the minor isomer. The difference in chemical shift increases in the order F (0.10) < Cl (0.17) < Br (0.23) for these epoxides. The difference in chemical shift for the two isomers increases in the same order for the diazetidines, and the differences are larger: F (0.48), Cl (0.57), Br (0.66). We have not separated the isomers of any diazetidine adducts, which decompose during silica gel chromatography, but addition of the lanthanide shift reagent Eu(fod)$_3$ (**12**) to the



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adducts from **4(F)** (major isomer, δ 5.46; minor isomer, δ 4.98) produced over twice as great a downfield shift for the major isomer (downfield) peak as for the other one, consistent with the assignment of the major peak as the *syn* adduct, so the hydrogen signal being observed is closer to the complexed europium. The difference in chemical shifts for the dioxetanes is F (0.40), Cl (0.17). The **8** and **9** adducts show the major isomer C*H*F signal upfield of the minor isomer, with a larger difference for the diazetidines than for the epoxides: epoxides from **8** (0.08), **9** (0.15); diazetidines **8** (0.63), **9** (0.45). Eu(fod)$_3$ addition to the diazetidines from **8** gave twice as large a downfield shift for the major isomer (δ 90.4) as for the minor (δ 91.0), again consistent with the major isomer being *syn*.

Table 3. Facial Selectivity for Additions to the Double Bond of Halogenated 3

	epoxidation[a]		diazetidination[b]		oxygenation[c]	
compd	ratio[d]	$\Delta\Delta G^{‡}$ [e]	ratio[d]	$\Delta\Delta G^{‡}$ [e]	ratio[d]	$\Delta\Delta G^{‡}$ [e]
4(F)	2.6	0.5_7	2.5	0.5_5	9.0	0.8_5
4(Cl)	3.0	0.5_9	2.8	0.6_1	24	1.2_3
4(Br)	2.5	0.5_0	2.3	0.5_0		
8	1.9	0.3_5	2.4	0.5_2	6.7[f]	0.7_3
9α	2.5	0.5_0	6.5	1.1	g	

[a]Reaction with MCPBA at 0 °C in CH_2Cl_2. [b]Reaction with **13** at 25 °C in CH_2Cl_2. [c]Reaction of the radical cation with O_2 at −78 °C in CH_2Cl_2. [d]*syn*/*anti* product ratio. [e]Unit, kcal/mol. [f]Anomalous relative carbon shifts compared to the other cases; see text. [g]See text.

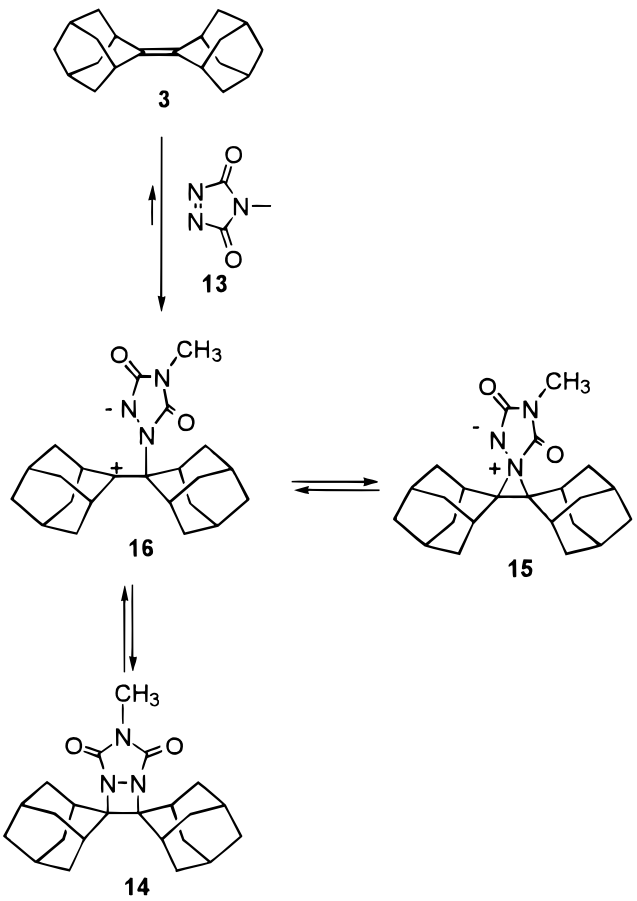
The facial selectivity data for 25 °C epoxidations of the halobiadamantylidenes with *m*-chloroperbenzoic acid appear in Table 3. The selectivity for **8** is within experimental error of that found by Srivastava and le Noble for 5-F-**1** (*syn*/*anti* 1.94 [$\Delta\Delta G° = 0.3_9$ kcal/mol]).[1b] The Cl > F > Br facial selectivity order for epoxidation of **4(X)** only represents small $\Delta G^{‡}$ changes, but the ratios can be measured rather accurately, and we do not doubt the order observed. le Noble and co-workers[1a] found the same order for reduction of 5-haloadamantanones by sodium borohydride in methanol at 0 °C: halogen *syn*/*anti* hydride attack ratio [$\Delta\Delta G^{‡}$, kcal/mol] F, 1.6_3 [0.27]; Cl, 2.0_3 [0.38]; Br, 1.4_4 [0.20]. This order is different from that for ease of oxidation. If the electron-donating ability of the alkyl groups were the only factor affecting facial selectivity, we would have expected the order to be the same. Although we do not know why the difference occurs, it suggests that more than one factor is probably contributing to the facial selectivity ratio; steric differences are an obvious possibility.

