π^*/σ^* Orbital Mixing. Synthesis and Excited-State Studies of 7-Chloro-2-(trimethylsiloxy)norbornene and 9-Chloro-3-methoxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene[1]

John J. Nash,[†] Dean V. Carlson,[†] Annette M. Kasper,[†] Dan E. Love,[‡] Kenneth D. Jordan,*[,‡] and Harry Morrison*[,†]

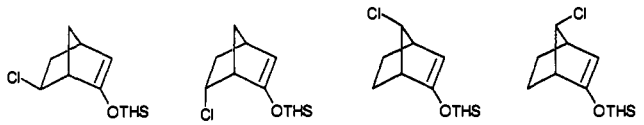
Contribution from the Departments of Chemistry, Purdue University, West Lafayette, Indiana 47907, and University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received September 4, 1992[⊗]

Abstract: *anti*-7-Chloro-2-(trimethylsiloxy)norbornene (AntiCl) and *syn*-7-chloro-2-(trimethylsiloxy)norbornene (SynCl) as well as the epimeric *exo*-9- and *endo*-9-chloro-3-methoxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (GExoCl and GEndoCl, respectively) have been synthesized, their electronic absorption and electron transmission (ET) spectra have been determined and their photochemistry at 254 nm has been studied. MO calculations have been carried out to aid in the interpretation of the spectra. In contrast to *exo*-6-chloro-2-(trimethylsiloxy)norbornene (ExoCl), the calculations show that the LUMO's of AntiCl and SynCl contain relatively little C–Cl σ^* character, similar to *endo*-6-chloro-2-(trimethylsiloxy)norbornene (EndoCl). This is consistent with the relatively low (compared to ExoCl) quantum efficiencies of disappearance for these compounds (Φ_{dis}(AntiCl) = 0.0072, Φ_{dis}(SynCl) = 0.0027). The ET spectra reveal that the π^* levels in all of the chloro-substituted compounds are appreciably stabilized relative to that of 2-(trimethylsiloxy)-norbornene (TMSNB). However, a natural bond orbital (NBO) analysis shows that much of this stabilization derives from electric field (*i.e.*, inductive) effects. Only in the case of ExoCl does the NBO analysis indicate sizable through-space (TS) and through-bond (TB) coupling between the π^* and C–Cl σ^* orbitals. Ab initio calculations on the extended chloro enol ethers GExoCl and GEndoCl (*i.e.*, γ-chlorides) show that the LUMO's of these molecules contain a small amount of C–Cl σ^* character. In addition, an NBO analysis shows that there are small TB interactions between the enol ether π^* and C–Cl σ^* orbitals in both GExoCl and GEndoCl. However, photoinduced cleavage of the C–Cl linkage following $\pi \rightarrow \pi^*$ excitation at 254 nm is not observed in these compounds.

I. Introduction

Orbital interactions between distal functionalities are important for a wide range of chemical processes, including electron transfer and excitation transfer.[2] As part of our continuing interest in the chemical consequences of orbital interactions in polyfunctional molecules as a potential mechanism for the photoactivation of distal functionalities,[3] we recently reported on the photochemistry and photophysics of the *exo* and *endo* isomers of 6-chloro-2-(trimethylsiloxy)norbornene (ExoCl and EndoCl, respectively).[4]



ExoCl EndoCl AntiCl SynCl

Ab initio calculations predict, and the ultraviolet absorption and electron transmission spectra give evidence for, the admixture of an appreciable C–Cl σ^* component in the predominantly π^* LUMO of ExoCl but not in that of EndoCl. The mixing of antibonding C–Cl σ^* character into the LUMO should facilitate C–Cl homolysis upon photochemical excitation, and such is indeed observed with ExoCl, which is approximately 8-fold more reactive than EndoCl.[4]

Herein, we extend our earlier studies to include the related pair of isomers *anti*-7- and *syn*-7-chloro-2-(trimethylsiloxy)-norbornene[5] (AntiCl and SynCl, respectively). In these two compounds, π^*/σ^* orbital mixing (σ^* refers to the C–Cl σ^* orbital unless specified otherwise) is expected to be significantly less important than in ExoCl. In fact, in the absence of the trimethylsiloxy moiety, such mixing would be symmetry forbidden. The presence of the trimethylsiloxy substituent lowers the symmetry, leading to the possibility of small interactions between the π^* and C–Cl σ^* orbitals. AntiCl and SynCl are herein characterized by means of their ultraviolet absorption and electron transmission spectra as well as by means of MO calculations. In addition, the quantum yields of disappearance upon $\pi \rightarrow \pi^*$ excitation have been measured.

The electronic coupling between the π^* (or π) and C–Cl σ^* (or σ) orbitals can occur by means of the through-space (TS) or through-bond (TB) mechanisms.[6] The TS coupling is defined as the coupling due to direct overlap between the localized π^* (or π) and C–Cl σ^* (or σ) orbitals, while the TB coupling mechanism involves coupling with the C–C σ and σ^* orbitals of the connecting bridge. It should be noted that the mixing of two localized antibonding orbitals (*i.e.*, π^* and C–Cl σ^*) is only relevant to experimental processes involving electron capture into these orbitals or from promotion of an electron to such orbitals (*i.e.*, following electronic excitation) and would generally be unimportant for ground-state processes.

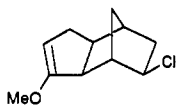
It is also of interest to determine whether there is appreciable

[†] Purdue University.
[‡] University of Pittsburgh.
[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1993.

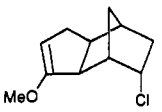
(1) Organic Photochemistry. 100. Part 99. Lu, Y.; Carlson, D.; Morrison, H. *J. Am. Chem. Soc.* **1993**, *115*, 115. Abstracted, in part, from the Doctoral Dissertation of John Nash, Purdue University, December 1991.
(2) See for example: Paddon-Row, M. N.; Jordan, K. D. In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1988; Chapter 3.
(3) Morrison, H. A. *Rev. Chem. Intermed.* **1987**, *8*, 125.
(4) Maxwell, B. D.; Nash, J. J.; Morrison, H. A.; Falcetta, M. L.; Jordan, K. D. *J. Am. Chem. Soc.* **1989**, *111*, 7914.
(5) Nash, J. J.; Morrison, H. *J. Org. Chem.* **1990**, *55*, 1141.
(6) (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (c) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696. (d) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245.

0002-7863/93/1515-8969$04.00/0

π^*/σ^* mixing between more remote π^* and C–Cl σ^* groups. To address this issue, *exo*-9- and *endo*-9-chloro-3-methoxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (denoted GExoCl and GEndoCl,



GExoCl



GEndoCl

respectively) have been prepared and studied spectroscopically, photochemically, and theoretically. In these "γ-chlorides", the C–Cl and enol ether moieties are separated by an additional methylene unit in comparison to the β-chlorides described above. A significant difference between the β-chlorides and the γ-chlorides is that the distance between the two functionalities in the γ-chlorides should preclude significant TS interactions. Consequently, any π^*/σ^* mixing should result primarily from TB coupling of the two functionalities.

II. Computational Methodology

The ab initio molecular orbital calculations were carried out using the Gaussian 86[7] or Gaussian 90[8] program. Several studies have appeared[9] that show that the STO-3G[10] basis set is adequate for describing TB coupling through norbornyl rings. However, more flexible basis sets might be expected to be important for describing TS coupling between the π^* and C–Cl σ^* (or between the π and C–Cl σ) orbitals. For this reason, MO calculations were carried out on TMSNB, ExoCl, EndoCl, AntiCl, and SynCl[11] using both the STO-3G and 3-21G[12] basis sets. The trends in the π^* orbital energies are similar with the two basis sets. For example, the π^* orbital of ExoCl is predicted to be 0.43 and 0.42 eV more stable than that of EndoCl with the STO-3G and 3-21G basis sets, respectively. For this reason, we will focus on the results obtained from the calculations with the STO-3G basis set using Hartree–Fock (HF)/STO-3G optimized geometries.[13]

Natural bond orbital[14] (NBO) calculations were carried out in order to "dissect" the interactions into their TS and TB components.[15] In the NBO calculations, the cannonical HF MO's are localized to generate localized bond and lone-pair orbitals. Although the energies of the π and π^* NBO's of norbornene are quite close to those of ethylene, the same is not true of the energies of the π and π^* NBO's of TMSNB or of the chlorine-substituted compounds because the electric fields due to the polar groups (*i.e.*, C–Cl and O–$SiMe_3$) cause shifts in the energies of the π and π^* NBO's. For this reason, the energies of the π and π^* NBO's, thus obtained, were compared with the corresponding energies of the π and π^* NBO's of the parent, nonhalogenated compounds in order to determine the inductive shifts caused by the electric field of the C–Cl group. The remaining interactions may be divided into hyperconjugation, TS coupling, and TB coupling. The hyperconjugative interaction causes a shift in the π^* (and in the σ^*) orbitals due to mixing with the orbitals of the norbornyl bridge (excluding any mixing with the NBO of the other chromophore). Diagonalization of the NBO matrices, with only the TS coupling between the chromophores "turned on", allows one to determine the shifts in the π^* (and σ^*) orbitals due to the TS and TB interactions. For example, comparison of the energies from such a calculation with the energies obtained from calculations containing only the hyperconjugative interactions (and the electric field shifts) gives the shifts due to TS coupling, while comparison with the energies obtained from the HF calculations gives the shifts in the π^* (and σ^*) energies due to TB coupling.

Alternatively, diagonalization of a 2×2 eigenvalue problem containing the π^* and σ^* NBO's gives the shifts due to TS coupling. Comparison with the results of the calculations containing only the hyperconjugative interactions can then be used to separate out the shifts due to TB coupling. If each type of interaction were relatively small, the contributions of the various interactions to the net shifts in the π^* (and π) levels would be independent of the scheme used to evaluate them. This is true, to a good approximation, for the systems studied here. Unless specified otherwise, the results presented in this study are obtained by means of the first scheme outlined above. Finally, it should be noted that the π/C–Cl σ^* and π^*/C–Cl σ mixing in the molecules studied here proved to be relatively unimportant, producing shifts in the π and π^* orbital energies less than 0.01 eV. Hereafter, we will concern ourselves only with π^*/σ^* and π/σ coupling.

It should be noted that, although the procedures outlined above give the shifts in the π^* (or π) and σ^* (or σ) energies due to TS and TB coupling, these shifts do not provide a direct measure of the electronic coupling between the chromophores. Only in the case of symmetrical chromophore–bridge–chromophore systems can the shifts be directly associated with the off-diagonal matrix element of an effective two-level problem.[16] However, for a series of closely related molecules, such as those studied here, we can associate large shifts with strong coupling and small shifts with weak coupling.

III. Results

A. Molecular Orbital Calculations. (i) Natural Bond Orbital (NBO) Analysis of the Electronic Interactions in the 6-Chloro- and 7-Chloro-2-(trihydrosiloxy)norbornenes. The individual contributions to the shifts in the π^* (due to C–Cl σ^*) and π (due to C–Cl σ) orbital energies of ExoCl, EndoCl, AntiCl, and SynCl[11] due to electric field effects, through-space (TS) coupling, and through-bond (TB) coupling, estimated by means of the NBO analysis, are presented in Table I. Only in the case of ExoCl are there significant TS and TB interactions, and then, only in the case of the π^* orbital. Note that the sum of the interactions (*i.e.*, electric field effect, TS coupling, and TB coupling) does not exactly reproduce the net HF shifts in all cases. This is due to the fact that the various interactions are not perfectly additive. Also, in estimating the shifts in the HF calculations (last column), the orbital energies are referenced relative to the parent, 2-(trihydrosiloxy)norbornene. In this way, hyperconjugative interactions are effectively "removed". Geometry changes introduced in the

(7) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. Gaussian 86. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.

