tained. Examination of the ^{1}H NMR spectrum (200 MHz) with the help of 2D ^{1}H/^{1}H and ^{1}H/^{13}C correlations confirmed this hypothesis: protons on C-5 and C-11 are both axial and the cyano group occupied an axial position.

After ensuring the correct relative stereochemistry at carbons 5 and 11 it was necessary to introduce the pentyl side chain in the proper equatorial configuration. According to the CN(*R*,*S*) method, this was possible by simple decyanation of alkylated amino nitrile as **13**. Indeed, cyano aminal **9** was alkylated with *n*-pentyl bromide after deprotonation by LDA-HMPA to give **13** in 62% yield. The cyano group of **13** was removed in a stereospecific manner using Na in liquid ammonia to give (+)-tetraponerine-8 (**1**) in 97% yield.[8]

Synthetic (+)-tetraponerine-8 (**1**) exhibited all analytical data (^{1}H and ^{13}C NMR, MS) in full agreement with those of natural material.[2a] The same optical rotation and sign were also obtained: $[\alpha]_D$ +99° (*c* 0.6, $CHCl_3$) [lit.[2a] $[\alpha]_D$ +102° (*c* 0.15, $CHCl_3$)]. The relative configuration of tetraponerine-8 being known[2] it was thus possible to assign the 5*R*,9*S*,11*R* absolute configuration to synthetic and natural (+)-tetraponerine-8.

Acknowledgment. We want to thank Drs. Braekman, Daloze, and Merlin for valuable discussions.

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[8] The direct alkylation of **9** by a nucleophilic reagent (as a Grignard reagent) would lead in the opposite to the introduction of the side chain in an axial position.[5a]

Photoactivation through (π* + σ*) LUMO Mixing. Photochemistry and Photophysics of the 7-Chloro-2-(trimethylsiloxy)norbornenes[1]

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Summary: The syn and anti isomers of 7-chloro-2-(trimethylsiloxy)norbornene have been synthesized and found to be comparably and minimally photoactive, a result which contrasts with previous observations for the *exo*- and *endo*-6-chloro-2-(trimethylsiloxy)norbornenes and which confirms the role of (π* + σ*) LUMO mixing as the source of relatively facile C–Cl photolytic cleavage of the *exo*-6-chloro isomer.

The chemical consequences of orbital interactions between distal functionalities have been extensively investigated for molecular ground states[2] but much less so for electronic excited states. As part of our continuing interest in such interactions as a 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] 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 EndoCl. Such mixing of an antibonding σ* orbital into the LUMO should facilitate C–Cl homolysis upon photochemical excitation and such is indeed observed for ExoCl, with EndoCl almost 9-fold less reactive.[4]

Table I. π*/σ* LUMO Mixing in 6-Chloro- and 7-Chloro-2-(trihydrosiloxy)norbornenes

molecule	LUMO constitution[a] % σ* C–Cl	 % π* C=C
ExoCl	27.3	53.6
EndoCl	3.9	66.9
AntiCl	3.7	67.6
SynCl	4.5	66.0

[a] 3-21G*//3-21G* calculations with the percentages calculated as previously described.[4]

However, orbital mixing is not uniquely capable of rationalizing photolytic dehalogenation of ExoCl and, for example, one can derive a plausible alternative involving electron transfer from an initially excited silyl enol ether chromophore.[4] Though arguments against this alternative have been presented,[4] ab initio calculations on the related pair of isomers, *syn*- and *anti*-7-chloro-2-(trimethylsiloxy)norbornene (SynCl and AntiCl, respectively) suggested that a study of the spectroscopic and photochemical properties of these compounds could provide a definitive test of the orbital mixing mechanism. This is so because, despite the similar relative orientation of the C–Cl bond to the trimethylsilyl enol ether functionality in ExoCl and AntiCl, the calculations (see below) predict much less orbital mixing in (and thus a lower reactivity for) the AntiCl isomer. One would also anticipate a diminution in the anti/syn reactivity ratio for the 7-chloro pair relative to that observed for the exo/endo 6-chloro pair. By contrast, were an electron-transfer mechanism operating, a consideration of the relative distances of C-7 and C-6 to C-2 of the silyl enol ether moiety (2.35 Å vs 2.43 Å by ab initio calculation) would suggest that C–Cl homolysis in AntiCl should be comparable to that observed for ExoCl. Furthermore, the particularly close approach of the chlorine atom to C-2 in SynCl (3.16 Å), relative to that in AntiCl (4.08 Å) could well be expected to produce a particularly facile homolysis in the syn isomer. As we will show below, our results are consistent with the conclusions predicted by the orbital mixing hypothesis.

Ab initio calculations[5] were performed on the trihydrosiloxy analogues of the four compounds (ExoCl,

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[1] Organic Photochemistry, Part 85. Part 84: Wu, Z. Z.; Morrison, H. *J. Am. Chem. Soc.* **1989**, *111*, 9267. We thank the National Science Foundation (Grant CHE 8700333) for suport of this research.

