Photochemical Transformations. 41. Epimerization and Solvolysis in the Ground-State and Excited-State Reactions of Some Bridged Bicyclic Benzylic Compounds[1]

Stanley J. Cristol,* Robert J. Opitz, and Ellen O. Aeling

Department of Chemistry, University of Colorado, Boulder, Colorado 80309

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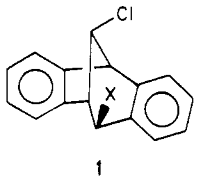
Ground-state carbocationic reactions of *syn*- and *anti*-8,4-dichloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dienes 1-, 2-, 3-, and 4-Cl have been studied, including epimerization at C-4, solvolysis, and, in the case of the anti 8-chloro epimers, Wagner–Meerwein rearrangement to the [2.2.2] isomer (6-Cl). The syn 8-chloro isomers give no [2.2.2] products. In addition, free-radical reductive removal of the C-4 chlorine in 1-Cl and 3-Cl is described, which proceeds without rearrangement. The photochemistry of these chlorides in acetonitrile and in acetic acid, both direct and sensitized, leads to epimerization and to photosolvolysis to amide or to acetate, with a photostationary state composition of chlorides distinctly different from the ground-state equilibrium composition and without C-8 bridge migration, that is, without interconversion from syn to anti 8-chloro compounds or the reverse. The photoepimerization and photosolvolysis results are consistent with the existence of intimate and solvent-separated ion pairs similar to those involved in ground-state reactions. However, in acetonitrile, irradiations of the syn 8-chloro compounds 1-Cl and 2-Cl gave the cis [2.2.2] product 5-Cl, while those of the corresponding anti 8-chloro compounds 3-Cl and 4-Cl gave no [2.2.2] products. These results are not consistent with those of corresponding ground-state intermediates.

For some time[2] members of our research group have been interested in the solvolysis of benzylic compounds attendant upon their irradiations and in the nature of the carbocations that are intermediates in these reactions, as well as in similar problems involving homobenzylic systems.[3] In simple benzylic systems, photosolvolyses proceed with principal racemization of chiral centers,[4-6] accompanied by a small amount of inversion, consistent with the formation of ion-pair or ion-molecule intermediates, and with major capture at the solvent-separated or free-ion stage. In addition, Jaeger and Angelos[5] studied ^{18}O scrambling in chiral acetates and demonstrated that there was significant front-side return from the postulated ion pair.

In a more complex system,[2] Wagner–Meerwein rearrangement was observed in the recovered substrate, as well as in the solvolysis product, again consistent with the intervention of an ion-pair intermediate, which could suffer return or proceed to solvolysis product. With homobenzylic systems, a variety of Wagner–Meerwein rearrangements has been noted.[3] We now report our results on irradiations of the *syn* and *anti*-8-chloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-4-yl systems 1–4, which are both benzylic and homobenzylic and contrast these results with those of ground-state analogues, as well as report radical reductions.



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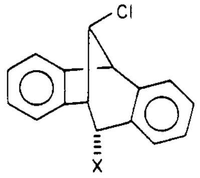

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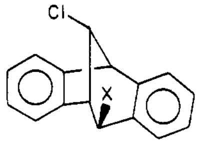

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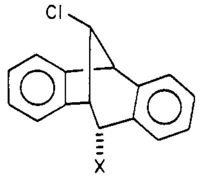

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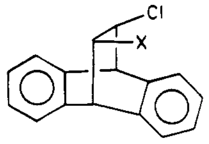

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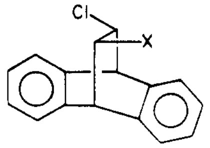