(8) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian 90. Gaussian, Inc., Pittsburgh, PA, 1990.

(9) Jordan, K. D.; Paddon-Row, M. N. *J. Phys. Chem.* **1992**, *96*, 1188 and references therein.

(10) Pople, J. A.; Hehre, W. J.; Stewart, R. F. *J. Chem. Phys.* **1969**, *51*, 2657.

(11) The calculations were carried out with the trihydrosiloxy derivatives to facilitate the computations. The energies of the σ and π orbitals do not deviate significantly from those computed for the trimethylsiloxy derivatives (see ref 4).

(12) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(13) Although the π^* orbitals of the molecules of interest here are unbound, the STO-3G and 3-21G basis sets are sufficiently compact that the lowest unfilled π^* orbitals are indeed those that correspond, in a Koopmans' theorem sense, to the anion states.

(14) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(15) See for example: (a) Falcetta, M. F.; Jordan, K. D.; McMurry, J. E.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1990**, *112*, 579. (b) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Am. Chem. Soc.* **1990**, *112*, 1710. (c) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Chem. Soc., Perkin Trans. 2* **1990**, 417. (d) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Chem. Soc., Perkin Trans. 2* **1990**, 425. Jordan, K. D.; Paddon-Row, M. N. *Chem. Rev.* **1992**, *92*, 395.

(16) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767.

Table I. NBO Analysis of the Contributions (eV) of Various Interactions to the π^* and π Orbital Energies of ExoCl, EndoCl, AntiCl, and SynCl[a,b]

	field effect		through-space interaction[c]		through-bond interaction		net shift from HF calculations[d]	
molecule	π^*	π	π^*	π	π^*	π	π^*	π
ExoCl	0.54	0.49	0.13	0.01	0.24	−0.01	0.85	0.44
EndoCl	0.39	0.31	0.01	0.00	−0.01	0.01	0.40	0.30
SynCl	0.46	0.35	0.00	−0.01	0.00	0.01	0.46	0.35
AntiCl	0.74	0.50	0.00	−0.01	0.00	−0.05	0.59	0.51

[a] Determined from STO-3G//STO-3G wave functions. [b] Positive shifts reflect stabilization of the π^* (or π) orbital whereas negative shifts reflect destabilization of the orbital. [c] The through-space interaction is defined to be the coupling that results from direct overlap between the π^* and C–Cl σ^* (or the π and C–Cl σ) NBO's. [d] Relative to the parent, 2-(trihydrosiloxy)norbornene.

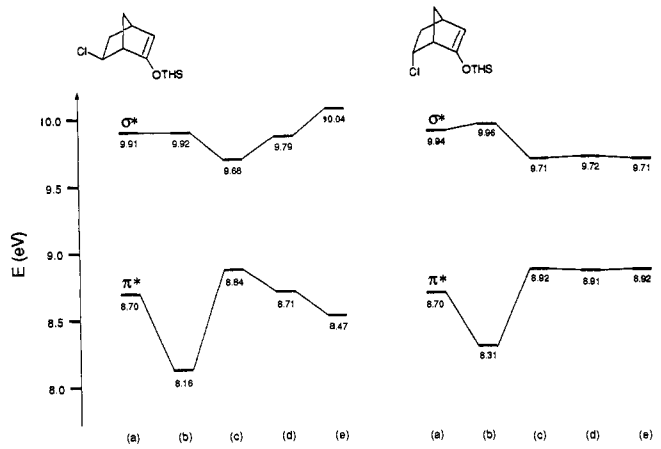


Figure 1. HF/STO-3G NBO interaction diagrams for the π^* and C–Cl σ^* orbitals of ExoCl and EndoCl. The steps in the figure are as follows: (a) the noninteracting, localized π^* and C–Cl σ^* basis NBOs (For the π^* NBO, the electric field caused by the trihydrosiloxy substituent is also included.), (b) inclusion of the electric field effect caused by the C–Cl group (for π^*) and by the enol ether group (for σ^*), (c) inclusion of all hyperconjugative interactions with the norbornyl bridge (For the π^* orbital, hyperconjugation with the trihydrosiloxy substituent is also included.), (d) inclusion of TS interactions between the two basis NBOs (π^* and C–Cl σ^*), (e) inclusion of TB interactions between the two basis NBOs (π^* and C–Cl σ^*).

norbornyl framework due to the presence of the C–Cl bond (which are particularly important in AntiCl) also cause deviations between the shifts determined from the sum of the separate interactions and those from the HF procedure. Correlation diagrams of the π^* and σ^* energy levels for ExoCl and EndoCl and AntiCl and SynCl, where the effects of the shifts due to hyperconjugation and TS and TB interactions are illustrated, are shown in Figures 1 and 2. It is clear from these figures that both TS and TB interactions are sizable in ExoCl but negligible in EndoCl, AntiCl, and SynCl.

(ii) NBO Analysis of the Electronic Interactions in *exo*-9-Chloro- and *endo*-9-Chloro-3-methoxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene. Contributions of electric field effects and through-space (TS) and through-bond (TB) coupling to the shifts in the π^* and π orbital energies of GExoCl and GEndoCl are presented in Table II. TS interactions are not important for either GExoCl or GEndoCl; however, there are calculable TB interactions between the π^* and C–Cl σ^* orbitals in both cases, with the TB coupling in GExoCl being larger, as expected. The TB coupling in GExoCl is 2.6 times smaller than that in ExoCl; the 0.05-eV TB coupling in GEndoCl compares with the absence of such coupling in EndoCl.

B. Synthesis, Photochemistry, and Photophysics of 7-Chloro-2-(trimethylsiloxy)norbornene. (i) Synthesis of *syn*- and *anti*-7-Chloro-2-(trimethylsiloxy)norbornene (SynCl and AntiCl). The

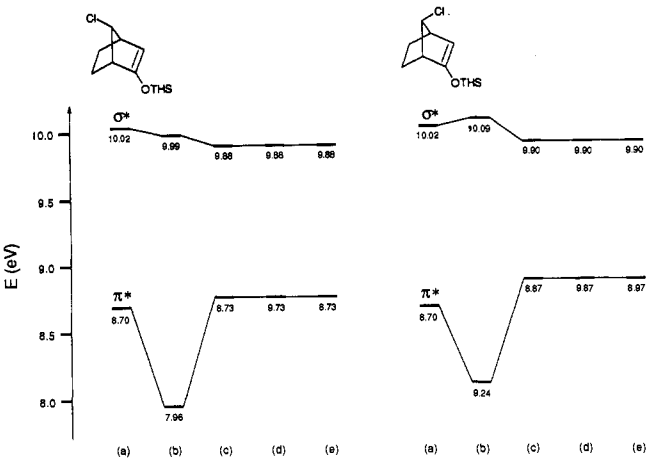


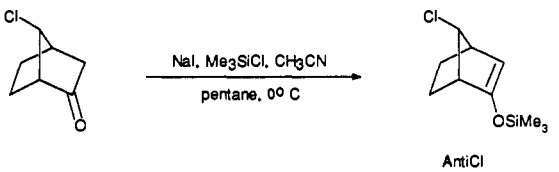
Figure 2. HF/STO-3G NBO interaction diagrams for the π^* and C–Cl σ^* orbitals of AntiCl and SynCl. The steps in the figure are as follows: (a) the noninteracting, localized π^* and C–Cl σ^* basis NBOs (For the π^* NBO, the electric field caused by the trihydrosiloxy substituent is also included.), (b) inclusion of the electric field effect caused by the C–Cl group (for π^*) and by the enol ether group (for σ^*), (c) inclusion of all hyperconjugative interactions with the norbornyl bridge (For the π^* orbital, hyperconjugation with the trihydrosiloxy substituent is also included.), (d) inclusion of TS interactions between the two basis NBOs (π^* and C–Cl σ^*), (e) inclusion of TB interactions between the two basis NBOs (π^* and C–Cl σ^*).

Table II. NBO Analysis of the Contributions (eV) of Various Interactions to the π^* and π Orbital Energies of GExoCl and GEndoCl[a,b]

	field effect		through-space interaction[c]		through-bond interaction		net shift from HF calculations[d]	
molecule	π^*	π	π^*	π	π^*	π	π^*	π
GExoCl	0.30	0.31	0.00	0.00	0.10	0.01	0.41	0.28
GEndoCl	0.21	0.21	0.00	0.00	0.05	0.00	0.26	0.19

[a] Determined from STO-3G//STO-3G wave functions. [b] Positive shifts reflect stabilization of the π^* (or π) orbital whereas negative shifts reflect destabilization of the orbital. [c] The through-space interaction is defined to be the coupling that results from direct overlap between the π^* and C–Cl σ^* (or the π and C–Cl σ) NBO's. [d] Relative to the parent, 3-methoxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene.

anti isomer was prepared by the silylation of *anti*-7-chloro-2-norbornanone[17] using iodotrimethylsilane generated *in situ* from sodium iodide and chlorotrimethylsilane in acetonitrile[18] (cf. eq 1). The *syn* isomer was prepared by an identical procedure using *syn*-7-chloro-2-norbornanone.[19]



AntiCl

(ii) Ultraviolet and Electron Transmission Spectroscopy. The UV absorption spectra of both AntiCl and SynCl, shown in Figure 3, show hyperchromicity and blue shifts compared to the parent, 2-(trimethylsiloxy)norbornene[4] (TMSNB). The vertical electron attachment energies determined from the electron transmission spectra (ETS)[20,21] of norbornene, AntiCl, SynCl, TMSNB, *exo*-2-chloronorbornane, and 7-chloronorbornane are presented in

(17) Lumb, J. T.; Whitham, G. H. *Chem. Commun.* **1966**, 400.
(18) Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron* **1987**, *43*, 2075.
(19) Roberts, J. D.; Johnson, F. O.; Carboni, R. A. *J. Am. Chem. Soc.* **1954**, *76*, 5692.
(20) Sanche, L.; Schulz, G. J. *Phys. Rev.* **1972**, *A5*, 1672.
(21) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

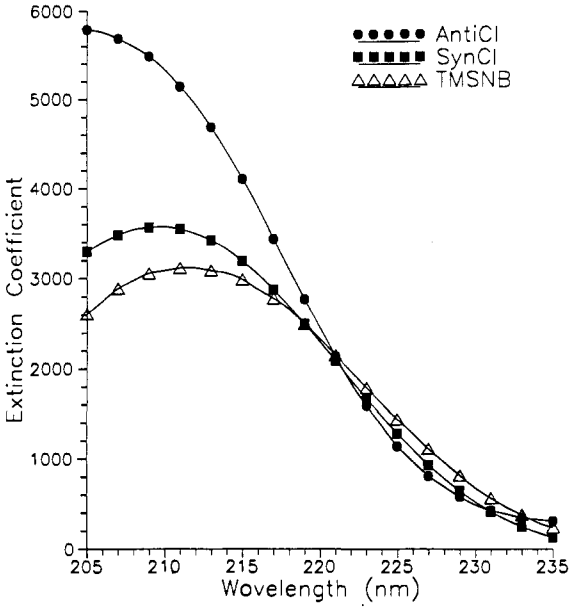


Figure 3. UV absorption spectra for TMSNB, AntiCl, and SynCl.