The *syn*/*anti* ratio is significantly higher for 4-F than for 5-F substitution, 2.6 for **4(F)** and 1.9 for **8**; so moving an F substituent from C_4 to C_5 has opposite effects on ease of electron removal and facial selectivity. We would expect the through-bond portion of the electronic effect to be smaller for epoxidation than for electron removal, because the importance of through-bond interaction between C(2) and the F ought to decrease with less stabilization of the C(2) orbital at the transition state, and there is clearly more C(2) orbital stabilization in the radical cation than at the epoxidation transition state. It seems possible to us that decreasing the importance of hyperconjugation (which makes the 5-F substitution more important than 4-F) might make the electronic effect be larger for 4-F. On the other hand, part of the facial selectivity might be steric in origin.

Reaction of **3** with *N*-methyltriazolinedione, **13**, to give the diazetidine **14** proceeds through aziridinium imide intermediate **15**,[28a] but kinetic studies show that **15** does not revert to starting materials significantly at room temperature,[28b] so that the facial selectivity should be that for bonding of **13** to the two faces, if rearrangement of **15** to the diazetidene **14** is rapid compared single-bond

(28) (a) Nelsen, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 5548. (b) Nelsen, S. F.; Klein, S. J. *J. Phys. Org. Chem.* **1997**, *10*, 456.

Scheme 1



rotation in the hypothetical singly C−N bonded intermediate **16** (see Scheme 1). Experimentally a similar pattern of results to that of the single-step epoxidations is observed, and the results for **4(X)** are essentially the same, as shown in Table 3. The difference between these reactions for **8** corresponds to under a 0.2 kcal/mol difference in $\Delta\Delta G^{\ddagger}$, which we believe is too small to interpret usefully.

