# Photochemical Transformations. 24. Comparison of "Ionic" Intermediates Produced Photochemically with Corresponding Ground-State Intermediates. Initial Studies in Some Chlorobenzooctadienyl Systems[1]

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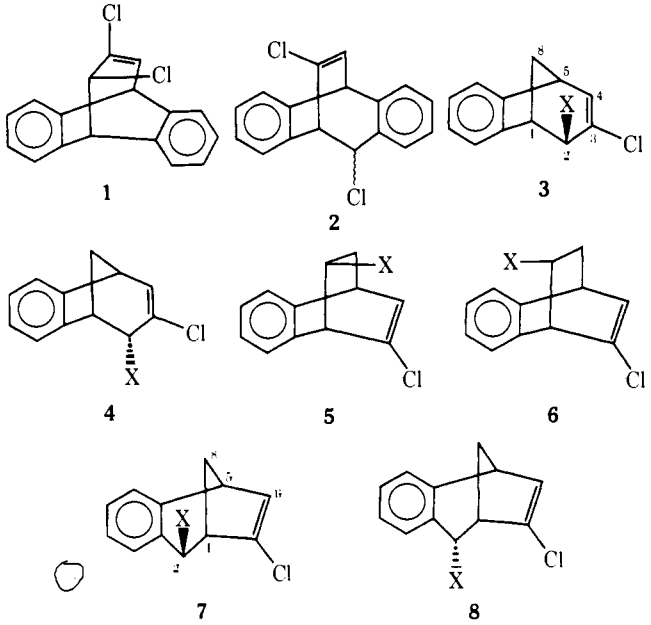
**Abstract:** Rearrangements and solvolyses in acetic acid and/or in acetonitrile have been studied with exo and endo 4-functionalized derivatives of 3-chloro-6,7-benzobicyclo[3.2.1]octa-2,6-diene (**3** and **4**, respectively) and their Wagner-Meerwein rearrangement isomers, the anti 7-functionalized 2-chloro-5,6-benzobicyclo[2.2.2]octa-2,5-dienes (**5**). Both ground-state and photochemical reactions with a variety of nucleofugal groups X have been investigated. Ground-state reactions appear to be "normal", **3** and **4** isomers being produced under kinetic control and a preponderance of **5** isomers produced upon equilibration. No mixing of this system with the syn-benzylic chlorobenzobicyclooctadienyl systems **6–8** is seen. The results are compatible with the idea that the lowest lying cationic intermediate in this system is the allylic cation **15** and that the benzo-bridged (phenonium ion) cation **14** is of low enough energy to be readily accessible in the equilibration studies. Direct irradiation of either of the allylic isomers **3** and **4** (X = Cl, $OCOCHCl_2$, and OMs) in acetonitrile led readily to the **5** isomers, without mixing of **6–8** systems, accompanied by photosolvolysis to **3**-$NHCOCH_3$ (water added). Solvent effects show that polar solvents favor such reactions, while radicals are produced from **3**-Cl in nonpolar solvents. With X = OH or OAc, only di-$\pi$-methane rearrangement was observed, and the latter type of rearrangement was observed as well with a variety of **3**-X and **4**-X compounds, with ketone-triplet sensitization. The unsensitized results seem inconsistent with reaction paths involving radical intermediates or concerted rearrangements, but can be rationalized by the assumption that reaction from the excited state leads to an intimate ion pair involving the bridged cation **14**, which may relax to **5**-X or **3**-X by ion-pair collapse or to the more stable allylic ion **15**, prior to or attendant upon formation of a solvent-separated ion pair.

Some time ago, members of this research group reported[2] that irradiation of **1** in a variety of solvents led to mixtures of the Wagner-Meerwein isomers *endo*- and *exo*-**2**. They proposed that ion pairs were produced photochemically from **1**, which recombined (after cationic rearrangement) to give **2**.