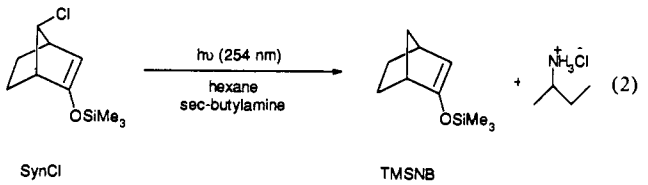
Table III. Vertical Electron Attachment Energies (eV) for ExoCl, EndoCl, AntiCl, SynCl, TMSNB, and 7-Chloronorbornane as Determined by Electron Transmission Spectroscopy

compound	attachment energies
ExoCl[a]	1.50, 2.60, 3.25
EndoCl[a]	1.80, 2.57, 3.30
AntiCl	1.60, 2.7
SynCl	1.75, 2.9
TMSNB[a]	2.20, 2.55, 3.42
7-chloronorbornane	2.20
exo-2-chloronorbornane[a]	2.30
norbornene[b]	1.70

[a] Reference 4. [b] Reference 22.

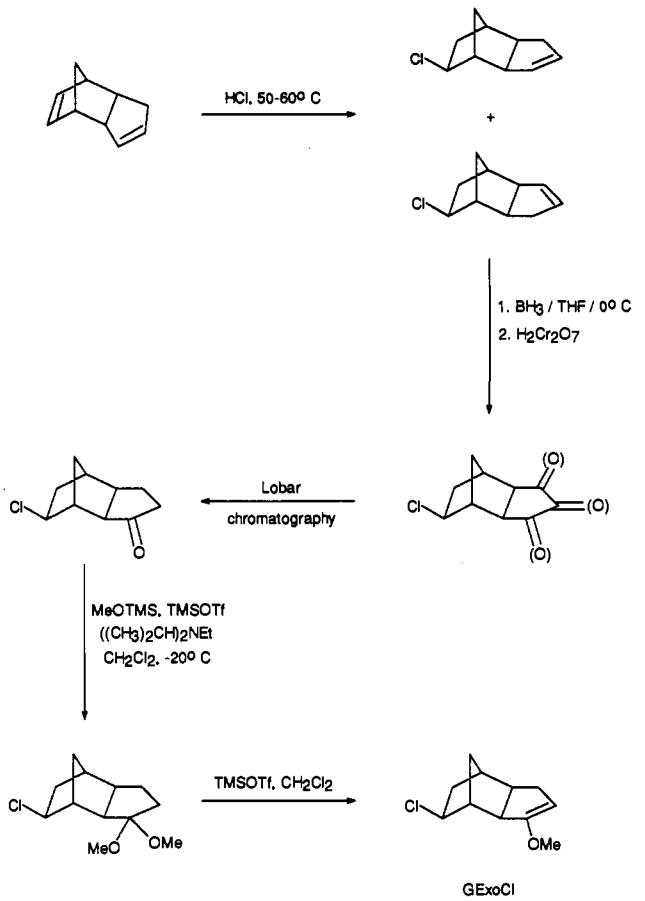
Table III. The results for ExoCl and EndoCl are also included for comparison. Note that, in addition to the low-lying anion state due to electron capture into the π^* orbital associated with the double bond, there are also anion states due to the C–Cl and trimethylsiloxy groups. In AntiCl and SynCl, the anion states due to electron capture into the C–Cl π^* orbital, and to various σ^* orbitals associated with the trimethylsiloxy group, apparently fall at roughly the same energy (*i.e.*, 2.7-2.9 eV). In norbornene, the π^* anion state falls at 1.70 eV. This is destabilized to 2.20 eV in TMSNB, placing the π^* anion state of this system close in energy to the C–Cl σ^* anion states of 7-chloronorbornane and *exo*-2-chloronorbornane.

(iii) Photoreaction of SynCl in Hexane. Irradiation at 254 nm for 4.0 h of 1.58×10^{-2} M solutions of SynCl in hexane with 1.0 mol equiv of (±)-*sec*-butylamine[23] (SBA), degassed with argon, produced one principal product in addition to HCl (cf. eq 2). The



product was identified as TMSNB via comparison of its GC/MS spectrum with that of an authentic sample. A quantum efficiency of disappearance was determined using the E/Z isomerization of 1-phenyl-2-butene as an actinometer.[24,25] The value determined was 0.0027 ± 0.0002.

Scheme I



(iv) Photoreaction of AntiCl in Hexane. Irradiation at 254 nm for 4.0 h of 1.99×10^{-2} M solutions of AntiCl in hexane with 0.83 mol equiv of (±)-*sec*-butylamine (SBA), degassed with argon, produced two principal products in addition to HCl. The products were identified as TMSNB and 2-norbornanone via comparison of GC/MS spectra with those of authentic samples. The quantum efficiency of disappearance determined was 0.0072 ± 0.0008.

C. Synthesis, Photochemistry, and Photophysics of 9-Chloro-3-methoxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene. (i) Synthesis of *exo*-9-Chloro-3-methoxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (GExoCl). The title compound was prepared in five steps as shown in Scheme I. The structure of the intermediate *exo*-9-chloro-*exo*-tricyclo-[5.2.1.$0^{2,6}$]decan-3-one was established by ^{1}H, ^{13}C, HETCOR, NOESY, HMBC, and INADEQUATE NMR analyses. The ^{1}H NMR spectrum shows a multiplet at δ 3.866, which was assigned to the *endo* proton attached to the carbon bearing the chlorine. The HETCOR spectrum shows that this proton, and consequently the chlorine, is attached to the carbon atom with a resonance at δ 60.2 in the ^{13}C NMR spectrum. In addition, the ^{13}C NMR spectrum shows a resonance at δ 219.4, which was assigned to the carbonyl carbon. The INADEQUATE spectrum clearly indicates that the carbon atom of the carbonyl and that bearing the chlorine are separated by *two* carbon atoms. This is consistent with the structure of the 3-keto isomer since the corresponding 5-ketone (as well as the 4-ketone) would show *three* intervening carbons between the carbon of the carbonyl and that bearing the chlorine. Additional confirmation for this assignment was obtained from HMBC and NOESY NMR experiments. The INADEQUATE spectrum is shown in Figure 4.

(22) Balaji, V.; Jordan, K. D.; Burrow, P. D.; Paddon-Row, M. N.; Patney, H. K. *J. Am. Chem. Soc.* **1982**, *104*, 6849.

(23) The presence of the amine is necessary to prevent more extensive decomposition of the starting materials and their dehalogenated products. Previous studies (see ref 4) have demonstrated that it plays no significant role in the photochemistry.

(24) Morrison, H.; Pajak, J.; Peiffer, R. *J. Am. Chem. Soc.* **1971**, *93*, 3978.

(25) Morrison, H.; Peiffer, R. *J. Am. Chem. Soc.* **1968**, *90*, 3428.

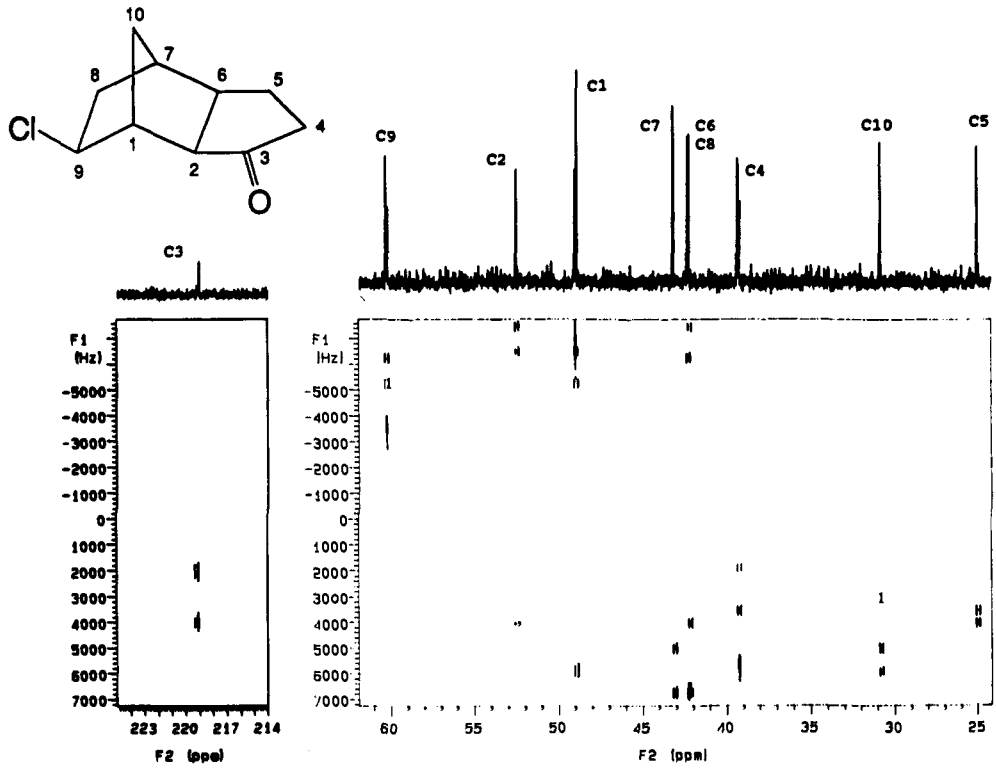


Figure 4. INADEQUATE NMR spectrum of *exo*-9-chloro-*exo*-tricyclo[5.2.1.$0^{2,6}$]decan-3-one.

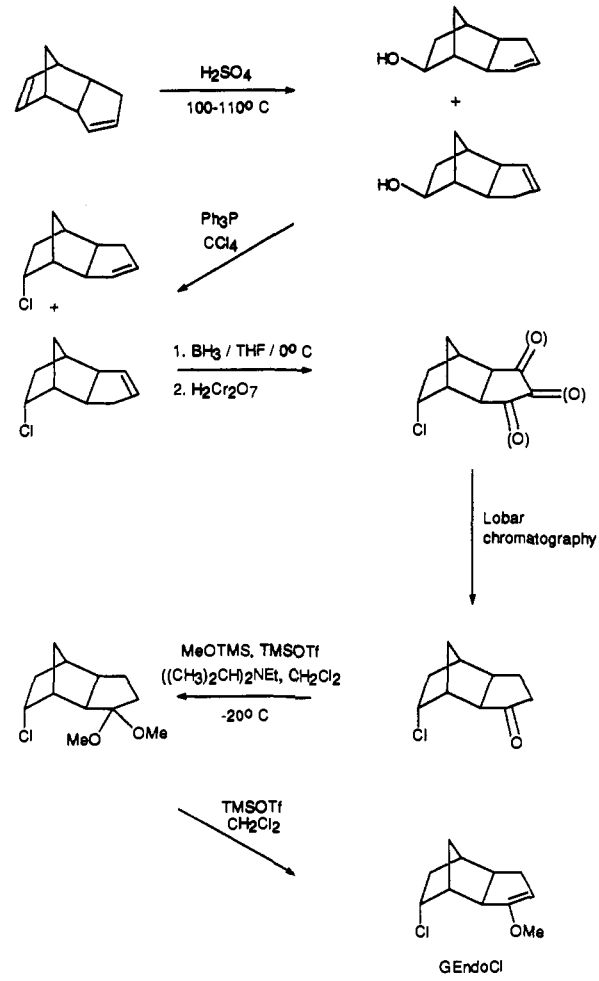
(ii) Synthesis of *endo*-9-Chloro-3-methoxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]-dec-3-ene (GEndoCl). The title compound was prepared in seven steps as shown in Scheme II. As for the *exo* isomer, the structure of the intermediate *endo*-9-chloro-*exo*-tricyclo[5.2.1.$0^{2,6}$]decan-3-one was identified by ^{1}H, ^{13}C, HETCOR, NOESY, HMBC, and INADEQUATE NMR analyses, with the INADEQUATE spectrum again confirming the presence of two carbon atoms separating the carbon atom of the carbonyl (δ 221.7) and the carbon atom bearing the chlorine (δ 58.6). As for the *exo* isomer, additional confirmation of the assigned structure was obtained from HMBC and NOESY NMR experiments.