The halogen effect on *syn* and *anti* transition states is what is needed to properly calculate the face selectivity for addition reactions to **3**, but the cases studied experimentally are too complex for reasonable transition state calculations. We have instead calculated halogen effects on models for cationic intermediates in electrophilic additions, using Cl^+ and Br^+,**3** adducts for simplicity. The [**3**,Cl]$^+$ pair is optimized by AM1 as the C_2-Cl, C_2'-carbocation in a C_1 unsymmetrical structure twisted 4.2° about the C_2,C_2' bond, $d(C_2C_2')$ = 1.492 Å, and having $d(C_2Cl)$ = 1.803 Å, $\alpha(C_2)$ [the average of the CC_2C bond angles] = 113.1°, $d(C_2'Cl)$ = 2.439 Å and $\alpha(C_2')$ = 119.9°. Stretching the C_2Cl bond leads to migration of Cl from C_2 to C_2', for which the transition state is the chloronium ion (C_{2v} symmetry, $d(C_2C_2')$ = 1.475 Å, d(CCl) = 1.987 Å, average $CC^{+\delta}C$ bond angle α = 118.85°), which lies 2.58 kcal/mol higher in enthalpy than the β-chloro cation.[29] AM1 optimizes [**3**,Br]$^+$ as the C_{2v} bromonium ion, known experimentally to be the result in solution from the work of Brown and co-workers.[30] The AM1 structure has $d(C_2,C_2')$ = 1.470 A, $d(C_2Br)$ = 2.151 Å, α = 118.5°, a shorter CC bond length than that of the best available experimental X-ray structure, (**3**,Br)$^+$(OTf^-)$_3$-$H_3O^+CH_2Cl_2$,[30] for which values averaged over the two (**3**,Br)$^+$ units in the unit cell, with quoted error in parentheses and range of most probable values in brackets: $d(C_2,C_2')$ = 1.492(15) [0.001] A, $d(C_2Br)$ = 2.114(10−20) [0.047] Å, α = 118.8(10) [0.6]°. Not surprisingly, *ab initio* calculations give a better CC distance (1.491), but the CBr distance (2.158) is slightly further from experiment; information on α was not provided.[30] Table 4 summarizes AM1-calculated enthalpy effects for γ-eq halogen substitution at C_4(*syn*) and C_{10}(*anti*) and for δ-F substitution at C_5(*syn*) and C_7(*anti*) on [**3**,Cl]$^+$(open) and [**3**,Br]$^+$(bromonium). The substantially larger *anti*,*syn* $\Delta\Delta H_f$ values calculated for [**3**,Cl]$^+$ than for [**3**,Br]$^+$ appear to be caused by greater pyramidality at C(2) in the former (α = 113.1 for the unsubstituted case) than the latter (α = 118.5). γ-eq-F substitution in the carbocationic ring of [**3**,Cl]$^+$, α = 119.9, causes $\Delta\Delta H_f$ = 0.18 kcal/mol, similar in size to that at the bromonium ions which also have flattened carbons. The $\Delta\Delta H_f$ calculated for γ-eq-F substitution on [**3**,Cl]$^+$ is similar in size to the $\Delta\Delta G^{\ddagger}$ observed for both epoxidation and diazetidination, although the drop-off in $\Delta\Delta H_f$ which is calculated as the halogen is changed is not observed. Interestingly, δ-F substitution is calculated to have the opposite effect, with the *anti* (7-F) compounds having lower enthalpy than the *syn* (5-F) ones. This result presumably incorporates a dipole effect; *syn* C_2-Hal, C_5-F has a less favorable dipole orientation than does the *anti* isomer. The dipole effect would be attenuated in solution, but it seems possible to us that this factor might contribute to the observed lower facial selectivities for 5-F- than 4-eq-F-substituted compounds. As pointed out above, the 5-F-substituted compounds should have larger Cieplak effects but show less facial selectivity.

Table 4. Summary of AM1 Calculations on *syn* and *anti* γ-eq-Halogen and δ-F-Substituted [3,Cl]$^+$ and [3,Br]$^+$

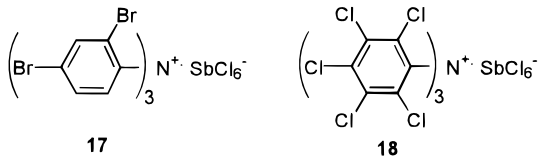
substit	[**3**,Cl]$^+$ (open) ΔH_f(*anti*) − ΔH_f(*syn*)[a]	[**3**,Br]$^+$ (bromonium) ΔH_f(*anti*) − ΔH_f(*syn*)[a]	Δd(CBr)[b], Å
γ-F	+0.53	+0.17	0.14, 0.14
γ-Cl	+0.39	+0.18	0.16, 0.14
γ-Br	+0.29	+0.14	0.17, 0.14
δ-F	−0.49	−0.13	0.23, 0.15

[a] In kcal/mol. [b] Value of $d(C_2'Br) - d(C_2Br)$ for *syn* substitution, followed by that for *anti* substitution. In all cases the halogenated ring has the smaller CBr distance, and the ions are "closed", with d(CC) 1.471 ± 0.0006, and α in the range 117.3 ± 0.1° except for the 5-F-**3** case, where α is 116.6°.

