(t), 57.6 (q, OCH_3), 70.6 (C-1), 88.5 (C-3); mass spectrum, *m/e* (rel intensity) 213 (M^+, 24.2), 182 ($M^+ - \cdot OCH_3$, 91.7), 170 ($M^+ - \cdot C_3H_7$, 13.6) 168 (8.8), 126 (100), 114 (28.5), 98 (24.5); high-resolution mass spectrum, *m/e* 213.2086 ($C_{13}H_{27}NO$ requires 213.20925). This substance was prepared independently by methylation of **81** by using CH_3I (1.2 equiv, Et_2O, reflux, 10 h). The synthetic and photochemically generated materials had identical physical and spectroscopic properties.

A dark control experiment was run in the following manner. A solution of 200 mg (0.73 mmol) of 1-methyl-2-(4-methyl-3-pentenyl)-pyridinium perchlorate (**73**) in 60 mL of CH_3OH was stirred for 2 h and hydrogenated (60 mg of PtO_2, 55 psi, 12 h). The solution was worked up in the same manner as for the photochemical reaction except for the molecular distillation step. GLC analysis (5% OV 101, 10 ft × $^1/_8$ in., 150 °C, 20 mL/min flow rate) indicated the presence of the reduced starting material **86** and the complete absence of other substances arising in the irradiation experiment.

2,2-Dimethyl-3-methoxycyclopentanone (76). A solution of 200 mg (1.57 mmol) of 2,2-dimethyl-3-hydroxycyclopentanone (**82**) and 1.1 g (4.80 mmol) of Ag_2O in 5 mL of CH_3I containing 0.5 mL of DMF was heated at 55 °C for 3 h. The solution was diluted with 300 mL of ether, filtered, and washed with water. The ethereal solution was dried and concentrated in vacuo to yield 127 mg (57.1% yield) of keto ether **76**. All physical and spectroscopic properties of this substance were identical with those of the material generated photochemically.

1-(Butylimino)-2,2-dimethyl-3-methoxycyclopentane (84). A solution of 120 mg (0.85 mmol) of 2,2-dimethyl-3-methoxycyclopentanone (**76**) and 373 mg (2.55 mmol) of *n*-butylamine in 45 mL of benzene containing 60 mg of *p*-toluenesulfonic acid was stirred at reflux with water removal through a molecular sieve (4 Å) column for 40 h. The solution was diluted with ether and extracted with 0.15% aqueous K_2CO_3. The ethereal solution was washed with water, dried, and concentrated in vacuo to yield 153 mg (78%) of the imine (**84**). For spectroscopic analysis, a portion of this material was further purified by preparative GLC (20% SE-30, 5 ft × $^5/_{16}$ in., 135 °C, 120 mL/min flow rate) (36.7% yield): ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 3 H, CH_3), 1.03 (t, 3 H, $C\mathit{H}_3(CH_2)_3N{=}$), 1.11 (s, 3 H, CH_3), 1.2–2.55 (m, 8 H), 3.15–3.55 (m, 3 H), 3.40 (s, 3 H, OCH_3); IR (neat) 1680 (C=N stretching), 1460, 1379, 1359, 1270, 1205, 1120, 1100, 990, 947 cm^{-1}; mass spectrum, *m/e* (rel intensity) 197 (M^+, 18), 182 ($M^+ - \cdot CH_3$, 19), 166 ($M^+ - \cdot OCH_3$, 28), 154 ($M^+ - \cdot C_3H_7$, 23), 124 (30), 110 (68), 73 (90), 69 (100); high-resolution mass spectrum, *m/e* 197.1767 ($C_{12}H_{23}NO$ requires 197.1781).

1-(Butylamino)-2,2-dimethyl-3-methoxycyclopentane (81). To a solution of 100 mg (0.51 mmol) of 1-(1-butylimino)-2,2-dimethyl-3-methoxycyclopentane in 4 mL of 1:1 methanol–THF was added 100 mg of $NaBH_4$. The resulting mixture was stirred for 30 min. The solution was concentrated in vacuo to yield a residue that was diluted with chloroform. The chloroform solution was washed with water, dried, and concentrated in vacuo to yield 95 mg (94%) of 1-(*N*-butylamino)-2,2-dimethyl-3-methoxycyclopentane. This material possesses physical and spectroscopic properties identical with those of the substance produced photochemically.