(iii) Ultraviolet and Electron Transmission Spectroscopy. In both GExoCl and GEndoCl, as well as GOMe, the wavelength for maximum absorption is below 200 nm. However, the observable portions of the spectra of all three compounds are nearly identical. The spectra are shown in Figure 5. The lowest vertical electron attachment energies determined from the electron transmission spectra of GExoCl, GOMe, and *exo*-2-chloronorbornane[4] are 2.10, 2.30, and 2.30 eV, respectively. In the first two molecules, the lowest energy feature is due to electron capture into the π^* orbital, while in the last molecule, it is due to electron capture into the C–Cl σ^* orbital. The ET spectrum of GExoCl also shows a peak near 2.5 eV presumably due to electron capture into the C–Cl σ^* orbital.

(iv) Photolysis of GExoCl and GEndoCl in Hexane or Methanol. Irradiation at 254 nm for 1.0 h of degassed 8×10^{-2} M solutions of GExoCl or GEndoCl in hexane or methanol gave only small amounts of decomposition of the enol ethers. In addition, there was no evidence for the dehalogenated product, GOMe, in either solvent for either substrate.

(v) Photolysis of GExoCl in Hexane or Methanol in the Presence of *o*-Xylene. Irradiation at 254 nm for 1.0 h of degassed hexane or methanol solutions containing 5.4×10^{-3} M GExoCl and 1.0×10^{-1} M *o*-xylene produced no observable products. The enol ether was found to be stable to the sensitization conditions and did not quench the fluorescence of *o*-xylene.

Scheme II



IV. Discussion

A. Theory. (i) NBO Analysis of the Interactions in the Rigid Norbornyl Framework. As noted previously, the NBO analysis reveals that the π and π^* orbitals of ExoCl, EndoCl, AntiCl, and SynCl are appreciably stabilized due to the electric field of the

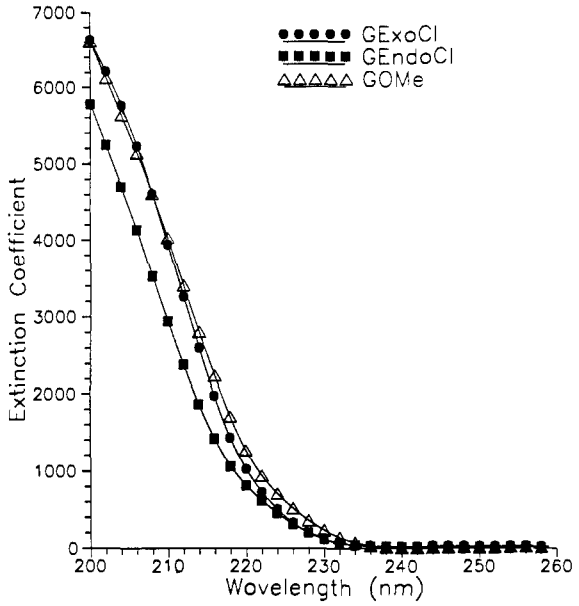


Figure 5. UV absorption spectra for GOMe, GExoCl, and GEndoCl.

C–Cl group (cf. Table I). The occupied π orbitals of all four compounds, and the π^* orbitals of EndoCl, AntiCl, and SynCl, are relatively unshifted by TS or TB interactions. However, ExoCl experiences a sizable (0.13 eV) stabilization of the unoccupied π^* orbital due to the direct TS coupling with the C–Cl σ^* orbital, and an even larger stabilization (0.24 eV) resulting from the TB coupling between these two orbitals. The particularly large TB coupling in this case is due to the "all-*trans*"[6] arrangement of the bonds involved in the coupling. TB coupling is expected to be smaller in EndoCl than in ExoCl due to the *cis* orientation of the C–Cl bond to the bridge. However, the near total absence of TB (and TS) coupling in EndoCl is somewhat surprising. An analysis of the NBO matrix elements of EndoCl reveals that there are individual pathways that lead to a significant (*ca.* 0.1 eV) shift of the π^* level due to TB coupling with the C–Cl σ^* NBO. The fact that the net TB coupling in this compound is much smaller than this must be due to a destructive interference between various pathways.

The relative unimportance of TS or TB coupling in both SynCl and AntiCl is consistent with the existence of an approximate nodal plane[26] between the C–Cl σ^* and silyl enol ether π^* orbitals in these molecules. In addition, calculations on model compounds show[27] that the orientation of the C–Cl and silyl enol ether moieties in SynCl is poorly suited for TS or TB coupling.

(ii) NBO Analysis of the Interactions in the Rigid Tricyclic Framework. NBO calculations on the model γ-chlorides, GExoCl and GEndoCl, also reveal significant shifts in the π and π^* orbitals of these molecules due to the electric field of the C–Cl group (cf. Table II). However, the magnitude of the electric field shifts in these molecules is reduced relative to the norbornyl silyl enol ethers, consistent with the increased distance between the chlorine atom and the olefinic carbon bearing the methoxy group in GExoCl and GEndoCl. TS coupling is unimportant in the π and π^* orbitals of both molecules due to the relatively large separation between the two functionalities. However, the π^* orbitals of GExoCl and GEndoCl are, in fact, shifted due to TB coupling with the C–Cl σ^* orbitals by 0.10 and 0.05 eV, respectively (cf. Table II). These values are, as expected, appreciably smaller than those of the TB coupling in ExoCl (0.23 eV). The apparently larger TB coupling in GExoCl than in GEndoCl can be attributed to the "all-*trans*"[6] arrangement of the bonds involved in the coupling in the former.

(26) The nodal plane between the π^* and C–Cl σ^* orbitals is approximate since the presence of the trimethylsiloxy substituent on the double bond reduces the symmetry in these molecules.

(27) Nash, J. J. Unpublished observations.

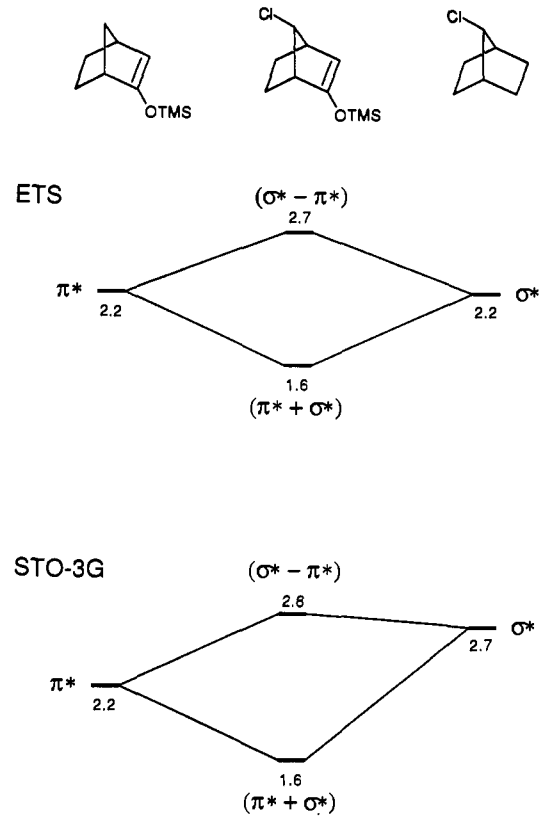


Figure 6. Experimental (ETS) attachment energies (eV) for AntiCl and reference compounds. Calculated energies (eV) for the trihydrosiloxy analogues are included for comparison. The calculated energies have been shifted by –7.1 eV to facilitate comparison with the experimental energies.

B. Spectroscopy. The λ_{max} of ExoCl occurs at 215 nm,[4] versus 211.5 nm[4] for TMSNB. The red shift for the $\pi \rightarrow \pi^*$ transition of ExoCl has been attributed to C–Cl σ^* character in the LUMO (π^*) of this molecule.[4] This is borne out by the calculations discussed above. The λ_{max} values of AntiCl (206 nm), SynCl (211 nm), and EndoCl (207.5 nm)[4] are all blue-shifted relative to that of TMSNB (by 5.5, 0.5, and 4.0 nm, respectively). The origins of the blue shifts in the $\pi \rightarrow \pi^*$ transitions in AntiCl, SynCl, and EndoCl are less clear, particularly in light of the fact that the electric field of the C–Cl group stabilizes the π^* orbitals more than the π orbitals in all of the chloronorbornenes.

In the context of Koopmans' theorem,[28] the vertical electron attachment energies may be associated with the energies of the unoccupied orbitals. The vertical electron attachment energies determined from ETS and the calculated orbital energies for AntiCl, SynCl, TMSNB, and 7-chloronorbornane are compared in Figures 6 and 7.

The LUMO energies obtained from the HF/STO-3G calculations closely reproduce the trends in the lowest attachment energies determined from ETS. The ETS measurements show that the LUMO of AntiCl is depressed by 0.60 eV relative to that of TMSNB, and that of SynCl is depressed by 0.45 eV. The calculated shifts (HF) for the LUMO's of AntiCl and SynCl (0.59 and 0.46 eV, respectively) are in excellent agreement with the ETS data. As noted previously, these shifts are due almost entirely to the electric field of the C–Cl bond. Previous ETS measurements on ExoCl[4] and EndoCl[4] have shown that the LUMO's of these molecules are depressed by 0.70 and 0.40 eV, respectively, relative to that of TMSNB. The calculated shifts for the LUMO's of ExoCl and EndoCl (0.85 and 0.40 eV, respectively) are also in good agreement with the ETS data. On the basis of the NBO calculations, about two-thirds of the shift

(28) Koopmans, T. *Physica* **1934**, *1*, 104.

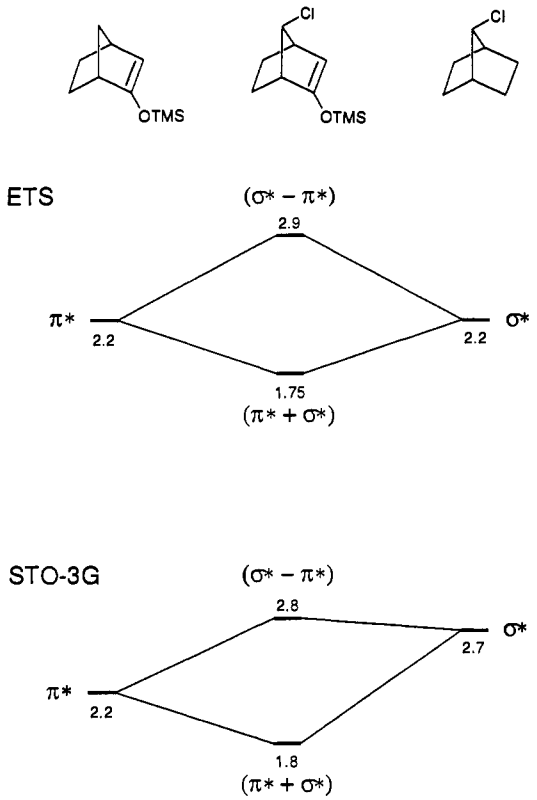


Figure 7. Experimental (ETS) attachment energies (eV) for SynCl and reference compounds. Calculated energies (eV) for the trihydrosiloxy analogues are included for comparison. The calculated energies have been shifted by −7.1 eV to facilitate comparison with the experimental energies.