These rearrangements were studied in more detail, as were the accompanying photosolvolysis reactions in acetonitrile and in aqueous acetonitrile, and these results have been reported recently.[3] Interest in photochemically induced molecular rearrangements involving carbocations has been developing since 1969,[4] and there has been an accompanying interest in photosolvolytic reactions.[4,5] We have also been interested in a comparison of the carbocationic intermediates produced, on the one hand, from ground-state reactants and, on the other hand, from excited-state intermediates. This present paper describes another system, in which it is possible to consider both stereochemistry and regiochemistry in such rearrangements.

The system we have chosen to study is that represented by the formulas **3–8**, that is, the chlorobenzobicyclo[3.2.1]octadienyl and chlorobenzobicyclo[2.2.2]octadienyl systems. Compounds in these systems with various nucleofugal groups X are (more or less) readily synthesized, which is of obvious attractiveness. Furthermore, Tanida and his co-workers[6] have studied the ground-state reactions of the dechloro analogues of these compounds, so that comparable structural data were available to us. Perhaps of more importance to us, their work showed that the allylic-anti system, analogous to **3**, **4**, and **5**, but without a chlorine atom on the double bond, was mechanistically insulated from the syn-benzylic system **6**, **7**, and **8**, when carbenium ion intermediates intervened. We decided to use the chloro compounds; they have the advantage that the electron-attracting chlorine atom makes the compounds less labile than their dechloro analogues and thus somewhat easier to handle.

One may assume (see below for confirmation) that these syn-benzyl and anti-allyl systems will similarly be mechanistically insulated in the ground state. An obvious point of interest is the question of whether the excess energy present in the excited states of systems such as this can be utilized in the photorearrangements or photosolvolyses to overcome the barriers insulating the systems in ground-state reactions. An additional advantage this system (**3** and **4**) was anticipated to have over the **1** system was the fact that the two faces of the allylic system are different (endo and exo). We anticipated that **3** and **4** would be subject[7] to photochemical and thermal allylic rearrangements. With appropriate (deuterium) labeling, it would be possible to see if these reactions are stereospecific, and, if so, whether they are suprafacial or antarafacial, a problem of interest in considering orbital symmetry effects. Of course mechanisms involving carbocationic intermediates produced photochemically are still so little understood (multiplicity, nature of intermediates, leaving group and environmental effects, etc.), that we hope that the general study of this

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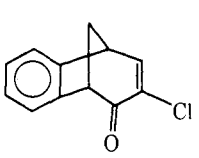
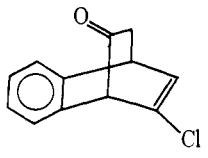
(and other) system(s) will bring some understanding to this relatively new area of photochemistry.

**The Allylic-Anti System. Ground-State Chemistry.** This system is readily entered by the preparation of 3,*exo*-4-dichloro-6,7-benzo-2,6-bicyclo[3.2.1]octadiene (**3**-Cl) by rearrangement of the addition product of dichlorocarbene to benzonorbornadiene, as described by Goldschmidt and Gutman.[8] **3**-Cl was converted to the corresponding alcohol **3**-OH with silver perchlorate in aqueous acetone.[8] Treatment of **3**-Cl with silver acetate in acetic acid gave **3**-OAc.[9] Oxidation of **3**-OH gave the ketone **9**, which on reduction with lithium



**9**



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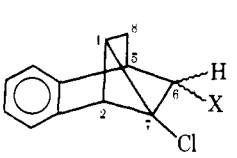
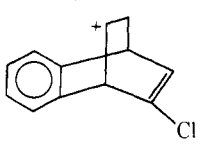


**11**

aluminum hydride gave the endo alcohol **4**-OH,[9] which was converted to **4**-OAc. Treatment of **3**-Cl with ferric chloride at 140 °C gave a mixture of **3**-Cl, **4**-Cl, and **5**-Cl in a ratio of approximately 30:14:56. It would appear that thermodynamic control leads largely, but not entirely, to the bicyclo[2.2.2]-octadiene system, although (see below) kinetic control gives largely **3**-X isomers. No syn (**6**-Cl) or benzylic (**7**-Cl or **8**-Cl) products were noted ($^1$H NMR analysis). The allylic isomers **3**-Cl and **4**-Cl were quite reactive toward silver perchlorate in aqueous acetone (see below for products) and thus could be removed from the rather inert **5**-Cl, which was then readily separated by chromatography from the alcohol produced from the hydrolysis. Pure **5**-Cl was thus available.