The dioxetane-forming addition reactions are significantly different from the other two studied because they involve olefin radical cation as an intermediate. In contrast to **4(F)** and **4(Cl)**, which undergo efficient cation radical chain catalyzed dioxygenation, little dioxetane forms from the 5-F-substituted compounds when they are treated with 10 mol % aminium salt **17** at −78 °C in methylene chloride. We believe that this is because the oxidizing power of **17** ($E^{\circ\prime}$ = 1.65 V vs SCE under the reaction conditions) is too low for efficient initiation and

(29) Large stretching of the C,Cl bond from the C_{2v} structure cannot be calculated by AM1 without employing UHF because gas phase cleavage to $\mathbf{3}^{\bullet+}$ and $Cl^{\bullet}$ is by far the most favorable process. UHF calculations are still unsatisfactory. The IIS keyword is required to achieve self-consistency at large distances. Although crossing of the enthalpy−distance curve obtained by stretching from the chlorine atom shift transition state with that obtained by moving the chlorine in from a large distance occurs at about a 3.9 Å CC midpoint, Cl distance, AM1 calculations using both the TS and NS01A transition state locating packages fail because dozens of negative force constants are found in this region. We gave up trying to locate a transition state, which would be for $\mathbf{3}^{\bullet+}$,$Cl^{\bullet}$ formation.

(30) Brown, R. S.; Nagorski, R. W.; Bennet, A. J.; McClung, R. E. D.; Aarts, G. H. M.; Klobukowski, M.; McDonald, R.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1994**, *116*, 2448.

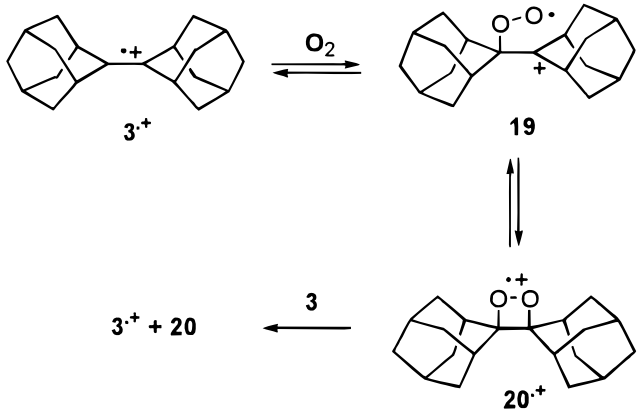


switched to using **18** ($E^{\circ\prime}$ = 2.32 V), generated *in situ* because it is not stable enough to isolate, to initiate these reactions. The dioxetane-forming reactions are significantly more selective than the addition reactions to the neutral compounds, partially because the temperature was lower, but also because $\Delta\Delta G^{\ddagger}$ is higher (Table 3). The oxygenation of these compounds involves formation of one C−O bond to give the β-peroxy carbocationic intermediate **19** (see Scheme 2).[6b] Although **19** has not been detected spectroscopically, it has been trapped, and rotation about the C−C bond in this intermediate before closure has been detected.[31] The initial C−O bond formation should be considered a nucleophilic attack of the olefin radical cation on oxygen, because both carbons of the radical cation are oxidized (one is oxygenated and the other increases in formal charge from $+^1/_2$ to +1), and chlorination of $\mathbf{3}^{\bullet+}$ detectably slows the oxygenation reaction.[31] If C−O bond formation to C(2) of the unsubstituted ring occurred, rotation about the single bond before closure would lead to scrambling of stereochemistry, but we expect significant selectivity for C−O bond formation to C(2) of the substituted ring, so the the carbocation is formed at C(2) of the unsubstituted ring. The ^{13}C NMR shifts for the dioxetanes from 5-F-**3** were anomalous because the major isomer (δ 91.4) appears downfield of the minor (δ 91.2). This might indicate that the *anti* adduct is formed in greater amount; we doubt that the true selectivity for the addition would be in this direction, and perhaps the products were being destroyed by **18**; the ratio observed reflects product reactivity. There is also a strange result for the other reaction catalyzed by **18**, that with α-5,5′-F_2-**3** (**9**), for which the epoxidation and diazetidination reactions give higher selectivity for than for 5-F-**3**, as expected, but roughly equal intensities of *syn* and *anti* *C*HF signals were observed by ^{13}C NMR for the dioxetanes. The product mixture was not separated, so we do not know whether more than one compound is formed. Because it has not been established whether the carbon frameworks in the dioxetane(s) formed have *syn* or *anti* F_2 substitution, we cannot comment usefully on why this unexpected NMR result was obtained. The high oxidizing power of **18** may be causing both anomalous results by reacting with the dioxetane products, but we do not have a satisfactory explanation for these results.