Effect of Acid on the Yield of 3-Methoxy-2,2-dimethylcyclopentanone (76) and 1-(Butylmethylamino)-2,2-dimethyl-3-methoxycyclopentane (85). Solutions of 200 mg (0.73 mmol) of 1-methyl-2-(4-methyl-3-pentenyl)pyridinium perchlorate (**73**) in 125 mL of methanol containing 0.0, 1 × 10^{-4}, and 1 × 10^{-2} M $HClO_4$ were irradiated with Corex-filtered light for 30 min. The crude photolysate derived by irradiation in methanol with no acid was acidified to ca. pH 2 with concentrated perchloric acid. The crude photolysates were then transferred to Parr medium-pressure reaction bombs and shaken under hydrogen atmospheres (55 psi) for 18 h. The solutions were filtered and concentrated in vacuo, yielding residues that were stirred with 70 mL of chloroform, 10 mL of saturated sodium bicarbonate, and 20 mL of water. The chloroform layers were separated, and the water layers were extracted again with 10 mL of chloroform. Each of the combined chloroform layers were washed with water, dried, and concentrated in vacuo to ca. 5 mL. To each of the concentrated solutions was added the biphenyl standard. GLC analysis (5% OV 101, 10 ft × $^1/_8$ in., 135 °C, 20 mL/min flow rate) give the relative yields of 2,2-dimethyl-3-methoxycyclopentanone (**76**) and 1-(butylmethylamino)-2,2-dimethyl-3-methoxycyclopentane (**85**) as follows: no acid, 1.0:1.0; 1 × 10^{-4} M $HClO_4$, 2.2:1.2; 1 × 10^{-2} M $HClO_4$, 2.9:1.3.

Acknowledgment. Support for this research by the National Science Foundation (CHE 80-90813) and the National Institutes of Health (GM-27251) is gratefully acknowledged. RS acknowledges the financial assistance provided by a grant from NIH (GM-19455) and guidance by Professors E. E. Hazen and F. A. Cotton for the X-ray crystallographic studies.

Photochemical Transformations. 32. Stereochemical Course and Stereochemical Requirement for Activation of Photosolvolysis and Photorearrangements in a Chlorobenzobicyclo[2.2.2]octadienyl System[1,2]

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Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80309. *Received April 5, 1982*

Abstract: The epimers 6-*anti*- and 6-*syn*-7-dichloro-2,3-benzobicyclo[2.2.2]octa-2,5-diene (**7**-Cl and **8**-Cl) have been subjected to irradiation in wet acetonitrile at 254 nm. The epimer **7**-Cl with chlorine anti to the benzene ring chromophore is photoactive, giving photo-Wagner–Meerwein isomerization and photosolvolysis to Wagner–Meerwein rearranged acetamides. Both the isomerization and the solvolysis (photo-Ritter reaction) are nonstereospecific, although migration of the syn chloroethenyl group occurs in modest preference to that of the anti benzo group. The syn chloride **8**-Cl is relatively photoinert, and no products attributable to photosolvolysis or photo-Wagner–Meerwein isomerization are produced.

A recent communication[3a] from this laboratory described the direct irradiation in acetonitrile or in acetic acid of some **7**-chloro derivatives of dibenzobicyclo[2.2.2]octadienes (**1**) and of 6-chloro and 6-methanesulfonoxy derivatives of 7-chloro-3,4-benzotricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**2** and **3**). These are all homobenzyl systems; that is, they have nucleofugal groups β to aromatic rings.

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(1) Paper 31: Cristol, S. J.; Graf, G. A. *J. Org. Chem.* **1982**, *47*, 5186.

(2) A portion of this work was described at the Spring 1981 meeting of the American Chemical Society in Atlanta, Georgia, and at the Tenth International Conference on Photochemistry in Iraklion, Crete, Greece, in September 1981.

(3) (a) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977. (b) Morrison, H.; Miller, A. *Ibid.* **1980**, *102*, 372.