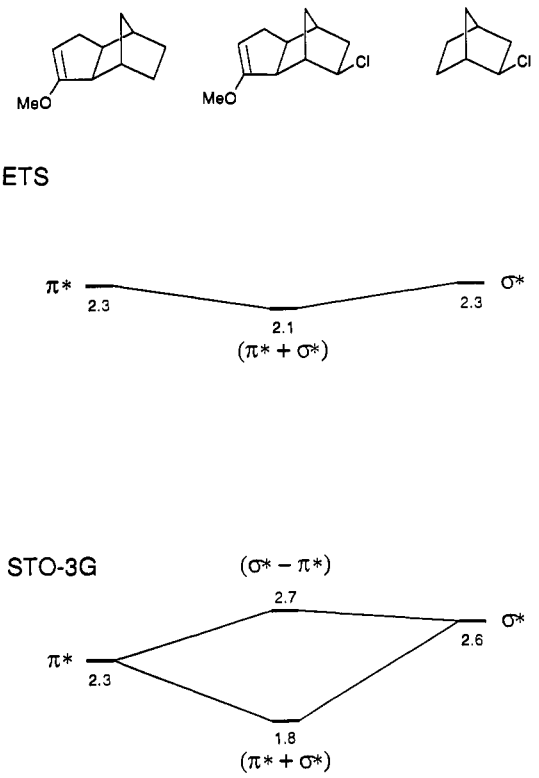


Figure 8. Experimental (ETS) attachment energies (eV) for GExoCl and reference compounds. Calculated energies (eV) are included for comparison. The calculated energies have been shifted by −7.0 eV to facilitate comparison with the experimental energies.

in the LUMO of ExoCl, and all of that in EndoCl, is due to the electric field effect.

The UV spectra of the γ-chlorides, GExoCl and GEndoCl (cf. Figure 5), are not particularly enlightening as the absorption maximum lies below 200 nm in both molecules.

The vertical electron attachment energies determined from ETS are compared in Figure 8 with the calculated orbital energies for GExoCl, GOMe, and *exo*-2-chloronorbornane. The lowest electron attachment energy of GExoCl is 0.20 eV smaller than that of the parent compound, GOMe, while the calculated shift (HF) for the LUMO (π^*) of GExoCl is 0.41 eV. The NBO analysis reveals that approximately 0.30 eV of this shift is due to the electric field effect and 0.10 eV is due to TB coupling.

C. Photochemistry. Photolysis of AntiCl[29] in hexane at 254 nm produced two products: TMSNB and 2-norbornanone. The trimethylsilyl enol ethers are extremely susceptible to degradation back to the respective ketones in the presence of electrophiles,[4] and incomplete scavenging of photogenerated HCl would explain the trace amount of 2-norbornanone observed in the photolysis via hydrolysis of TMSNB. Photolysis of SynCl produced a single product: TMSNB.

The quantum efficiencies of disappearance of AntiCl and SynCl in hexane are 0.0072 ± 0.0008 and 0.0027 ± 0.0002, respectively. These should be compared to the quantum efficiencies of disappearance of ExoCl and EndoCl of 0.066 and 0.0079,[4] respectively. It is not surprising that the quantum efficiency of disappearance is so large for ExoCl given the importance of both TS and TB coupling in this substrate. Likewise, the relative lack of photoactivity[30] in AntiCl and SynCl can be attributed to the lack of TS and TB coupling between the π^* and C–Cl σ^* orbitals in these molecules and, in fact, one might well ask why these compounds (and EndoCl) show what little reactivity they do. It is possible that the Forster (dipole–dipole) coupling mechanism is operative and is responsible for the relatively small photodestruction observed in these compounds.

No products resulting from photoinitiated C–Cl cleavage are observed upon photolysis of GExoCl and GEndoCl in either hexane or methanol, even though the NBO analysis (cf. Table II) indicates that the TB mechanism leads to a small level of π^*/σ^* coupling in these molecules.[31]

V. Experimental Section

Chemicals. THF (Fisher) and diethyl ether (Mallinckrodt) were distilled from sodium benzophenone ketyl. Acetonitrile, pentane, and hexane (Burdick and Jackson, Distilled in Glass) were dried over 4-Å molecular sieves for a period of 1 week before use. Methylene chloride (Fisher) was dried over 4-Å molecular sieves before use. Dimethylformamide (Fisher), pyridine (Fisher), and (±)-*sec*-butylamine (Kodak) were distilled from calcium hydride under N_2 and stored over 4-Å molecular sieves. Triethylamine (Mallinckrodt) was distilled from LAH under N_2 and stored over 4-Å molecular sieves. Sodium iodide (Mallinckrodt) was dried at 80 °C for 1 week before use. *o*-Xylene (Matheson) was distilled before use. (*E*)-1-Phenyl-2-butene (Pfaltz and Bauer) was purified by preparative gas chromatography (25% XF-1150, 16 ft × 1/4 in., T = 140 °C, flow = 40–60 mL/min). Tetradecane (Kodak) was washed with concentrated sulfuric acid, water, aqueous potassium hydroxide, water, and brine, dried over anhydrous magnesium sulfate, and distilled under N_2 from calcium hydride. The following

(29) We have evidence from earlier triplet quenching and triplet sensitization studies that the photochemistry observed in ExoCl and EndoCl derives from the singlet excited state (see ref 4). We expect the same to be true of AntiCl and SynCl.

(30) We are assuming that radiationless decay in these closely related molecules is relatively constant. This allows us to relate the quantum efficiencies with the excited-state reactivity.

(31) It is possible that there is a barrier in the potential energy surface leading to the dissociation products and the lack of reactivity is a consequence of the relative energies of the excited-state surfaces and the wavelength of excitation used in these experiments. Further analyses of the excited-state potential surfaces for the photodissociation of these substrates are planned.

chemicals were used as received from Aldrich: norbornene, anhydrous lithium chloride, chlorotrimethylsilane, platinum oxide, 1 M BH_3–THF complex, trimethylsilyl triflate, triphenylphosphine, methoxytrimethylsilane, *N,N*-diisopropylethylamine.

Instrumentation. ^1H NMR and ^{13}C NMR spectra were obtained using a Varian Gemini 200 (200 MHz), a General Electric QE-300 (300 MHz), a Varian VXR-500 (500 MHz), or a Varian model VXR-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm relative to TMS. Infrared spectra were obtained using a Perkin-Elmer 1420 ratio recording spectrophotometer or a Perkin-Elmer model 1800 FT-IR. Ultraviolet spectra were recorded using a Perkin-Elmer model Lambda 3B spectrophotometer. Low-resolution mass spectra were obtained using a Finnigan Automated Gas Chromatograph EI/CI Mass Spetrometer. High-resolution spectra were recorded on a Kratos model MS-50. EI mass spectra were recorded at 70 eV. CI spectra were recorded at 70 eV with isobutane gas at a pressure of 0.30 Torr. Gas chromatography utilized Varian models 3300, 1400, and 1200 chromatographs for qualitative or preparative work and a Varian model 3700 or a Hewlett-Packard 5710A FID chromatograph with Hewlett-Packard 3390A digital integrators for quantitative studies. Columns used were (A) 20 ft × 0.125 in., 5% SE-30 on 60/80 AW-DMCS Chromosorb W, (B) 15 ft × 0.125 in., 20% Carbowax 20M on 100/120 AW-DMCS GasPack W, (C) 50 m × 0.25 mm, GB-20M capillary, 0.25-μm film thickness, (D) 30 m × 0.25 mm, DB-1 capillary, 0.25 μm film thickness, and (E) 16 ft × 0.25 in., 25% XF-1150 on 60/80 AW Chromosorb P. Lobar chromatography was performed with a Bioanalytical Systems Miniprep 1200 system, with an ISCO 1840 UV–vis absorbance detector and recorder and an E. M. Reagents LiChroprep Si 60 (size A, 40–63 μm) Lobar column. Photochemical studies employed a Rayonet model RPR-100 reactor and quartz photolysis tubes. Deoxygenation was accomplished by bubbling argon through the solutions for at least 15 min. The absorbances of all photolysis solutions were ≥2. The technique of electron transmission spectroscopy, used to determine the vertical electron affinities, has been described in refs 20 and 21. The EAs reported here are expected to be accurate to ±0.05 eV.

Syntheses. ***anti*-7-Chloro-2-norbornanone.**[32] A 5.516-g sample (29.2 mmol) of *syn*-7-bromo-2-norbornanone[33] and 1.604 g (37.8 mmol) of anhydrous LiCl were combined under nitrogen. These were dissolved with stirring in 17.6 mL of dimethylformamide added by syringe under nitrogen. The mixture was then refluxed for 7 h.

The mixture was cooled to room temperature, diluted with 200 mL of water, and extracted with 3 × 100 mL of ether. The extracts were combined, washed with 50 mL of water, 50 mL of saturated sodium bicarbonate, and 50 mL of brine, then dried over sodium sulfate. The ether was removed under vacuum and the residual oil distilled to give a slightly yellow liquid: bp 69–73 °C (1.7 mmHg) (lit.[34] 95–104 °C (13 mmHg)). The liquid was purified by flash chromatography on silica gel (1:1 hexane/ether) to give 1.535 g (10.6 mmol, 36%) of waxy, white *anti*-7-chloro-2-norbornanone. The purity by GC analysis on column A at 140 °C was approximately 91%: mp 74–77 °C (lit.[35] 86–90 °C). IR[36] (CCl_4): 2981, 2959, 1757, 1467, 1448, 1407, 1305, 1280, 1256, 1156, 1123, 1078, 928, 860, 826 cm^{-1}. ^1H NMR[36] ($CDCl_3$, 200 MHz): 4.193 (bs, C7 *syn*-H, 1H), 2.710 (m, C1 H, C4 H, 2H), 2.273–2.164 (m, C5 *exo*-H, C6 *exo*-H, C3 *exo*-H, C3 *endo*-H, 4H), 1.580–1.508 (m, C6 *endo*-H, C5 *endo*-H, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 212.2 (C2), 62.9 (C7), 55.8 (C1), 45.8 (C3), 42.1 (C4), 24.4 (C5), 21.2 (C6).

***anti*-7-Chloro-2-(trimethylsiloxy)norbornene (AntiCl).** The title compound was prepared according to the procedure of Cazeau et al.[37] A 0.397-g sample (2.97 mmol) of *anti*-7-chloro-2-norbornanone and 2.7 mL of dry pentane were combined under nitrogen. The solution was stirred and cooled in an ice bath. Triethylamine (0.55 mL, 4.0 mmol) and chlorotrimethylsilane (0.50 mL, 4.0 mmol) were then syringed into the flask under nitrogen. Sodium iodide (0.615 g, 4.10 mmol) dissolved in 5.0 mL of dry acetonitrile was added dropwise at 0 °C over 10 min. Upon complete addition of the sodium iodide, the mixture was stirred at room temperature overnight.