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The exo-4-syn-8-chloro compound 1-Cl is the principal kinetic product[7] of addition of chlorine to dibenzobarrelene, although small amounts of the endo isomer 2-Cl are also produced. It had also been shown previously[7] that 1-Cl could be converted to 2-Cl in a mixture of *o*-cresol and liquid sulfur dioxide, but we found that ferric chloride catalyzed epimerization was more convenient. In carbon tetrachloride and in the presence of a trace of ferric chloride, conversion to the endo epimer 2-Cl was essentially complete (^{1}H NMR analysis) within 5 min. Even after several hours, the reaction mixture did not contain measurable amounts of the [2.2.2] isomer 5-Cl. These results are consistent with those reported earlier[8] on the corresponding acetate 1-OAc, where epimerization to endo epimer 2-OAc occurs readily and rearrangement to the cis [2.2.2] product was not seen. When either the exo (3-Cl) or endo (4-Cl) anti 8-chloro compound was similarly treated with ferric chloride for 5 min, mixtures of 3-Cl and 4-Cl were produced, with the exo epimer predominating in a ratio approximating 4:1, and in the latter case, with measurable amounts of the trans [2.2.2] isomer 6-Cl present. After 2 h, the reaction mixtures contained more than 80% of 6-Cl. These results are similarly analogous to those of the anti-8-chloro 4-acetates,[8] where measurable

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(1) Previous paper in series: Cristol, S. J.; Opitz, R. J. *J. Org. Chem.*, in press.

(2) Cristol, S. J.; Schloemer, G. C. *J. Am. Chem. Soc.* **1972**, *94*, 5916.

(3) For a review of early work, see: Cristol, S. J.; Bindel, T. H. *Org. Photochem.* **1983**, *6*, 327-415.

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amounts of both exo (**3**-OAc) and endo (**4**-OAc) acetates were produced rapidly and conversion to the trans [2.2.2] isomer **6**-OAc ultimately occurred in acetic acid, catalyzed by strong acids.

The reduction of **1**-Cl with tri-*n*-butyltin hydride (initiated with azobisisobutyronitrile) led cleanly to **1**-H, without C-8 bridge migration or benzo ring migration. This radical[9] reduction parallels the hydrogenolysis of **1**-Cl, which also[7] gives **1**-H, and it has been shown previously[10] that [2.2.2] radicals rearrange to [3.2.1] radicals, so that failure to see [2.2.2] products is not unexpected. Similar reduction of **3**-Cl gave only **3**-H as product; that is, no rearrangements occurred.

When **1**-Cl or **2**-Cl (or mixtures of **1**-Cl and **2**-Cl) were irradiated in acetonitrile, either directly (254 nm) or with acetone sensitization, epimerization was observed to occur, giving rise to approximately equal amounts of **1**-Cl and **2**-Cl, as well as to lesser amounts of exo amide **1**-NHAc. Rearrangement to the cis [2.2.2] isomer **5**-Cl occurred slowly, and ultimately a photostationary composition of dichlorides containing about 12–15% of **5**-Cl was produced. Similar experiments were carried out with **3**-Cl and **4**-Cl. Here, again, exo-amide was formed (**3**-NHAc), and an approximately equal mixture of **3**-Cl and **4**-Cl resulted, but no rearrangement to [2.2.2] isomers was observed, even with long exposures.

When **1**-Cl was irradiated with 254-nm light in acetic acid-d_4, it was converted to a mixture with **2**-Cl about twice as fast as it was converted to its solvolysis product **1**-OAc-d_3. The steady-state mixture contained **1**-Cl and **2**-Cl in a ratio of about 2:3. No endo acetate **2**-OAc-d_3 was produced initially. After significant conversion of the chlorides to **1**-OAc, the endo acetate began to appear. Thus it seems to be due to epimerization of the acetate, rather than to substantial formation directly by solvolysis (cf. infra). Similar irradiation of the anti-endo dichloride **4**-Cl gave both epimerization and solvolysis. In this case, the processes occurred at about the same rate. In the steady state, exo predominated over endo by a factor of 3:2. The acetate product was exo (**3**-OAc-d_3) and epimerization of the acetate was not observed.