Conclusions

The order of $E^{\circ\prime}$ and vIP for **4(X)**, F > Cl ≅ Br, is most consistent with a detectable resonance contribution through the σ-framework. The more difficult oxidation of **8** than **4(F)** despite the fluoro substituent being one carbon atom more removed from the double bond is consistent with the Whiffen effect, that σ-hyperconjugative destablilization proceeding through two pathways is more than double the same effect through one pathway. AM1 calculations predict these results. The facial selectivity for epoxidation and diazetidine formation from **4(X)** is in the order Cl > F > Br, and **8** is less selective than

Scheme 2



4(F) for both reactions, which is not what would be predicted from the Cieplak effect. Steric as well as electronic factors probably contribute to these results. Cation radical catalyzed chain dioxetane formation from **4(F)** and **4(Cl)** is significantly more face selective than epoxidation or diazetidine formation, as expected on electronic grounds; σ,π interaction should be larger in the radical cation.

Experimental Section

Biadamantylidene (3) was prepared by the method of Meijer and Wynberg[32] in 86% yield: m 183−4 °C, lit.[31] mp 184−7 °C; ^{13}C NMR ($CDCl_3$) δ 133.5 (2 × C_v), 39.0 (8 × $C_\beta H_2$), 37.3 (2 × $C_\delta H_2$), 32.2 (4 × $C_\alpha H_2$), 28.6 (4 × $C_\gamma H_2$).

4-eq-Chlorobiadamantylidene (4(Cl)) was prepared from **3** and *N*-chlorosuccinimide by the method of Wynberg and coworkers[33] in 75% yield: mp 138−40 °C, lit.[33] mp 144−145 °C). ^{13}C NMR ($CDCl_3$) δ 137.2, 130.9, 68.5, 39.7, 39.6, 39.5_1, 39.5_1, 39.3, 38.9, 37.1, 35.8, 32.6, 32.2, 30.6, 30.5, 28.4, 28.3_6, 27.7 [18 signals observed for this 20-carbon compound, so 2 signals are unresolved]; HRMS calcd for $C_{20}H_{27}Cl$ 302.1801, found 302.1807.

4-eq,4′-eq-Dichlorobiadamantylidene (5). A mixture of adamantylidene (**3**, 650 mg, 2.42 mmol) and *N*-chlorosuccinimide (630 mg, 4.86 mmol) in 200 mL of methylene chloride was stirred at room temperature for 72 h, and the mixture was diluted with methylene chloride, washed with water, dried with magnesium sulfate, and concentrated to a powder. Silica gel chromatography using 10:90 methylene chloride:hexane as eluent removed some **4(Cl)**, and more was removed by recrystallization from methanol to give 700 mg of a white solid which appeared by NMR to be a mixture of **5** isomers (mp 121−6 °C, 86%): ^{13}C NMR ($CDCl_3$) δ 134.6, 67.8_2, 67.7_8, 67.7, 39.9, 39.6, 39.4, 39.3, 39.2, 38.7, 38.6, 38.5_2, 38.5_0, 35.4_6, 32.7, 32.6, 32.5, 31.1, 30.8, 30.3, 27.5, 27.4.