The mixture was diluted with 10.0 mL of dry pentane, the stirring was discontinued, and the pentane extract was removed by syringe under a slight positive pressure of nitrogen. The extraction process was repeated two additional times (5.0 mL each) and the pentane extracts were combined. The pentane and residual iodotrimethylsilane were removed via distillation, and the residual oil was distilled at reduced pressure to give 0.201 g (0.93 mmol, 24%) of AntiCl: bp 58 °C (0.95 mmHg). The purity of this compound via GC analysis on column A at 140 °C was 88%. IR (neat): 3081, 2960, 2910, 2874, 1612, 1331, 1302, 1282, 1254, 1220, 1184, 1147, 1118, 944, 903, 876, 848, 822, 806, 771, 747 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 4.756 (dd, C3 H, J = 1.4 and 2.2 Hz, 1H), 3.804 (m, C7 *syn*-H, 1H), 2.681 (m, C1 H, 1H), 2.514 (m, C4 H, 1H), 2.017–1.921 (m, C5 *exo*-H, C6 *exo*-H, 2H), 1.288–1.192 (m, C5 *endo*-H, C6 *endo*-H, 2H), 0.181 (s, $Si(CH_3)_3$, 9H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 159.2 (C2), 105.4 (C3), 66.2 (C7), 50.4 (C1), 46.3 (C4), 24.2 (C5), 21.1 (C6), –0.3 ($Si(CH_3)_3$). MS EI m/e (%): 216/218 (M^+, 1.3/0.5), 181 (M – Cl, 27), 73 ($Si(CH_3)_3^+$, 100). MS CI m/e (%): 217/219 (M + 1, 26/10), 181 (M + H – HCl, 100). High-resolution MS EI (m/e): calcd, 216.0737; found, 216.0733.

***syn*-7-Chloro-2-(trimethylsiloxy)norbornene (SynCl).** The title compound was prepared according to the procedure of Cazeau *et al.*[37] A 0.762-g sample (5.27 mmol) of *syn*-7-chloro-2-norbornanone[34] and 4.5 mL of dry pentane were combined under nitrogen. The solution was stirred and cooled in an ice bath. Triethylamine (0.92 mL, 6.6 mmol) and chlorotrimethylsilane (0.82 mL, 6.5 mmol) were then syringed into the flask under nitrogen. Sodium iodide (0.955 g, 6.4 mmol) dissolved in 7.0 mL of dry acetonitrile was added dropwise at 0 °C over 10 min. Upon complete addition of the sodium iodide, the mixture was stirred at room temperature overnight.

The mixture was diluted with 10.0 mL of dry pentane, the stirring was discontinued, and the pentane extract was removed by syringe under a slight positive pressure of nitrogen. The extraction process was repeated two additional times (10.0 and 5.0 mL), and the pentane extracts were combined. The pentane and residual iodotrimethylsilane were removed via distillation, and the residual oil was distilled at reduced pressure to give 0.569 g (2.62 mmol, 54%) of SynCl: bp 60–61 °C (1.2 mmHg). The purity of this compound via GC analysis on column D at 140 °C was 94%. IR (neat): 3088, 2960, 2914, 2876, 1620, 1464, 1342, 1308, 1274, 1254, 1244, 1226, 1188, 1150, 1120, 952, 934, 922, 878, 848, 784, 766 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 4.717 (d, C3 H, J = 3.2 Hz, 1H), 3.778 (m, C7 *anti*-H, 1H), 2.854 (m, C1 H, 1H), 2.630 (m, C4 H, 1H), 1.850–1.737 (m, C5 *exo*-H, C6 *exo*-H, 2H), 1.379–1.295 (m, C5 *endo*-H, C6 *endo*-H, 2H), 0.249 (s, $Si(CH_3)_3$, 9H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.3 (C2), 101.5 (C3), 72.0 (C7), 52.1 (C1), 47.6 (C4), 25.8 (C5), 22.5 (C6), –0.2 ($Si(CH_3)_3$). MS EI m/e (%): 216/218 (M^+, 2.5/0.8), 181 (M – Cl, 12), 73 ($Si(CH_3)_3^+$, 100). MS CI m/e (%): 217.219 (M + 1, 100/34), 181 (M + H – HCl, 7). High-resolution MS EI (m/e): calcd, 216.0737; found, 216.0739.

***anti*-7-Chloro-2-norbornene.** The title compound was prepared using the procedure of Brown and Rao.[38] A 5.76-g sample (51.3 mmol) of potassium *tert*-butoxide was added to 30 mL of dry THF with stirring. *exo*-2-Chloro-*anti*-7-chloronorbornane[39] (5.06 g, 30.6 mmol) was then added in one portion and the mixture refluxed for 1 h.

The mixture was cooled and poured into 50 mL of water. The mixture was then extracted with 4 × 30 mL of pentane, and the extracts were combined and washed with 5 × 40 mL of water and finally dried over Na_2SO_4. The pentane was removed via distillation through a 15-cm Vigreux column and the residual oil distilled at reduced pressure to give 2.55 g (19.8 mmol, 65%) of a colorless liquid: bp 42.5–46 °C (22 mmHg) (lit.[40] 70.5–71.5 °C (60 mmHg)). GC analysis on column D at 100 °C showed a mixture of six products in a 4.0:33.3:5.5:5.0:2.6:1.0 ratio. The major isomer was identified as *anti*-7-chloro-2-norbornene via comparison of the IR spectrum with the IR spectrum reported previously.[34]

7-Chloronorbornane.[34] A 1.47-g sample (11.4 mmol) of impure *anti*-7-chloro-2-norbornene (*vide supra*) and 50 mL of dry ether were combined, and a small portion of PtO_2 (0.071 g) was added. The mixture was then stirred vigorously under a positive pressure of hydrogen for 2 h.

The catalyst was removed via filtration and the ether removed via distillation. Distillation of the residue at reduced pressure afforded 1.16 g (8.88 mmol, 77%) of white, waxy 7-chloronorbornane: bp 51–52 °C (18 mmHg), mp 42.5–44 °C (lit.[41] 41–44 °C). GC analysis on column A at 140 °C showed approximately 99% purity. IR[34] (neat): 2954, 2913, 2872, 1473, 1453, 1314, 1259, 1139, 988, 939, 827, 816, 781, 748

(32) Lumb, J. T.; Whitham, G. H. *Chem. Commun.* **1966**, 400.
(33) Zalkow, L. H.; Oehlschlager, A. C. *J. Org. Chem.* **1964**, *29*, 1625.
(34) Roberts, J. D.; Johnson, F. O.; Carboni, R. A. *J. Am. Chem. Soc.* **1954**, *76*, 5692.
(35) Gassman, P. G.; Hornback, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 7010.
(36) Werstiuk, N. H.; Timmins, G.; Cappelli, F. P. *Can. J. Chem.* **1980**, *58*, 1709.
(37) Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron* **1987**, *43*, 2075.
(38) Brown, H. C.; Rao, C. G. *J. Org. Chem.* **1979**, *44*, 1348.
(39) Uemura, S.; Onoe, A.; Okano, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3702.
(40) Tanida, H.; Hata, Y. *J. Org. Chem.* **1965**, *30*, 977.
(41) Weiss, R. G.; Snyder, E. I. *J. Org. Chem.* **1970**, *35*, 1627.

cm^{-1}. ^1H NMR[42] ($CDCl_3$, 200 MHz): δ 3.91 (bs, C7 H, 1H), 2.19 (m, C1 H, C4 H, 2H), 1.95 (m, C2 *exo*-H, C3 *exo*-H, 2H), 1.58 (m, C2 *endo*-H, C3 *endo*-H, 2H), 1.29 (m, C5 H, C6 H, 4H). ^{13}C NMR[42] ($CDCl_3$, 50 MHz): δ 66.5 (C7), 42.2 (C1 and C4), 27.3 (C5 and C6), 26.7 (C2 and C3).

exo-9-Chloro-exo-tricyclo[5.2.1.$0^{2,6}$]decan-3-one. A 9.99-g (59.2 mmol) mixture of *exo*-9-chloro-*exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene and *exo*-9-chloro-*exo*-tricyclo[5.2.1.$0^{2,6}$]dec-4-ene[43] was dissolved with stirring in 15 mL of dry THF. The mixture was then cooled to 0 °C in an ice bath.

A 30.0-mL solution (30.0 mmol) of 1.0 M borane–THF complex was then added by syringe under nitrogen. The mixture was stirred at 0 °C for an additional 1 h and finally quenched via the careful addition of 15 mL of water. A chromic acid solution (prepared by dissolving 12.95 g of sodium dichromate monohydrate in 53 mL of water and 9.7 mL of H_2SO_4)[44] was placed in the dropping funnel and added dropwise over 20 min. The ice bath was removed and the mixture stirred an additional 19 h at room temperature.

The mixture was diluted with 100 mL of water and extracted with 4 × 100 mL of ether. The extracts were combined, washed with 50 mL of water, 50 mL of saturated sodium bicarbonate, and 50 mL of brine, and finally dried over Na_2SO_4. The ether was removed under vacuum and the residual oil distilled at reduced pressure to give 7.35 g (39.8 mmol, 67%) of a colorless liquid: bp 105–109 °C (0.82 mmHg). GC analysis on column C at 175 °C showed approximately 83% purity of a mixture of the three chloro ketones in a 1.1:3.0:1.0 ratio. The title compound was separated from the other isomers via Lobar chromatography (eluent = 40% hexane/45% ether/15% ethyl acetate). Analysis of the isolated sample by GC on column C at 175 °C showed approximately 95% purity. IR (neat): 2965, 2887, 1738, 1473, 1445, 1408, 1321, 1297, 1258, 1170, 1158, 1026, 948, 898, 886, 809, 761 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.866 (m, C9 *endo*-H, 1H), 2.696 (bs, C1 H, 1H), 2.260 (m, C4 H, C5 *endo*-H, C7 H, C6 H, 5H), 2.056 (d, C2 H, J = 7.5 Hz, 1H), 1.944 (m, C8 *endo*-H, 1H), 1.818 (m, C8 *exo*-H, 1H), 1.698 (d, C10 *syn* (to Cl)-H, J = 10.8 Hz, 1H), 1.412 (m, C5 *exo*-H, 1H), 1.158 (d, C10 *anti* (to Cl)-H, J = 10.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 219.4 (C3), 60.2 (C9), 52.5 (C2), 48.9 (C1), 43.1 (C7), 42.2 (C6), 42.2 (C8), 39.3 (C4), 30.8 (C10), 25.0 (C5). UV (hexane): λ_{max} = 294 nm (20). MS EI m/e (%): 184/186 (M^+, 35/9), 149 (M − Cl, 12), 66 ($C_5H_6^+$, 100). MS CI m/e (%): 185/187 (M + 1, 100/24). High-resolution MS EI (m/e): calcd, 184.0655; found, 184.0651.

exo-9-Chloro-3-methoxy-exo-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (GExoCl). The title compound was prepared using the procedures of Tsunoda[45] and Gassman.[46] A 0.46-g sample (2.5 mmol) of *exo*-9-chloro-*exo*-tricyclo-[5.2.1.$0^{2,6}$]decan-3-one and 1.0 mL of dry CH_2Cl_2 were combined in a small flask. The mixture was stirred, cooled to −20 °C, and 4.9 μL (0.025 mmol) of trimethylsilyl triflate and 0.76 mL (5.5 mmol) of methoxytrimethylsilane were added by syringe under nitrogen. The mixture was then stirred an additional 3 h at −20 °C.

The mixture was quenched with 0.2 mL (2.5 mmol) of dry pyridine, poured onto 10 mL of saturated sodium bicarbonate, and extracted with 3 × 15 mL of ether. The extracts were combined and dried over a 1:1 mixture of Na_2CO_3 and Na_2SO_4. The ether was removed under vacuum, and the residual oil (presumably the dimethyl acetal) was immediately dissolved in 4.2 mL of dry CH_2Cl_2 in a small flask. The mixture was stirred, and 0.52 mL (3.0 mmol) of *N,N*-diisopropylethylamine was added by syringe under nitrogen. The mixture was again cooled to −20 °C, and 0.53 mL (2.7 mmol) of trimethylsilyl triflate was added dropwise by syringe over about 5 min. The cooling bath was removed and the mixture stirred at room temperature for an additional 18.5 h.