The reactions to give epimer and acetolysis product (**1**-OAc) from either **1**-Cl or **2**-Cl could be sensitized with acetone (300-nm light). The dichlorides are substantially transparent at this wavelength. The steady-state ratio of **1**-Cl to **2**-Cl was about 1:1 under these conditions; no isomerization to [2.2.2] dichloride was observed in the sensitized or unsensitized reactions, even on extended irradiations, nor was any transformation of syn-8-chloro to anti-8-chloro compounds (or the reverse) seen.

The two exo acetates (**1**-OAc and **3**-OAc) were irradiated in acetic acid-d_4. With the syn acetate (**1**-OAc) exchange was about 10 times as fast as epimerization (steady state about 1:1), while, with the anti acetate (**3**-OAc), approach to the steady state (about 4:1 exo:endo) was somewhat more rapid than exchange.

The photosolvolysis of benzylic halides has been shown[11] to occur from both singlet and short-lived triplet states. The experiments described herein, in which both direct irradiation and sensitization result in epimerization and photosolvolysis, suggest that this is also true for the **1**–**4** systems, but our experiments do not rule out the possibility of intersystem crossing from the excited singlet to a short-lived triplet. While it is clear that the solvolysis of benzylic systems involves the formation of ion pairs[3–6,11] and the capture of free cations or the cations in solvent-separated ion pairs[4–6] by solvent, details of the reactions remain obscure. It is not clear whether excitation leads directly to a π,π^* excited state which later suffers electron transfer to a zwitterionic state, as is the process[12] in homobenzylic systems, whether the electron transfer occurs on irradiation, or indeed whether excitation transfer is more properly to be considered as energy transfer rather than electron transfer. Further, the multiplicity of the direct irradiation path is obscure. Nonetheless, the experiments reported above, combined with those reported earlier, allow for certain conclusions and for a partial understanding of these and presumably related reactions.

First, the formation of exo acetate or exo amide from the photosolvolyses and the absence of significant amounts of endo epimers are consistent with results of ground-state solvolyses[1,13] and of photosolvolyses–rearrangements of [2.2.2] systems.[1] This observation leads to the conclusion that a "normal" cation is produced by the time capture by solvent occurs. The photoepimerization of **1**-Cl to **2**-Cl, which occurs somewhat faster than photoacetolysis, is also similar to that in the ground-state acetolysis, where it was observed[13a] that the rate of exo to endo epimerization was about 1.5 times that of solvolysis of **1**-Cl, again suggesting that an almost "normal" ion pair is produced in the photoreaction. The ground-state acetolysis,[13a] like the ferric chloride catalyzed isomerization, leads to complete epimerization in the ion-pair return component of the reaction. This may be largely the result of the fact that the formation of ion pairs from **2**-Cl is slower than that from **1**-Cl. In the photoreaction, reactivity is, of course, induced by light absorption, and, as the two epimers have similar chromophores, the steady-state ratio contains substantial amounts of both epimers.

The two exo acetates **1**-OAc and **3**-OAc also showed both epimerization and exchange, although they were not as photoactive as the chlorides. It is of interest that epimerization was observed in both cases to proceed at rates competitive with solvolysis. This may be contrasted with results in the 1-(3,5-dimethoxyphenyl)ethyl system studied by Jaeger and Angelos[5] or with 3,5-dimethoxybenzyl-*1-d* acetate,[14] where only return without racemization was observed. Their experiments were carried out in aqueous methanol and in 2,2,2-trifluoroethanol, solvents of significantly higher ionizing power than that of acetic acid and acetonitrile. That return would be less likely to compete with solvation in the more polar solvents in the relatively loose intimate ion pair on the path to epimerization may reasonably be suggested.

A comparison of **1**-OAc and **1**-Cl in acetic acid indicates that loss of acetate, leading to exchange, is somewhat faster than loss of chloride, compared with return to give epimerization. This can be rationalized by the assumption that acetate ion in acetic acid can, by proton transfer from solvent, become acetic acid whose loss into the solvent cage is much more facile than that of anion. Thus ion-pair return should occur more frequently with the chloride than with the acetate, as is observed.