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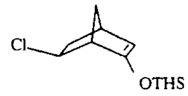


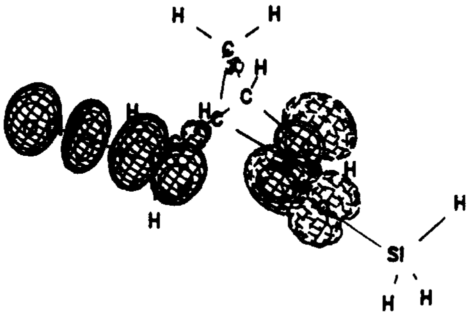
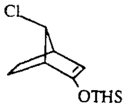


Figure 1. Delta plot showing the changes in electron density resulting from $S_0 \rightarrow S_1$ excitation of ExoCl;[4] dashed and solid contours correspond to loss and gain of electron density, respectively.[8]



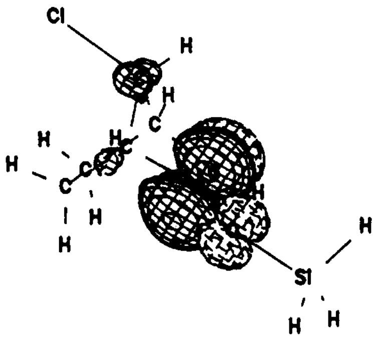


Figure 2. Delta plot showing the changes in electron density resulting from $S_0 \rightarrow S_1$ excitation of AntiCl; dashed and solid contours correspond to loss and gain of electron density, respectively.[8]

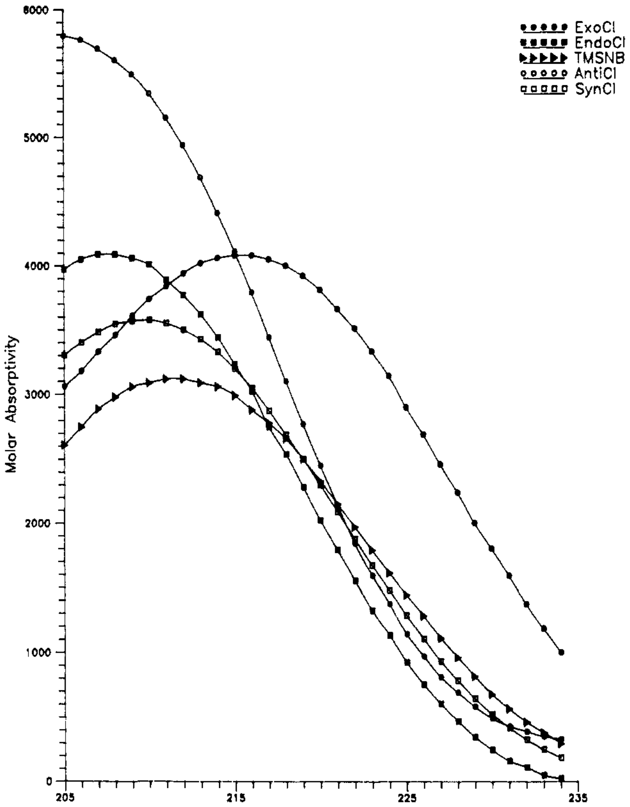


Figure 3. Absorption spectra for TMSNB, ExoCl, EndoCl, AntiCl, and SynCl.

EndoCl, AntiCl, SynCl[6] with the 3-21G* basis set.[7] The results are presented in Table I, and it is evident that the C–Cl σ^* contribution to the LUMO is greatly reduced in the 7-chloro series. This is particularly well seen in the Delta plots[8,9] for the $S_0 \rightarrow S_1$ transitions of ExoCl and AntiCl presented in Figures 1 and 2 and is explicable both in terms of the virtually symmetrical relationship of the orbitals of the enol ether and C–Cl group in the 7-chloro epimers and by the diminished C–Cl/C=C dihedral angle in AntiCl (34.5°) vs ExoCl (70.6°).[10]

Samples of AntiCl and SynCl were prepared by the triethylamine-catalyzed trimethylsilylation[4,11] of the corresponding 7-chloro-2-norbornanones.[12] The UV absorption spectra for these and related compounds are shown in Figure 3, and it is evident that the bathochromic shift (relative to 2-(trimethylsiloxy)norbornene, TMSNB, λ_{max} = 211.5 nm) of ca. 4 nm which characterizes the absorption maximum for ExoCl (λ_{max} = 215 nm) is absent in both of the 7-chloro isomers (λ_{max} = 206 and 211 nm for AntiCl and SynCl, respectively). (These, in fact, show hypsochromic shifts in their absorption maxima relative to TMSNB, as does EndoCl.)