***syn*- and *anti*-Eα-4-eq,4′-eq-Dichlorobiadamantylidene Epoxide (6 and 7).** Using the proceedure given below, 300 mg (0.9 mmol) of the above **5** mixture was epoxidized with 218 mg (1.0 mmol) of *m*-chloroperbenzoic acid. Silica gel chromatography using 50:50 methylene chloride:hexane as eluent gave 200 mg of a mixture of epoxides, and silica gel chromatography using 10% ethyl acetate in hexane gave a mixture of two α-substituted olefin epoxides (major isomer, ~85%, ^{13}C NMR ($CDCl_3$) δ 73.8, 64.7, 39.9, 37.0, 34.5, 34.4, 30.9, 30.6, 30.1, 26.3; minor isomer δ 64.5, 39.8, 39.6, 37.4, 35.8, 34.9, 30.5 30.3, 28.6). Recrystallization allowed isolation of the major isomer, mp 204−6 °C, shown to be **6** by X-ray crystallography.[34]

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(34) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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4-eq-Fluorobiadamantylidene (4(F)). A solution of **4(Cl)** (170 mg, 0.56 mmol) in 180 mL of acetonitrile was treated with silver fluoride (400 mg, 3.15 mmol) in a flask wrapped with aluminum foil to exclude light, the mixture was sonicated for 9 h, solids were removed by filtration through Celite, solvent was removed by distillation under vacuum, and the residue was recrystallized from ethanol. Chromatography on 80−200 mesh silica gel, eluting with 10:90 methylene chloride: hexane, gave 140 mg of **4(F)** (90%): m 184−6 °C; ^{1}H NMR ($CDCl_3$) δ 4.50 (dt, J = 51.3, 3.7 Hz, C_4HF), 3.11 (m), 2.87 (dt, J = 10.3 Hz, 2.9, 2H), 2.83 (m), 2.14 (3 H), 1.77−1.92 (m, 12H), 1.58−1.69 (m, 6H), 1.48 (m, 2H); ^{13}C NMR ($CDCl_3$) 137.4, 129.3 ($^3J_{CF}$ = 10.5 Hz, C_2), 95.5 ($^1J_{CF}$ = 183 Hz, C_4HF), 39.7, 39.6, 39.5, 38.9, 37.1, 36.9 ($^2J_{CF}$ = 19 Hz, C_3H), 35.9 ($^3J_{CF}$ = 8 Hz, C_9H_2), 33.1, 32.7 ($^2J_{CF}$ = 19 Hz, C_5H), 32.6, 32.3, 31.1, 30.5, 28.4, 27.4 [2 signals not resolved]; HRMS calcd for $C_{20}H_{27}F$ 286.2097, found 286.2095.

4-eq-Bromobiadamantylidene (4(Br)). A solution of **4(OH)** (mp 188 °C, prepared by the method of Wynberg and co-workers,[9] 610 mg, 2.14 mmol) in 60 mL of 48% hydrobromic acid was refluxed for 16 h, cooled, and added to 60 g of ice water. The product was extracted with 3 × 120 mL portions of hexane, dried over magnesium sulfate, filtered, and concentrated, followed by sublimation (100 °C, 0.5 Torr) to give 500 mg (78%) of 4-eq-Br-**3**, dec 120−3 °C: ^{1}H NMR ($CDCl_3$) δ 4.5 (br s, 1H), 3.1 (br s, 1H), 2.9 (m, 3H), 1.6−2.4 (m, 22H); ^{13}C NMR ($CDCl_3$) δ 137.2, 131.2, 65.4, 40.1, 39.7, 39.6, 39.5$_2$, 39.4$_7$, 37.1, 33.2, 32.5, 32.2, 31.3, 30.6, 28.3, 27.8 [4 signals not resolved]; HRMS calcd for $C_{20}H_{27}Br$ 346.1296, found 346.1310.