The epimerizations and the solvolyses are thus reasonably well rationalized by the assumptions of the inter-

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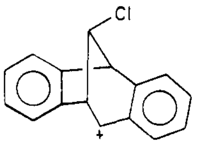
(14) Footnote 15 in ref 5.

vention of ion pairs in which **7** is the cationic component from **1** and **2** species and **8** from **3** and **4** species and that there is no **7** $\rightleftharpoons$ **8** transformation. On the other hand, we have no rationalization for the [3.2.1] to [2.2.2] rearrangement observed in the irradiation of **1**-Cl and **2**-Cl in acetonitrile. Two aspects are particularly interesting and confusing. The fact that the cis dichloride (**5**-Cl) is the only one produced (from **1**-Cl and **2**-Cl) and that the trans dichloride is not seen in any of the irradiations seem to rule out the bridged ions **9** and **10** as intermediates, as our experiments and the treatment of **2**-Cl with ferric chloride show that either **9** is not readily formed in equilibration with **7** or is not captured in ground-state reactions to give the [2.2.2] cis dichloride in a meaningful amount. The failure of the attempted acid-catalyzed rearrangement[8] of **1**-OAc and **2**-OAc to **5**-OAc leads to a similar conclusion.



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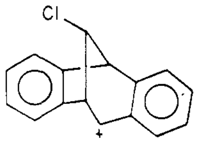

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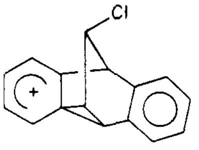

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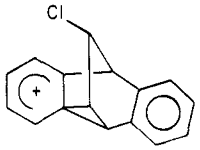

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On the other hand, the ground-state rearrangements of **3**-Cl and **4**-Cl to the trans dichloride **6**-Cl and the corresponding experiments with the acetates, which proceed to **6**-OAc, stand in contrast to the failure to observe this rearrangement in the photoreaction. Clearly this result is inconsistent with the idea of a "normal" cationic intermediate in this part of the photochemical process, but we have no basis for further speculation at this time. Another confusing aspect of this reaction is the stereochemistry of the rearrangement, which is opposite to that which is observed as the major fate of [2.2.2] to [3.2.1] photorearrangements,[1] where **5**-Cl gives largely **3**-Cl and **4**-Cl and **6**-Cl gives largely **1**-Cl and **2**-Cl. These latter reactions are singlet reactions and the fact that the reverse rearrangements do not follow the same course may be due to multiplicity differences. Clearly a sound basis for understanding these peculiar problems remains to be discovered.

Experimental Section

Irradiation was done in a Rayonet Srinivasan–Griffin photochemical reactor equipped with either 254-nm or 300-nm lamps, either in quartz (254 nm) or Pyrex (300 nm) NMR tubes. The samples were deoxygenated with N_2 bubbling.

CH_3CN was distilled from CaH_2 prior to use.

Where samples were purified by dry-column chromatography,[15] Woelm silica gel was used in a nylon column. Fractions were found by examination with a UVS-11 Mineralight, cut, and extracted with ether. Extraction residues after evaporation of solvent were weighed and analyzed by ^1H NMR.

^1H NMR spectra were determined on 60- or 90-MHz NMR spectrometers with Me_4Si as internal reference. Mass spectra were obtained on a Varian MAT CH-5 or CH-7 spectrometer.

Identification of dibenzobicyclo[3.2.1]octa-2,6-diene derivatives (**1**-X to **4**-X) was based on comparisons of ^1H NMR spectra with those of authentic samples.[1,16]

***exo*-4-*syn*-8-Dichloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-diene (1-Cl)** was prepared as described earlier,[7] as was the endo isomer (**2**-Cl).[1]

***exo*-4-*anti*-8-Dichloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-diene (3-Cl)** was prepared as described earlier,[17] as was the endo isomer (**4**-Cl).[1]

Reaction of 1-Cl with Ferric Chloride. A few milligrams of $FeCl_3$ were added to a solution of 47 mg (0.17 mmol) of **1**-Cl in 5 mL of CCl_4. After being stirred for 2 h, the mixture was washed twice with water and then dried ($MgSO_4$). ^1H NMR analysis of the filtrate showed endo dichloride **2**-Cl, containing a barely visible amount of **1**-Cl, whose absorbance was too small to integrate.