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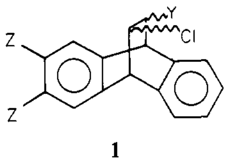

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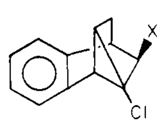

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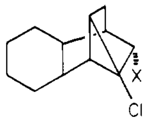

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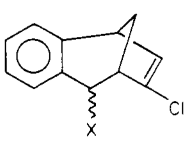

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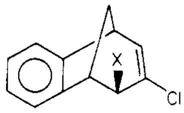
The aromatic rings are the light-absorbing chromophores. It was reported that photosolvolysis and photorearrangement seemed only to occur when the excited chromophore and the nucleofuge were anti and the photo-Wagner–Meerwein migrations in the **1** compounds were largely, but not exclusively, syn to the nucleofuge. Irradiation of *anti*-**2** derivatives led to compounds **4** (solvolysis and rearrangement) and a cyclopropylcarbinyl to homoallyl rearrangement, while the syn epimers **3** gave no such reactions. Morrison and Miller[3b] have similarly observed a large preference for anti activation in a benzo-2-norbornenyl system. In contrast,[4] the homobenzyl allylic species, **5**-Cl, **6**-Cl, **5**-OMs, and **6**-OMs, showed little stereochemical difference in their photoreactions to give solvolysis products **5** or photo-Wagner–Meerwein rearrangement products **7**-Cl or **7**-OMs. Obviously, excitation transfer from aromatic ring to allylic system does not suffer the same stereochemical constraints as the nonallylic systems, presumably a consequence of the chloroethenyl moiety. It was therefore of interest to study the photoreactions of **7** and **8** species to see if the homoallylic systems (which of course are also homobenzylic) retained or lost the stereochemical freedom of the allylic systems. In this paper, we report our results with **7**-Cl and **8**-Cl.



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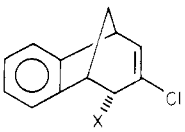

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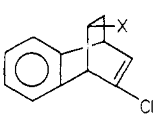

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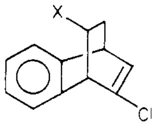

8

Compound **7**-Cl was prepared, as described earlier,[4a] by the reaction of **5**-Cl[5] with ferric chloride. The anti tricyclic chloride **2**-Cl was prepared by treatment of the known[4a] syn tricyclic methanesulfonate **3**-OMs with lithium chloride. Treatment of **2**-Cl with ferric chloride gave **8**-Cl.[6]

Irradiation of the syn epimer **8**-Cl at 254 nm in acetonitrile-d_3 containing 2% deuterium oxide was monitored from time to time for up to 100 h. No photosolvolysis or photorearrangement products were noted. The mild degradation led to no identifiable or isolable products. On the other hand, similar irradiation of the anti epimer **7**-Cl produced both photosolvolysis and rearrangement products. In the ground-state heterolytic reactions[4a] of **7**-Cl, only allylic isomers (**5** and **6**) are produced. This, of course, is typical of Wagner–Meerwein rearrangements, where anti participation is general. In contrast to the ground-state reaction, the stereochemistry of the photo-Wagner–Meerwein reactions was not clean. Moreover, the benzylic products, **4**-Cl and **4**-NHCOCH$_3$, which result from syn migration, were favored over the allylic products **5**-Cl and **5**-NHCOCH$_3$ (anti migration products) by a ratio of about 5 to 2. Analysis involved the separation of chlorides from amides by column chromatography, selective hydrolysis of **4**-Cl to **4**-OH, leaving **5**-Cl and **7**-Cl unreacted, and measurements of the compositions of the various fractions by weighing and ^{1}H NMR spectroscopy.

The homobenzylic chloroethylenic system represented by **7**-Cl and **8**-Cl is thus similar to the dibenzobicyclooctadiene system **1** and the tricyclic systems **2** and **3** and dissimilar from the homobenzylic allylic systems **5** and **6** in having what appears to be a strict stereochemical requirement for an anti disposition of "chromophores" in the intramolecular transmission of excitation from the donor light-absorbing chromophore to the acceptor reaction site. It was assumed[3a] that the anti activation occurs as an intramolecular electron transfer from the π,π^* excited state of the aromatic ring to the lobe of the σ^* orbital of the carbon–nucleofuge bond, which extends anterior to the carbon atom, or to an orbital that combines the overlapping π^* and σ^* orbitals. The σ^* orbital of the carbon–chlorine bond has lobes extending from both the carbon and chlorine atoms along the bond axis,[8] but models of **7**-Cl and **8**-Cl show that a line extended along the chlorine–carbon bond axis in **7**-Cl intersects the perpendicular from the plane of the benzene ring at a distance of 1.5 Å from the ring and almost bisects the suprafacial lobes of the π and π^* orbital systems. On the other hand, a similar construct along the carbon–chlorine bond axis of **8**-Cl intersects the perpendicular at a distance greater than 4.0 Å at its closest approach to the ring and is exo to the ring of carbon nuclei. If one assumes that these differences are reflected as extra work involved in electron removal from the excited benzene ring, the requirement for anti activation may be understood. Obviously, the carbon–chlorine bond in **8**-Cl has the same attitude with respect to the double bond as the analogous bond has to the benzene ring in **7**-Cl. Thus the lack of photoactivity in **8**-Cl indicates that the isolated chloroethenyl group cannot operate as a simple relay point for the presumed electron-transfer process.