***syn*(α)- and *anti*(*β*)-5,5′-difluorobiadamantylidene (9)** were prepared by the Barton method of decomposing cyclic azo sulfides.[11] The ketazine of was prepared in 85% yield by refluxing 5-fluoroadamantan-2-one[1a] with hyadrazine monohydrate in *tert*-butyl alcohol. The thiazolidine was prepared in 47% yield by bubbling hydrogen disulfide through the azine in benzene containing *p*-toluenesulfonic acid, and it was oxidized to the thiadiazine in 97% yield using lead tetraacetate.[11] A mixture of the thiadiazene (1.25 g, 3.43 mmol) and triphenylphosphine (2.11 g, 8.06 mmol) was heated at 125−130 °C under nitrogen, and the product mixture was cooled, dissolved in methylene chloride, and reacted with methyl iodide (1.5 g) to methylate the residual triphenylphosphine. The crude product was chromatographed on 300 g of silica gel (230−400 mesh) using 10% CH_2Cl_2/hexane (1400 mL) followed by 12% CH_2Cl_2/hexane (1200 mL) followed by 15% CH_2Cl_2/hexane (1400 mL) giving 300 mg of each isomer and 40 mg of a mixture (62% yield): HRMS calcd for $C_{20}H_{26}F_2$ 304.2003, found 304.2003. The less polar isomer (silical gel TLC R_f 0.34, 33% CH_2Cl_2/hexane) was *anti*-5,5′-F_2-**3**: ^{13}C NMR ($CDCl_3$) δ 131.9, 92.2 ($^1J_{CF}$ = 184 Hz, C(5)H), 43.6 ($^2J_{CF}$ = 17 Hz, C(4,9)H_2), 42.2 ($^2J_{CF}$ = 17 Hz, C(6)H_2), 37.8 ($^4J_{CF}$ = 2 Hz, C(8,10)H_2), 34.2 ($^3J_{CF}$ = 10 Hz, C(1,3)H), 31.7 ($^3J_{CF}$ = 10 Hz, C(7)H). Identity proven by X-ray crystallography of crystals grown by slow evaporation from pentane.[34] *syn*-5,5′-F_2-**3**, R_f 0.28, m 156−9 °C; ^{13}C NMR ($CDCl_3$) δ 131.9, 92.1 ($^1J_{CF}$ = 184 Hz, C(5)H), 43.6 ($^2J_{CF}$ = 17 Hz, C(4,9)H_2), 42.3 ($^2J_{CF}$ = 17 Hz, C(6)H_2), 37.9 ($^4J_{CF}$ = 2 Hz, C(8,10)H_2), 34.2 ($^3J_{CF}$ = 10 Hz, C(1,3)H), 31.8 ($^3J_{CF}$ = 10 Hz, C(7)H).

5-Fluorobiadamantylidene (8) was prepared by the same route as the difluoro compound, except that hydrazone of 5-fluoroadamantan-2-one was prepared by refluxing a 5-fold excess of hydrazine monohydrate with 5-fluoroadamantan-2-one and condensing with adamantanone to give the monofluoroazine, dec 233 °C, empirical formula established by HRMS, in 83% yield. This compound was carried on through the thiadiazolidine (m 180−182 °C, 85%) and the thiazoline (m 144−6 °C, 90%) to give **8**, mp 159−161 °C, in 59% yield from the thiazoline: HRMS calcd for $C_{20}H_{27}F$ 286.2097, found 286.2097; ^{1}H NMR ($CDCl_3$) δ 3.14 (br s, 2H), 2.85 (br s, 2H), 2.30 (br s, 1H), 1.54−1.89 (complex, 22 H); ^{13}C NMR ($CDCl_3$) δ 135.6, 129.6, 92.8 ($^1J_{CF}$ = 182 Hz, C(4)H), 43.9 ($^2J_{CF}$ = 17 Hz, C(H4,9)H_2), 42.5 ($^2J_{CF}$ = 17 Hz, C(6)H_2), 39.6, 39.5, 38.0 ($^4J_{CF}$ = 2 Hz, C(8,10)H_2), 34.0 ($^3J_{CF}$ = 10 Hz, C(1,3)H), 32.4, 32.1 ($^2J_{CF}$ = 9 Hz, C(7)H), 29.8, 28.5.