Reaction of 2-Cl with Ferric Chloride. When 55 mg of **2**-Cl in 5 mL of CCl_4 was treated as above, ^1H NMR analysis of the filtrate showed only starting material.

Reaction of 3-Cl with Ferric Chloride for 5 min. A solution of 81 mg of **3**-Cl in 5 mL of CCl_4 was treated with $FeCl_3$ as above, except that the mixture was quenched with water after only 5 min of reaction. ^1H NMR analysis of the filtrate obtained from this procedure showed a 5:1 mixture of starting material and endo epimer **4**-Cl.

Reaction of 4-Cl with Ferric Chloride for 5 min. Dichloride **4**-Cl (30 mg, 0.1 mmol) in 3 mL of CCl_4 was treated for 5 min as above. ^1H NMR analysis of the resulting filtrate showed a mixture that was approximately 70% exo dichloride **3**-Cl, 20% **4**-Cl, and 10% [2.2.2] dichloride **6**-Cl.[16]

Reaction of 3-Cl with Ferric Chloride for 2 h. When a solution of 54 mg of **3**-Cl in 3 mL of CCl_4 was treated as above for 2 h, ^1H NMR analysis showed a mixture of 80–85% [2.2.2] dichloride **6**-Cl and 15–20% **3**-Cl.

Reaction of 4-Cl with Ferric Chloride for 2 h. A similar treatment of 94 mg of **4**-Cl in 3 mL of CCl_4 for 2 h gave a product comprising 80–85% **6**-Cl and 15–20% **3**-Cl.

Reaction of 1-Cl with Tri-*n*-butyltin Hydride. A solution of 274 mg (1.00 mmol) of **1**-Cl, 370 mg (1.27 mmol) of tri-*n*-butyltin hydride, and 27.5 mg (0.17 mmol) of azobisisobutyronitrile was heated at reflux for 5 h, after which several milliliters of CCl_4 were added to quench any remaining tri-*n*-butyltin hydride. The solvent was evaporated, and the residue was purified by dry-column chromatography with 3% ether in hexanes as eluent. A fraction with R_f 0.6 proved to be the only one with significant amounts of material. NMR analysis of the material obtained showed it to be a mixture of tri-*n*-butyltin chloride and **1**-H.[7] No **3**-H[17] was found. The amount of **1**-H was estimated (by NMR) to be about 200–240 mg.

Reaction of 3-Cl with Tri-*n*-butyltin Hydride. A similar experiment with 276 mg of **3**-Cl was performed. Only one band—the fastest moving one—had a significant amount of material in it. NMR analysis showed that it was a mixture of tri-*n*-butyltin chloride and **3**-H.[17] No **1**-H was present. By NMR, this fraction contained an estimated 200 mg of the reduced product.

Direct Irradiation of 1-Cl in Acetonitrile. A solution of 20 mg of **1**-Cl in 1 mL of CD_3CN was irradiated at 254 nm. After 1.3 h, NMR peaks for epimer **2**-Cl and [2.2.2] dichloride **5**-Cl were visible and made up 25% and 15% of the dichlorides, respectively. After 2.5 h, these compounds made up about 55% of the material of interest. After 6.5 h, the peaks of the dichlorides were greatly diminished in the NMR spectrum. At this stage, water was added to the sample, and it was then washed with ether. The ether solution was dried ($MgSO_4$). Evaporation of the solvent gave a brown solid whose ^1H NMR spectrum was substantially identical (with the exception of the acetyl methyl absorbance) with that of **1**-NHAc.[1]

Direct Irradiation of 2-Cl in Acetonitrile. Similar irradiation of 23 mg of **2**-Cl in 1 mL of CD_3CN was carried out. After 1.3 h, epimer **1**-Cl and [2.2.2] product **5**-Cl were visible in the NMR spectrum, making up about 40% of the dichlorides. Compound **1**-Cl was present in about twice the amount of **5**-Cl. After 6.5

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h, the peaks of the dichlorides had substantially disappeared.