The presumed electron transfer results in a zwitterionic biradical, represented by **9**, and rapid decay of that species by loss of chloride ion can be anticipated.[4,9] This would result (see Scheme I) in the excited-state cation biradical **10** intermediate (paired with chloride ion). One plausible mode of decay of **10** involves double-bond participation to give the tricyclic excited-state cation biradical **11**, and continuation gives **12**, whose return to ground state gives the benzylic ion **13**, the progenitor of the major products **4**. Alternatively, return to the ground state from **11** would give the analogous tricyclic cation, which is known[6] to isomerize to **13**. Another plausible mode[4] involves decay from **10** to the ground-state bridged ion **14**, which is known[4] to give products of structure **5** via the allylic cation **15**. It seems remarkable that the competition for the two migration directions is so close, but we are unaware of analogies in the literature, other than work in our own laboratory[3a] regarding migratory aptitudes of unsaturated radical cation groups vs. other unsaturated groups toward radical centers. It seems possible that the slight preference for **11** formation might be due to the greater ability of the chloroethenyl group to "donate" an electron compared to that of the electron-deficient aromatic ring. The results cannot, however, be rationalized so simply, as the radical **16**, which is analogous to **10** except that the aromatic ring has its complete component of π electrons, is known[10] to rearrange to **17** via chloroethenyl migration in preference to rearrangement to **18** via aromatic ring migration (none of the product from **18** was observed). These

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(4) (a) Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 5707; (b) *Ibid.* **1980**, *102*, 5577.

(5) Goldschmidt, Z.; Gutman, W. *Tetrahedron* **1974**, *30*, 3327.

(6) The ground-state chemistry linking **2**, **3**, **4**, and **8** species has been investigated[7] in detail.

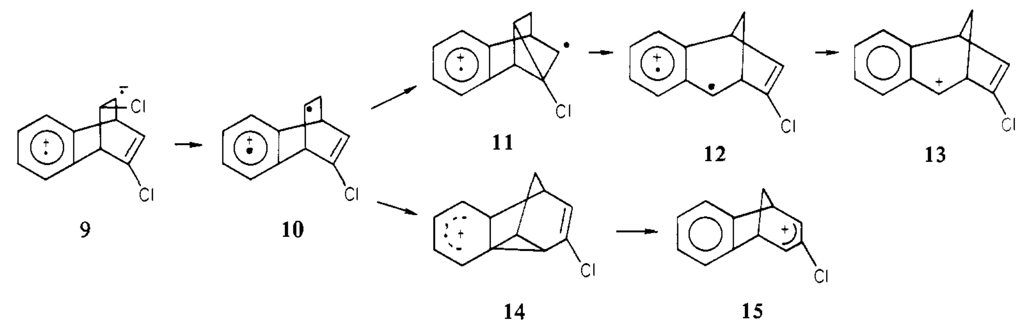
(7) Dickenson, W. A. Ph.D. dissertation, University of Colorado, Boulder, 1981.

(8) Jorgenson, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York and London, 1973; p 108.

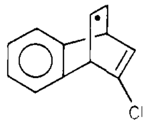
(9) For references see: Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. Cristol, S. J.; Barbour, R. V. *J. Am. Chem. Soc.* **1968**, *90*, 2832.

(10) Cristol, S. J.; Klein, M. W.; Hendewerk, M. H.; Daussin, R. D. *J. Org. Chem.* **1981**, *46*, 4992.

Scheme I



results on the neutral radical, compared to those we report on **7**-Cl, also make it clear that radical **16** is not involved in the photoreaction[10] and that the driving force for the rearrangement must originate in a source different from those affecting either ground-state cation or ground-state radical processes. We hope that a study of substituent effects on migration aptitudes, now in progress in our laboratory, may shed some light on this and other problems of photostereochemistry and photoregiochemistry.