Separate 4.0-h photolyses with 254-nm light of ca. 2×10^{-2} M solutions of AntiCl and SynCl in hexane (4.0 mL), with 0.8–1.0 molar equiv of (±) *sec*-butylamine added as an acid scavenger,[13] resulted in the formation of one and the same principal product observable by GC in each case, i.e.,the dehalogenated silyl enol ether, TMSNB. (Trace amounts of 2-norbornanone were also observed with AntiCl).[14] Quantum efficiencies for disappearance of the two substrates were determined using (*E*)-1-phenyl-2-butene actinometry[15] and were found to be 0.0069 ± 0.0008 and

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(6) The same symbols are herein used for the trihydrosiloxy and trimethylsiloxy derivatives. Calculations have been performed on the former in each case.

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(12) Satisfactory spectral and analytical data have been obtained on all new compounds.

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

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0.0025 ± 0.0003 for AntiCl and SynCl, respectively. By comparison, the quantum efficiencies for loss of ExoCl and EndoCl are 0.66 ± 0.001 and 0.0079 ± 0.0005, respectively.[4]

It is evident from these results that neither of the 7-chloro epimers show the theoretical and spectral characteristics associated with the relatively photoactive ExoCl, and that they are indeed both comparable in reactivity to EndoCl. Perhaps of even more significance is the fact that the relative reactivity of the respective isomer pairs has markedly diminished from ϕ_{dis}(ExoCl)/ϕ_{dis}(EndoCl) = 8.7 to ϕ_{dis}(AntiCl)/ϕ_{dis}(SynCl) = 2.8. All of these observations are consistent with our proposal[4] that, for these compounds, C–Cl photolytic cleavage derives from π^*/σ^* mixing in their lowest unoccupied molecular orbitals, and therefore delocalized excitation in their electronic excited states.[3]

Use of Metal Carbonyl Complexes To Achieve High Enantioselectivity in the Asymmetric Allylboration of Unsaturated Aldehydes

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Summary: The enantioselectivity of the asymmetric allylborations of aromatic and propargylic aldehydes is significantly enhanced by using metal carbonyl derivatives **4** and **8** as substrates.

Transition metal carbonyl complexes of unsaturated organic substrates have found numerous applications in organic synthesis.[1] For example, arene–chromium tricarbonyl complexes, among others, are highly activated toward nucleophilic attack; transition metal stabilized benzylic, allylic, and propargylic cations have found widespread application in stereocontrolled nucleophilic substitution reactions,[1b,2] and metal carbonyl units have been used as bulky substituents on *chiral substrates* enabling the diastereoselectivity of C–C bond forming reactions at adjacent positions to be enhanced.[1a,3] The electronic and/or steric influence of the metal on the unsaturated organic ligand is of course central to the success of these and many other applications. *We report herein a new and extremely useful effect of metal carbonyl complexes, specifically the ability of such complexes to enhance the enantioselectivity of the asymmetric allylborations of unsaturated (aryl and propargylic) aldehydes.* The reactions we report are unique in that they are among the first examples[4] in which metal carbonyl ligands of *achiral substrates* lead to an enhancement of the enantiofacial selectivity of a chiral reagent. This is in contrast to the vast majority of previously reported examples in which it is the diastereoface selectivity of the *metal carbonyl containing chiral substrates* that is enhanced.[1-3]

Previous studies from our laboratories have established that the asymmetric allylborations of aromatic aldehydes (e.g., benzaldehyde) proceed with only moderate enantioselectivity (55–72% ee for reactions with **1–3** in THF).[5] We thus decided to explore the use of the benzaldehyde chromium tricarbonyl complex **4** as a surrogate for C_6H_5CHO.[6] In the event, we were delighted to find that the asymmetric allylboration of **4** with (*R*,*R*)-**1** (toluene, −78 °C, 4-Å sieves) followed by oxidative decomplexation ($h\nu$, O_2, CH_3CN) provided (*S*)-**5** in greater than 90% yield and 83% ee.[7a] The (*E*)-crotylboration of **4** with (*R*,*R*)-**2** was even more selective, providing **6** with an ee of 92% (98:2 anti:syn; 90% yield).[7b] It is noteworthy that the sense of asymmetric induction is the same with or without the $Cr(CO)_3$ unit;[8] this substituent has simply led to an increase in the energy difference ($\Delta\Delta G^\ddagger$) between the favored (leading to the indicated enantiomers of **5** and **6**) and disfavored transition states.

Encouraged by these results, we examined the asymmetric allylboration of 2-decynal–dicobalt hexacarbonyl complex **8**.[9,10] This substrate was chosen for study since

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(7) (a) The reactions of benzaldehyde and **1–3** are more selective in THF than in toluene, while those of benzaldehyde–$Cr(CO)_3$ (**4**) display the highest selectivity in toluene. (b) The reaction of (*Z*)-crotylboronate **3** and **4** in toluene (−78 °C) provides **7** with 41% ee, while the reaction of **3** and PhCHO proceeds in only 25% ee under the same conditions. Thus, even though the enantioselectivity of the (*Z*)-crotylboration is enhanced (in toluene) by using **4** as a surrogate for PhCHO, the % ee does not exceed that obtained in the reaction of **3** and PhCHO in THF (55% ee). Reasons for the abberant behavior of **3** compared to **1** or **2** with **4** as a substrate are unclear at present.

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