Epoxidation of Biadamanylidines. A solution of 1.1 equiv of *m*-chloroperbenzoic acid in methylene chloride was cooled to 0 °C, and a solution of the olefin in methylene chloride was added dropwise over 30 min. After being stirred at 0 °C for 2 h, the solution was allowed to warm to room temperature and washed with a aqueous sodium thiosulfate and sodium bicarbonate, the combined aqueous solutions were back-extracted with methylene chloride, and the organic layers were dried over magnesium sulfate, filtered, and concentrated. From **4(F)**: product ratio determined by ^{1}H NMR integration of the *syn* epoxide C*H*F signal at 4.77 (d, J = 70 Hz); *anti* expoxide signal at 4.67 (d, J = 70 Hz) 2.6:1. From **4(Cl)**: *syn* epoxide C*H*Cl signal at 4.51 (br s); *anti* expoxide signal at 4.34 (br s) 3.0:1. From **4(Br)**: *syn* epoxide C*H*Cl signal at 4.77 (br s); *anti* expoxide signal at 4.54 (br s) 2.5:1. From **8**: ^{13}C NMR integration of the *syn* epoxide *C*HF signal at 91.7 (d, J = 185 Hz); *anti* expoxide signal at 91.8 (d, J = 185 Hz) 1.9:1. From **9**α; *syn* epoxide *C*HF signal at 91.2, *anti* at 91.3 δ, ratio 2.5:1.

Diazetidine Formation from Biadamantylidenes. Roughly equal amounts of olefin and *N*-methyltriazolinedione[36] were stirred in chloroform for 12 h, and the solution was concentrated and chromatographed on silica gel using 25:75 ethyl acetate:hexane as eluant. From **4(F)**: 85% of the mixture of diastereomers, dec 140−3 °C, *syn* diazetidine 5.46 (dt, J = 49, 4 Hz, CHF); *anti* diazetidine 4.98 (dt, J = 49, 4, CHF), methyl signals overlap, ratio 2.5:1. From **4(Cl)**: 78% of the mixture of diastereomers, dec 128−30 °C, *syn* diazetidine 5.11 (br s, CHCl); *anti* 4.54 (br s CHCl), ratio 2.8. From **4(Br)**: 100% of the mixture of diastereomers, *syn* diazetidine 5.44 (br s, CHBr); *anti* 4.78 (br s CHBr), ratio 2.3. From **8**: *syn* 90.4 (d, J = 184 Hz); *anti* 91.0 (d, J = 185 Hz) 2.4:1. From **9**α: *syn* 90.2 (d, J = 185 Hz); *anti* 90.6 (d, J = 185 Hz), ratio 6.5:1.

Dioxetane Formation from Biadamantylidenes. A solution of biadamantylidene in methylene chloride was cooled in a dry ice bath and a stream of dioxygen was bubbled through it for 30 min; then 10−15 mol % of triarylaminium salt dissolved in methylene chloride was added dropwise, the solution was stirred and bubbled with oxygen at dry ice temperature for 2 h, the reaction was quenched with aqueous sodium bicarbonate after the dry ice bath had been removed, the aqueous layer was extracted with methylene chloride, and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated. From **4(F)**: 10 mol % of tris(2,4-dibromophenyl)aminium hexachloroantominate, product ratio determined by ^{1}H NMR integration of the *syn* dioxetane C*H*F signal at 4.77 (d, J = 50 Hz); *anti* expoxide signal at 4.37 (d, J = 50 Hz) 9.0:1. From **4(Cl)**: 10 mol % of tris(2,4-dibromophenyl)aminium hexachloroantimonate, *syn* dioxetane C*H*Cl signal at 4.47 (br s); *anti* dioxetane signal at 4.30 (br s) 24:1. From **4(Br)**: 10 mol % of tris(2,4-dibromophenyl)aminium hexachloroantimonate, very little reaction occurred; olefin:dioxetane ratio approximately 7:1. Usable data were not obtained for this system. From **8**: major dioxetane *C*HF signal at 91.4 (d, J = 180 Hz): minor one at 91.2 (d, J = 180 Hz) 8.1:1. From **9**α, using 20 mol % of **18**, a 1:1 ratio of signals at 91.2 (J = 184 Hz):90.5 (J = 184 Hz).

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Supporting Information Available: ^{1}H NMR spectra of **4(F)**, **4(Br)**, **8**, and **9*β*/9**α mixture and ^{13}C NMR spectra of **8**, **9**α, and **9*β*** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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