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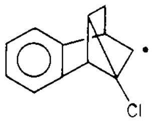

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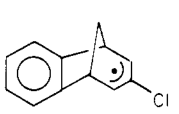

18

Experimental Section

Preparation of *anti*-6,7-Dichloro-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-ene (2-Cl). A solution of 601 mg (2.11 mmol) of the syn tricyclic methanesulfonate,[4a] **3**-OMs, and 2.51 g (59 mmol) of lithium chloride in 17 mL of dimethylformamide was heated at 100 °C for 50 h. The solution was diluted with 60 mL of water and extracted with 60 mL of ether. The ether extract was washed with aqueous sodium bicarbonate twice, water, aqueous cupric nitrate twice, and water twice and dried ($MgSO_4$). Filtration and evaporation of solvent gave 430 mg (91%) of a yellow oil, which ^1H NMR analysis indicated was 80% **2**-Cl, 15% benzylic chlorides **4**-Cl (about 5:2 exo:endo), and about 5% benzylic formates **4**-OCHO. Pure **2**-Cl, mp 73–74 °C, was crystallized from ether/hexanes mixed solvent from the colorless oil obtained by column chromatography on silica gel of the product mixture. ^1H NMR[11] ($CDCl_3$): δ 7.2 (m, 4, aromatic H), 3.8 (s, 1, H-6), 3.3 (d, 1, H-5, $J_{5,8_{anti}} = 5$ Hz), 2.8 (d, 1, H-2, $J_{2,1} = 8$ Hz), 2.7 (ddd, 1, H-8 anti, $J_{8_{anti},1} = 3$, $J_{8_{anti},5} = 5$, $J_{8_{anti},8_{syn}} = 12$ Hz), 2.2 (dm, 1, H-1, $J_{1,2} = 8$ Hz), 1.1 (d, 1, H-8 syn, $J_{8_{syn},8_{anti}} = 12$ Hz). Anal. Calcd for $C_{12}H_{10}Cl_2$: C, 64.03; H, 4.48. Found: C, 63.98; H, 4.59.

Preparation of 6-*syn*-7-Dichloro-2,3-benzobicyclo[2.2.2]octa-2,5-diene (8-Cl). A solution of 1.35 g (6.00 mmol) of the antitricyclic chloride, **2**-Cl, and 200 mg (1.23 mmol) of ferric chloride in 50 mL of carbon tetrachloride was heated at 55 °C for 26 h. After the solution was cooled, it was extracted with water. The aqueous phase was extracted with three portions of carbon tetrachloride. The combined organic layers were washed twice with water and dried ($MgSO_4$). Filtration and evaporation of solvent gave 1.44 g of a dark yellow oil. ^1H NMR analysis showed that this oil contained **8**-Cl, **2**-Cl, and *exo*-**4**-Cl in a 4:3:2 ratio as well as lesser amounts of **3**-Cl and *endo*-**4**-Cl. The chlorides other than **8**-Cl were selectively solvolyzed in 4.5 days with a stoichiometric amount of silver acetate in acetic acid. The resulting mixture of **8**-Cl and benzylic acetates **4**-OAC (predominantly exo) contained no **4**-Cl and only traces of **2**-Cl and **3**-Cl. The mixture was methanolyzed in a solution of 0.1 M sodium methoxide in methanol that was heated at reflux for 10 min. This solution was then diluted with water and extracted with three portions of ether. The combined ether layers were washed with water and brine and dried ($MgSO_4$). Filtration and evaporation of the solvent gave a mixture of **8**-Cl and the epimers of **4**-OH that was separated by column chromatography on silica gel to give nearly pure **8**-Cl as a clear oil. ^1H NMR ($CDCl_3$): δ 7.2 (m, 4, aromatic H), 6.5 (dd, 1, H-5, $J_{5,1} = 2$, $J_{5,4} = 7$ Hz), 4.4 (dt, 1, H-7, $J_{7,1} = 3$, $J_{7,8_{syn}} = 3$, $J_{7,8_{anti}} = 9$ Hz), 4.1 (t, 1, H-1, $J_{1,7} = 3$, $J_{1,5} = 2$ Hz), 4.0 (dt, 1, H-4, $J_{4,8_{syn}} = 3$, $J_{4,8_{anti}} = 3$, $J_{4,5} = 7$ Hz), 2.5 (ddd, 1, H-8 anti, $J_{8_{anti},8_{syn}} = 12$, $J_{8_{anti},7} = 9$ $J_{8_{anti},4} = 3$ Hz), 1.6 (dt, 1, H-8 syn, $J_{8_{syn},7} = 3$, $J_{8_{syn},8_{anti}} = 12$, $J_{8_{syn},4} = 3$ Hz). Mass spectrum (peak, *m/e* (relative intensity)): M, 224 (32); M + 2, 226 (19); M − 35, 189 (40); M − 62, 162 (100).