Workup of the above gave a brown solid whose ^{1}H NMR spectrum was substantially that of 1-NHAc-d_3.

Direct Irradiation of 3-Cl in Acetonitrile. A similar irradiation of 18 mg of 3-Cl in 0.5 mL of CD_3CN was conducted. After 1 h, a small amount of endo epimer 4-Cl was formed, as indicated by the NMR spectrum. After 2 h, the exo:endo ratio was 3:1, and after 5 h, it was 2:1. The peaks of the dichlorides decreased in intensity, so that by 5 h only a small amount remained. After irradiation, water was added to the sample, and it was extracted with $CDCl_3$. An NMR spectrum of the $CDCl_3$ extract was almost identical with that[1] of 3-NHAc (except for the absence of the acetyl methyl protons).

Direct Irradiation of 4-Cl in Acetonitrile. Dichloride 4-Cl (27.3 mg, 0.10 mmol) was treated in the same way as the exo epimer 3-Cl. There was a small amount of exo epimer 3-Cl apparent after 1 h, while after 2 h it had become almost one-third of the total dichlorides. After 5 h, the irradiated sample was treated with water as above, and an NMR spectrum showed amide 3-NHAc-d_3 here also.

Direct Irradiation of a Mixture of 3-Cl and 4-Cl in Acetonitrile. A solution of 13 mg of 3-Cl and 14 mg of 4-Cl in 0.5 mL of acetonitrile-d_3 was irradiated at 254 nm. NMR analyses of the dichloride mixture at various times from 0 to 17 h gave ratios of 3-Cl to 4-Cl of 47:53, which were invariant within the limits of our accuracy (± 3%). No [2.2.2] dichlorides were apparent.

Sensitized Irradiation of 1-Cl in Acetonitrile. A solution of 22 mg of 1-Cl in 1.5 mL of 20% acetone-d_6 in CD_3CN was irradiated at 300 nm. The irradiation sample showed NMR peaks of 2-Cl and 5-Cl. After 19 h, the ratio of 2-Cl to 5-Cl was about 2:1. A dark sample was unreactive.

Sensitized Irradiation of 2-Cl in Acetonitrile. A solution of 15 mg of 2-Cl in 1.5 mL of 20% acetone-d_6 in CD_3CN was irradiated as above. After 19 h, 3 times as much 1-Cl as 5-Cl appeared to be present. A dark sample was unreactive.

Sensitized Irradiation of a Mixture of 1-Cl and 2-Cl in Acetonitrile. A solution of 10.4 mg of 1-Cl and 10.9 mg of 2-Cl in 1 mL of 20% acetone-d_6 in CD_3CN was irradiated at 300 nm and analyzed by NMR from time to time over a period of 40 h. The ratio of 1-Cl to 2-Cl remained close to 1:1 while the amount of 5-Cl increased to 12% in 40 h.

Sensitized Irradiation of 3-Cl and 4-Cl in Acetonitrile. Dichloride 3-Cl (36 mg, 0.13 mmol) was dissolved in 1 mL of 20% acetone-d_6 in CD_3CN and irradiated at 300 nm. After 11 h, a small amount of endo epimer 4-Cl was formed, as indicated by the NMR spectrum. After 22 h, about 15% of 4-Cl had been formed. No peaks for any [2.2.2] dichlorides were visible in the NMR spectrum.

In a similar experiment with 58 mg of 4-Cl, after 11 h, a small amount of exo epimer 3-Cl was formed, as indicated by the NMR spectrum. After 22 h, about 15% of 3-Cl had been formed. No peaks for any [2.2.2] dichlorides were visible in the NMR spectrum.