The mixture was quenched with 0.50 mL of 1 M NaOH and stirred vigorously for 5 min. A 13-mL portion of dry pentane was then added and the pentane extract removed via syringe. The extract was then stored in a freezer for several hours to precipitate the *N,N*-diisopropylethylammonium triflate. The precipitate was removed via filtration and the pentane removed via distillation through a 15-cm Vigreux column. The residual oil was then distilled at reduced pressure to yield 0.32 g (1.6 mmol, 64%) of a colorless liquid, GExoCl. GC analysis on column D at 140 °C showed approximately 96% purity. IR (neat): 3071, 2936, 2894, 2847, 1649, 1465, 1440, 1358, 1328, 1302, 1276, 1258, 1230, 1177, 1068, 1040, 1028, 994, 948, 897, 873, 781, 734, 678, 656 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 4.435 (m, C4 H, 1H), 3.894 (m, C9 *endo*-H, 1H), 3.564 (s, OCH_3, 3H), 2.482 (m, C1 H, C2 H, C5 *endo*-H, 3H), 2.049 (bs, C7 H, 1H), 1.969–1.474 (m, C8 H, C10 H, C6 H, C5 *exo*-H, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.9 (C3), 95.6 (C4), 61.4 (C9), 56.8 (OCH_3), 51.1 (C2), 48.7 (C1), 43.0 (C7), 42.6 (C8), 41.3 (C6), 34.5 (C5), 28.7 (C10). MS EI m/e (%): 198/200 (M^+, 4/1), 97 (100). MS CI m/e (%): 199/201 (M + 1, 40/11), 97 (100). High-resolution MS EI (m/e): calcd, 198.0811; found, 198.0809.

endo-9-Chloro-exo-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene and endo-9-chloro-exo-tricyclo[5.2.1.$0^{2,6}$]dec-4-ene. A 11.9-g (79.2 mmol) mixture of *exo*-9-hydroxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene and *exo*-9-hydroxy-*exo*-tricyclo-[5.2.1.$0^{2,6}$]dec-4-ene[47] was dissolved in 128 mL of dry CCl_4, and 25.4 g (96.8 mmol) of triphenylphosphine was added in one portion with stirring. The mixture was then brought to reflux for 17 h.

The mixture was cooled to room temperature and diluted with 240 mL of dry pentane. The precipitate was removed via filtration and the solvent removed under vacuum. The residual oil was then distilled through a 15-cm Vigreux column at reduced pressure to give 8.17 g (48.4 mmol, 61%) of a colorless liquid: bp 51.5–53.5 °C (0.60 mmHg). GC analysis on column D at 100 °C showed approximately 93% purity. ^{13}C NMR analysis showed the presence of two isomeric chloro olefins. IR (neat): 3049, 2958, 2894, 2843, 1448, 1353, 1321, 1310, 1274, 1259, 1238, 951, 925, 891, 788, 744, 701, 649 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 5.727 (m, 1H), 5.490 (m, 1H), 4.230 (m, 1H), 2.929–1.092 (m, 10H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 132.8, 132.8, 132.0, 131.9, 60.8, 60.4, 55.4, 49.8, 47.9, 47.2, 43.6, 43.4, 40.8, 40.5, 40.4, 39.8, 39.2, 35.7, 31.7, 31.6.

***endo*-9-Chloro-*exo*-tricyclo[5.2.1.$0^{2,6}$]decan-3-one.** A 3.07-g (18.2 mmol) mixture of *endo*-chloro olefins (*vide supra*) was dissolved in 2.4 mL of dry THF. The mixture was then cooled to 0 °C in an ice bath.

A 9.0-mL solution (9.0 mmol) of 1.0 M borane–THF complex was then added by syringe under nitrogen. The mixture was stirred at 0 °C for an additional 1 h and finally quenched via the careful addition of 5 mL of water. A chromic acid solution (prepared by dissolving 4.28 g of sodium dichromate monohydrate in 16.5 mL of water and 3.2 mL of H_2SO_4) was placed in the dropping funnel and added dropwise over 15 min. The ice bath was removed and the mixture stirred an additional 18 h at room temperature.

The mixture was diluted with 50 mL of water and extracted with 5 × 50 mL of ether. The extracts were combined, washed with 50 mL of saturated sodium bicarbonate and 50 mL of brine, and finally dried over Na_2SO_4. The ether was removed under vacuum and the residual oil distilled at reduced pressure to give 2.41 g (13.1 mmol, 72%) of a colorless liquid: bp 90.5–92 °C (0.73 mmHg). GC analysis on column C at 175 °C showed approximately 71% purity of a mixture of the three chloro ketones in a 1.5:1.8:1.0 ratio.

A 7.50-g (40.6 mmol) mixture of chloro ketones (several runs) was placed in a small flask and 21 mL of ether and 17 mL of saturated sodium bisulfate solution were added. The mixture was stirred at room temperature for 23 h and diluted with a small portion of ether, and the precipitate was removed via filtration. The ether was removed under vacuum and the residual oil again treated with sodium bisulfite as described above. This mixture was stirred at room temperature for 21 h and the precipitate removed via filtration. The ether extract was separated off and the aqueous phase back-extracted with 10 mL of ether. The extracts were combined and washed with 10 mL of brine, then dried over Na_2SO_4. The ether was removed under vacuum and the residual oil distilled at reduced pressure to give 1.79 g (9.69 mmol) of a colorless liquid. GC analysis on column C at 175 °C showed approximately 49% purity of a mixture of two chloroketones in a 8.2:1.0 ratio. GC analysis showed only a trace of the 4-keto isomer.

The title compound was separated from the other isomer via Lobar chromatography (eluent = 40% hexane/45% ether/15% ethyl acetate). Analysis of the isolated sample by GC on column D at 150 °C showed approximately 84% purity. The major impurity (10%) was the isomeric 5-keto chloride. IR (neat): 2962, 2883, 1733, 1473, 1448, 1409, 1310, 1302, 1286, 1258, 1248, 1199, 1171, 953, 922, 903, 862, 758 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.209 (dt, C9 *exo*-H, J = 10.4 and 4.0 Hz, 1H), 2.870 (d, C2, H J = 9.0 Hz, 1H), 2.723 (d, C1 H, J = 4.1 Hz, 1H), 2.424 (m, C6 H, 1H), 2.237 (m, C7 H, C4 H, C8 *exo*-H, C5 *endo*-H, 5H), 1.382 (m, C5 *exo*-H, 1H), 1.232 (m, C10 H, C8 *endo*-H, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 221.7 (C3), 58.6 (C9), 48.4 (C2), 46.8 (C1), 43.5 (C7), 42.8 (C6), 40.1 (C8), 38.9 (C4), 33.7 (C10), 25.3 (C5). UV (hexane): λ_{max} = 294 nm (15). MS EI m/e (%): 184/186 M^+, 39/10),

(42) Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Org. Chem.* **1980**, *45*, 4936.
(43) Bruson, H. A.; Riener, T. W. *J. Am. Chem. Soc.* **1945**, *67*, 1178.
(44) Fry, A. J.; Farnham, W. B. *J. Org. Chem.* **1969**, *34*, 2314.
(45) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron* **1980**, *21*, 1357.
(46) Gassman, P. G.; Burns, S. J. *J. Org. Chem.* **1988**, *53*, 5574.
(47) Bruson, H. A.; Riener, T. W. *J. Am. Chem. Soc.* **1945**, *67*, 723.

149 (M – Cl, 10), 66 ($C_5H_6^+$, 100). MS CI *m/e* (%): 185/187 (M + 1, 100/23). High-resolution MS EI (*m/e*): calcd, 184.0655; found, 184.0657.

endo-9-Chloro-3-methoxy-exo-tricyclo[5.2.1.0^{2,6}]dec-3-ene (GEndoCl). The title compound was prepared using the procedures of Tsunoda[45] and Gassman.[46] A 0.36-g sample (1.9 mmol) of *endo*-9-chloro-*exo*-tricyclo-[5.2.1.0^{2,6}]decan-3-one and 1.0 mL of dry CH_2Cl_2 were combined under nitrogen. The solution was stirred and cooled to –20 °C, and 5.0 μL (0.026 mmol) of trimethylsilyl triflate and 0.75 mL (5.4 mmol) of methoxytrimethylsilane were added by syringe under nitrogen. The mixture was then stirred an additional 3 h at –20 °C.

The mixture was quenched with 0.2 mL (2.5 mmol) of dry pyridine, poured onto 10 mL of saturated sodium bicarbonate, and extracted with 3 × 15 mL of ether. The extracts were combined and dried over a 1:1 mixture of Na_2CO_3 and Na_2SO_4. The ether was removed under vacuum, and the residual oil (presumably the dimethyl acetal) was immediately dissolved in 3.3 mL of dry CH_2Cl_2. The solution was stirred, and 0.41 mL (2.4 mmol) of *N,N*-diisopropylethylamine was added by syringe under nitrogen. The mixture was again cooled to –20 °C, and 0.42 mL (2.2 mmol) of trimethylsilyl triflate was added by syringe dropwise over about 5 min. The cooling bath was removed and the mixture stirred at room temperature for an additional 16.5 h.

The mixture was quenched with 0.39 mL of 1 M NaOH and stirred vigorously for 5 min. The mixture was then diluted with 10 mL of dry pentane and the pentane extract removed via syringe. The pentane was removed via distillation through a 15-cm Vigreux column. The residual oil was then distilled at reduced pressure to yield 0.17 g (0.86 mmol, 44%) of a colorless liquid, GEndoCl. GC analysis on column D at 140 °C showed approximately 92% purity. IR (neat): 3070, 2955, 2845, 1649, 1465, 1448, 1356, 1318, 1303, 1292, 1278, 1261, 1247, 1225, 1200, 927, 892, 857, 823, 778, 746, 661 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.465 (m, C4 H, 1H), 4.257 (dt, C9 *exo*-H, *J* = 10.5 and 4.2 Hz, 1H), 3.573 (s, OCH_3, 3H), 3.235 (m, C2 H, 1H), 2.587 (m, C5 *endo*-H, 1H), 2.450 (m, C1 H, 1H), 2.257 (m, C6 H, C8 *endo*-H, 2H), 1.965 (m, C7 H, 1H), 1.845 (m, C5 *exo*-H, 1H), 1.629 (m, C10 *anti* (to olefin)-H, 1H), 1.206 (m, C8 *exo*-H, C10 *syn* (to olefin)-H, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 159.9 (C3), 95.3 (C4), 60.0 (C9), 56.7 (OCH_3), 46.1 (C2), 45.7 (C1), 43.7 (C7), 42.2 (C6), 40.1 (C8), 35.1 (C5), 31.9 (C10). MS EI *m/e* (%): 198/200 (M$^+$, 4/1), 97 (100). MS CI *m/e* (%): 199/201 (M + 1, 100/29). High-resolution MS EI (*m/e*): calcd, 198.0811; found, 198.0807.

exo-Tricyclo[5.2.1.0^{2,6}]decan-3-one. A 2.01-g sample (15.0 mmol) of *exo*-tricyclo[5.2.1.0^{2,6}]dec-3-ene[48] was dissolved with stirring in 5.0 mL of dry THF. The mixture was then cooled to 0 °C in an ice bath.