Small-Scale Irradiations of 6-*syn*- and 6-*anti*-7-Dichloro-2,3-benzobicyclo[2.2.2]octa-2,5-diene (8-Cl and 7-Cl). A solution of 42 mg of **8**-Cl in 0.5 mL of acetonitrile-d_3 containing 2% deuterium oxide was prepared. The solution was filtered into a quartz NMR tube and purged with a slow stream of nitrogen for several minutes. This tube was then irradiated at 254 nm in a Rayonet Srinivasan-Griffin photochemical reactor. It was monitored both before and periodically during the irradiation by ^1H NMR. After 100 h of irradiation, over 80% of the starting material remained. A trace of *exo*-**4**-OH was observed; however, a trace of the antitricyclic chloride, **2**-Cl, had been present in the starting material, and *exo*-**4**-OH is known[3,7] to be produced efficiently from that chloride under these conditions. The antitricyclic chloride disappeared early in the irradiation, and after that disappearance was complete, no additional *exo*-**4**-OH was produced. It was concluded that no products of photochemical reaction of **8**-Cl had been observed. In contrast, similar irradiation of **7**-Cl for 26.3 h showed measurable amounts of photochemical products.

Large-Scale Irradiation of 6-*anti*-7-Dichloro-2,3-benzobicyclo[2.2.2]octa-2,5-diene (7-Cl). A solution of 796 mg (3.54 mmol) of **7**-Cl in 800 mL of acetonitrile was purged with a stream of nitrogen and then irradiated at 254 nm in a Rayonet Srinivasan-Griffin photochemical reactor for 3 h. After evaporation, the crude product was submitted to dry column chromatography (about 93 g of silica gel) and eluted first with 10 mL of ether followed by 130 mL of 5% ether in hexanes. Four overlapping bands, encompassing the entire column, were separated and extracted with ether, followed by a 1:1 mixture of methanol and methylene chloride to give 91 mg of crude amides *endo*- and *exo*-**4**-$NHCOCH_3$ and **5**-$NHCOCH_3$, 23.7 mg of less pure amides, 539 mg of a mixture of **7**-Cl, *endo*-**4**-Cl, and *exo*-**4**-Cl (92:1:3), and 151 mg (0.67 mmol) of **7**-Cl. The latter weight and all further weights are estimates based on the purity of compounds by NMR and the experimental weights.

The 539-mg mixture of **7**-Cl and *endo*- and *exo*-**4**-Cl was treated with 6 mL of 50% aqueous acetone and heated at reflux for 34 h. The product was then extracted with methylene chloride, dried ($MgSO_4$), and evaporated. The crude material was eluted through a column containing about 80 mL of silica gel with 2% ether in hexanes to give 16.4 mg (0.079 mmol) of *exo*-**4**-OH, possibly contaminated with a trace of *endo*-**4**-OH, and 416 mg (1.85 mmol) of **7**-Cl, contaminated with traces of *exo*-**4**-Cl and **5**-Cl. The amounts of the latter two were estimated to be about 2 and 4 mg, respectively.

The 91-mg mixture of amides was transferred to a preparative TLC plate with 0.5-mm depth of silica gel and eluted three times with 75% ether in hexanes. A band containing 28.0 mg (0.113 mmol) of equal amounts of *exo*-**4**-$NHCOCH_3$ and **5**-$NHCOCH_3$ was found, as well as a smaller upper band containing about 1.2 mg (0.005 mmol) of *endo*-**4**-$NHCOCH_3$. A considerable amount of *endo*-**4**-$NHCOCH_3$ was lost in the separation, as ^1H NMR analysis on the amides indicated that it comprised roughly 20% of the crude amides. This analysis accounted for 77% of the starting **7**-Cl, and summation indicated that the isolated benzylic to allylic product ratio was 2.5:1.

Acknowledgment. This work was begun with support from the National Science Foundation (Grant CHE80-11933) and completed with support from the Office of Basic Energy Sciences, U.S. Department of Energy (Contract DE-AC02-79ER10366). S.J.C. is indebted to the John Simon Guggenheim Memorial Foundation and to the Council on Research and Creative Work of the University of Colorado for fellowship support.

Registry No. **2**-Cl, 75920-62-6; **7**-Cl, 72182-74-2; **8**-Cl, 84171-12-0.

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[11] ^1H NMR spectra were obtained with a Varian Associates EM-390 instrument.