Direct Irradiation of 1-Cl in Acetic Acid. A solution of 50 mg of 1-Cl in 1.5 mL of acetic acid-d_4 was irradiated at 254 nm. The results tabulated below were observed, using intensities of the H-4 proton absorbances.

time (h)	% 1-Cl	% 2-Cl	% 1-OAc	% 2-OAc
0	100	0	0	0
0.3	80	14	7	0
1.0	64	24	12	0
3.7	54	32	15	0
11	52	33	12	trace
34	48	33	13	6
77	34	35	18	13
100	24	36	23	17
150	20	33	22	25

It has previously been reported[13a] that 1-Cl and 2-Cl have half-lives of 12 h and 110 h, respectively, for solvolysis in HOAc at 75 °C. Little of the observed solvolysis listed above can be attributed to ground-state reaction at the temperature of the photoreaction (<35 °C), except perhaps at the longer reaction times.

Direct Irradiation of 4-Cl in Acetic Acid. Irradiation of a solution of 49 mg of 4-Cl in 1.5 mL of acetic acid-d_4 was treated as above, leading to the results tabulated below.

time (h)	% 4-Cl	% 3-Cl	% 3-OAc
0	100	0	0
0.3	82	9	9
1.0	67	14	18
1.7	53	22	26
3.7	41	29	29
11	25	35	40
34	22	31	47
77	20	30	50
100	17	26	57

The long-time irradiations contained small amounts of 4-OAc.

Sensitized Irradiation of 1-Cl and 2-Cl in Acetic Acid. A solution of 15 mg of 1-Cl in 1.5 mL of 20% acetone-d_6 in acetic acid-d_4 was irradiated at 300 nm. The reaction was monitored by NMR. The irradiated sample gave, as products, endo chloride 2-Cl and exo acetate 1-OAc in approximately equal amounts. After 20.6 h of irradiation, the amounts of products approximately equaled the amount of starting material. A similar experiment with 14 mg of 2-Cl was conducted. The amounts of products (1-Cl and 1-OAc) were about equal to the amount of starting material, after about 40 h.

Direct Irradiation of 1-OAc in Acetic Acid. A solution of 53 mg of 1-OAc in 1.5 mL of acetic acid-d_4 was irradiated, after deoxygenation. The photoreaction was folllowed by ^{1}H NMR spectroscopy. The H-4 absorptions were integrated to determine epimerization, and the acetate peak was integrated relative to the H-4 protons to determine exchange with the solvent. The following results were obtained.

time (h)	% 1-OAc	% 2-OAc	% loss of acetate absorption at 2.0 ppm
0	100	0	0
0.3	95	5	10
2.3	91	9	30
4.3	90	10	50
11.3	88	12	70
34.3	80	20	80
77	80	20	85

By 34 h, the sample was quite dark and thus it is not certain that the 4:1 ratio of exo:endo is a steady state, although a preference for exo is apparent.

Direct Irradiation of 3-OAc in Acetic Acid. A solution of 48 mg of 3-OAc in 1.5 mL of acetic acid-d_4 was treated as above, giving the following results:

time (h)	% 3-OAc	% 4-OAc	% loss of acetate absorption at 2.0 ppm
0	100	0	0
0.3	95	5	50
2.3	75	25	65
4.3	71	29	71
11	62	38	87
34	56	44	92
77	54	46	92

By 34 h, the sample was quite dark.

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Registry No. 1 (X = Cl), 2197-98-0; 1 (X = H), 2415-40-9; 1 (X = $NHCOCD_3$), 98687-80-0; 1 (X = OAc), 2197-95-7; 2 (X = Cl), 2197-99-1; 2 (X = OAc), 2197-97-9; 3 (X = Cl), 2198-00-7; 3 (X = H), 2198-10-9; 3 (X = $NHCOCD_3$), 98757-21-2; 3 (X = OAc), 3123-86-2; 4 (X = Cl), 98719-14-3; 4 (X = OAc), 2415-38-5; 5 (X = Cl), 6476-47-7; 6 (X = Cl), 6476-15-9; $FeCl_3$, 7705-08-0; tri-*n*-butyltin hydride, 688-73-3.