A 7.5-mL solution (7.5 mmol) of 1.0 M borane–THF complex was then added by syringe under nitrogen. The mixture was stirred at 0 °C for an additional 1 h and finally quenched via the careful addition of 4 mL of water. A chromic acid solution (prepared by dissolving 3.5 g of sodium dichromate monohydrate in 13.6 mL of water and 2.6 mL of H_2SO_4) was placed in the dropping funnel and added dropwise over 15 min. The ice bath was removed and the mixture stirred an additional 18 h at room temperature.

The mixture was diluted with 100 mL of water and extracted with 100 mL and 4 × 50 mL of ether. The extracts were combined, washed with 50 mL of saturated sodium bicarbonate and 50 mL of brine, and dried over Na_2SO_4. The ether was removed under vacuum and the residual oil distilled at reduced pressure to give 1.44 g (9.59 mmol, 64%) of a colorless liquid: bp 69–75 °C (1.2 mmHg). GC analysis on column D at 100 °C showed approximately 91% purity of a mixture of the two ketones in a 5.4:1.0 ratio.

The title compound was separated from the other isomer via Lobar chromatography (eluent = 60% hexane/40% ether). Analysis of the isolated sample by GC on column D at 100 °C showed >99% purity. IR[49] (neat): 2953, 2875, 1732, 1463, 1409, 1317, 1297, 1248, 1163, 1087, 871, 829 cm^{-1}. ^{1}H NMR[49] ($CDCl_3$, 300 MHz): δ 2.464 (bs, C1 H, 1H), 2.110 (m, C2 H, C7 H, C6 H, C4 H, C5 *endo*-H, 6H), 1.511 (m, C8 *exo*-H, C9 *exo*-H, 2H), 1.397 (m, C5 *exo*-H, 1H), 1.169 (m, C8 *endo*-H, C9 *endo*-H, 2H), 1.079 (m, C10 H, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 222.5 (C3), 55.2 (C2), 43.3 (C7), 43.2 (C6), 40.0 (C1), 38.8 (C4), 34.0 (C10), 28.2 (C8), 28.0 (C9), 25.4 (C5). UV (hexane): λ_{max} = 295 nm (16). High-resolution MS EI (*m/e*): calcd, 150.1045; found, 150.1042.

3-Methoxy-exo-tricyclo[5.2.1.0^{2,6}]dec-3-ene (GOMe). The title compound was prepared using the procedures of Tsunoda[45] and Gassman.[46] A 0.561-g sample (3.74 mmol) of *exo*-tricyclo[5.2.1.0^{2,6}]decan-3-one and 1.0 mL of dry CH_2Cl_2 were combined under nitrogen. The mixture was stirred and cooled to –25 °C, and 7.2 μL (0.037 mmol) of trimethylsilyl triflate and 1.03 mL (7.47 mmol) of methoxytrimethylsilane were added by syringe under nitrogen. The mixture was then stirred an additional 4 h at –25 °C.

The mixture was quenched with 0.08 mL (1 mmol) of dry pyridine, poured onto 10 mL of saturated sodium bicarbonate, and extracted with 3 × 10 mL of ether. The extracts were combined and dried over a 1:1 mixture of Na_2CO_3 and Na_2SO_4. The ether was removed under vacuum, and the residual oil (presumably the dimethyl acetal) was immediately dissolved in 3.6 mL of dry CH_2Cl_2. The solution was stirred, and 0.45 mL (2.6 mmol) of *N,N*-diisopropylethylamine was added by syringe under nitrogen. The mixture was cooled to –20 °C, and 0.46 mL (2.4 mmol) of trimethylsilyl triflate was added by syringe dropwise over about 5 min. The cooling bath was removed and the mixture stirred at room temperature for an additional 18.5 h.

The mixture was quenched with 0.43 mL of 1 M NaOH and stirred vigorously for 5 min. The mixture was then diluted with 11 mL of dry pentane and the pentane extract removed via syringe. The extract was then stored in a freezer overnight to precipitate the *N,N*-diisopropylethylammonium triflate.

The salt was removed via filtration, and the pentane was removed via distillation through a 15-cm Vigreux column. The residual oil was then distilled at reduced pressure to yield 0.26 g (1.8 mmol, 48%) of a colorless liquid, GOMe. GC analysis on column C at 120 °C showed approximately 99% purity. IR (neat): 3069, 2950, 2870, 2844, 1649, 1459, 1356, 1303, 1293, 1276, 1249, 1229, 1194, 1174, 1049, 1029, 995, 947, 857, 774, 667. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.383 (m, C4 H, 1H), 3.553 (s, OCH_3, 3H), 2.513 (ddd, C5 *endo*-H, *J* = 15.4, 9.6, and 2.2 Hz, 1H), 2.412 (bd, C2 H, *J* = 6.4 Hz, 1H), 2.235 (bs, C1 H, 1H), 2.110 (m, C6 H, 1H), 1.919 (bs, C7 H, 1H), 1.828 (dq, C5 *exo*-H, *J* = 18.1 and 2.9 Hz, 1H), 1.469 (m, C8 *exo*-H, C9 *exo*-H, C10 *anti*-H, 3H), 1.146 (m, C8 *endo*-H, C9 *endo*-H, 2H), 1.006 (dt, C10 *syn*-H, *J* = 9.9 and 1.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.6 (C3), 94.6 (C4), 56.7 (OCH_3), 53.7 (C2), 43.4 (C7), 42.6 (C6), 38.9 (C1), 35.1 (C5), 31.9 (C10), 28.5 (C9), 28.4 (C8). MS EI *m/e* (%): 164 (M$^+$, 17), 97 (100). MS CI *m/e* (%): 165 (M + 1, 100). High-resolution MS EI (*m/e*): calcd, 164.1201; found, 164.1204.

Photolysis of AntiCl with (±)-sec-Butylamine in Hexane. Three solutions of 1.99 × 10^{-2} M AntiCl, 4.0 mL in volume, were prepared for photolysis in three quartz tubes. To the solutions was added 6.7 μL (0.83 equiv) of SBA. The solutions were degassed with argon for 15 min. One solution was wrapped with several layers of aluminum foil and subjected to the same conditions as the irradiated tubes. Analysis of the irradiated solutions by GC on column A at 140 °C revealed the presence of two products, 2-norbornanone (1.8%) and TMSNB (6.2%), as evidenced by GC/MS analysis and comparison with authentic mass spectra. Additionally, the hydrogen chloride that was presumably produced precipitated as the hydrochloride salt of SBA. The dark control solution did not contain any precipitated hydrochloride salt, and GC analysis showed only the presence of AntiCl.

Quantum Efficiency of the Disappearance of AntiCl in Hexane. Two solutions, 4.0 mL in volume, of 1.99 × 10^{-2} M AntiCl in hexane with 0.83 mol equiv of SBA in matched quartz tubes were degassed and irradiated with 254-nm light for 4.0 h. The actinometer used for the experiment was (*E*)-1-phenyl-2-butene; its quantum efficiency for *E* → *Z* isomerization is 0.20. Two solutions (4.0 mL) of the actinometer (2.43 × 10^{-2} M) in hexane in matched quartz tubes were degassed and irradiated for the first 5.0 min and last 5.0 min of the photolysis. After analysis for isomerization by GC on column B at 150 °C, correction for the back-reaction (*Z* → *E*), and correction for differences in the percentage of light absorbed by the actinometer and AntiCl, the average intensity was calculated at 3.77 × 10^{16} photon/s. Analysis by GC of the photolysis of AntiCl on column A at 140 °C with tetradecane as an internal standard gave an average Φ_{dis} = 0.0072 ± 0.0008.

Quantum Efficiency of the Disappearance of SynCl in Hexane. Three solutions, 4.0 mL in volume, of 1.58 × 10^{-2} M SynCl in hexane with 0.83 mol equiv of SBA in matched quartz tubes were degassed and irradiated with 254-nm light for 4.0 h. Solutions (4.0 mL) of (*E*)-1-phenyl-2-butene in hexane (2.50 × 10^{-2} M) in matched quartz tubes were degassed and irradiated for the first 5.0 min and last 5.0 min of the photolysis to serve as the actinometer. The (*E*)-1-phenyl-2-butene solutions were analyzed by GC on column C at 130 °C. The SynCl solutions were analyzed by GC on column A at 140 °C with tetradecane as an internal

(48) Bartlett, P. D.; Schneider, A. *J. Am. Chem. Soc.* **1946**, *68*, 6.
(49) Dzhemileva, G. A.; Odinokov, V. N.; Dzhemilev, U. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, *1*, 149.

standard. The average for the three determinations of the quantum efficiency was 0.0027 ± 0.0002.

Photolysis of GExoCl and GEndoCl in Hexane. Two separate solutions of GExoCl and GEndoCl in hexane (8×10^{-2} M), 1.0 mL in volume, were prepared for photolysis in quartz tubes. To each of these solutions was added 5 μL of tetradecane as an internal standard. Two other solutions, which served as dark controls, of GExoCl and GEndoCl were prepared in an analogous manner. These tubes were wrapped in several layers of aluminum foil and subjected to the same conditions as the irradiated tubes. The solutions were degassed with argon for 15 min and irradiated at 254 nm for 1.0 h. Analysis of the solutions by GC on column D at 140 °C revealed only small amounts of decomposition of the enol ethers in the irradiated tubes, while the dark controls were unreactive under the photolysis conditions. In addition, there was no evidence for the dehalogenated product, GOMe.

Attempted Photosensitization of GExoCl in Hexane. A solution of GExoCl (5.4×10^{-3} M), 4.0 mL in volume, which was also 0.10 M in *o*-xylene, was prepared for photolysis. The tube was degassed with argon for 15 min and irradiated at 254 nm for 56 min. Analysis by GC on column D at 140 °C periodically showed no observable loss of the enol ether. In addition, in separate control experiments, the enol ether was shown to be stable to photolysis in the presence of *o*-xylene and did not quench the fluorescence of *o*-xylene.

Photolysis of GExoCl and GEndoCl in Methanol. Solutions of GExoCl and GEndoCl (8×10^{-2} M) in methanol, containing 0.1 equiv of (±)-*sec*-butylamine, were prepared in separate quartz tubes. Two other solutions, which served as dark controls, were prepared in an analogous manner. These were wrapped in several layers of aluminum foil and subjected to the same conditions as the irradiated tubes. The solutions were degassed with argon for 15 min and irradiated at 254 nm for 1.0 h. Analysis of the solutions by GC on column D at 140 °C revealed only small amounts of decomposition of the enol ethers in the irradiated tubes, while the dark controls were unreactive under the photolysis conditions. In addition, there was no evidence for the dehalogenated product, GOMe.

Attempted Photosensitization of GExoCl in Methanol. A solution of GExoCl (6.6×10^{-3} M), 4.0 mL in volume, which was also 0.10 M in *o*-xylene, was prepared for photolysis. A small portion of solid sodium bicarbonate was added to the tube. The tube was degassed with argon for 15 min and irradiated at 254 nm for 56 min. Analysis by GC on column D at 140 °C showed no observable loss of the enol ether. In addition, in separate control experiments, the enol ether was shown to be stable to photolysis in the presence of *o*-xylene and did not quench the fluorescence of *o*-xylene.

Acknowledgment. We thank the National Science Foundation (Grants CHE-9007569 and CHE-8922601) for support of this research. Some of the calculations were performed on an FPS model 500 EA in the Chemistry Department at the University of Pittsburgh. Funding for this system was provided by a grant from the National Science Foundation.