Treatment of **3**-OAc with perchloric acid in acetic acid gave a mixture of **3**-, **4**-, and **5**-OAc (11:9:80 respectively). The acetate was not isolated, but was methanolyzed to give a mixture from which **5**-OH was readily separated.[9] Methanesulfonates and dichloroacetates of **3**-OH, **4**-OH, and **5**-OH were prepared in the usual fashion for such derivatives.

Oxidation of **5**-OH gave the ketone **10**, which on treatment with lithium aluminum hydride gave an approximately equimolar mixture of **5**-OH and **6**-OH ($^1$H NMR spectral analysis). We were unable to separate the mixture of alcohols or that of the methanesulfonate derivatives by crystallization or chromatography. However, **5**-OMs was much more reactive toward solvolysis than was **6**-OMs and thus could be reacted away in acetic acid (see below for products), leaving **6**-OMs, which was then readily isolated; this therefore represented an entry into the syn-benzylic system. Indeed acetolysis[10] of **6**-OMs led to a mixture of **7**-OAc and **8**-OAc. No **6**-OAc, **11**-OAc, or members of the anti-allylic system were found. Thus (a) kinetic control in the syn-benzylic system gave the benzylic isomers and (b) the mechanistic insulation of the syn-benzylic and anti-allylic systems in ground-state reactions has been demonstrated, starting from either side. In this way, ions **12** and **13**, either of which would mix these systems,[11] are



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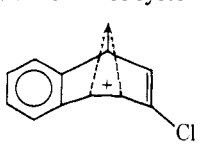
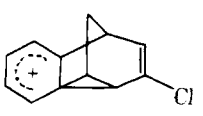
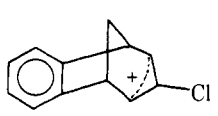


**13**



**14**



**15**

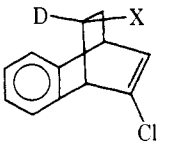
excluded as (relatively) low-energy intermediates in these carbenium ion rearrangements.

Acetolysis of the *anti*-methanesulfonate **5**-OMs in the presence of sodium acetate gave a mixture of **3**-OAc and **4**-OAc in a ratio of 4.7:1, while **4**-OMs gave the two acetates in a ratio of 15:1 or greater. The fact that these solvolyses all gave mixtures of both exo and endo isomers in these kinetically controlled experiments makes it clear that **14** cannot be the sole intermediate cation, but that **15** must be involved in the reactions. Tanida and co-workers[6] studied the dechloro analogue of **5**-OTs and found that acetolysis also gave complete rearrangement to the [3.2.1] allylic system with exo product favored over endo in a ratio of 4.9:1. They proposed that the allylic cation dechloro-**15** intervened as the sole intermediate with exo (axial) capture favored by stereoelectronic control. Thus the ion analogous to **14** (still partially bonded to the leaving alkanesulfonate group) was assumed to be a transition state on the route to the **15** analogue. Our results can be accommodated to the same model, but the **3** ⇄ **4** ⇄ **5** equilibrations in the chloride and acetate systems described above, where **5**-Cl or **5**-OAc are the predominant isomers on equilibration and the **6** epimers are not observed, suggest that ion **14** does not lie much above **15** in energy content or that the reverse of the Tanida mechanism occurs—that is, a geitonodesmic[12] reaction obtains in the [3.2.1] to [2.2.2] rearrangement.

The substantially greater amount of exo product in the solvolysis of **4**-OMs over that observed with **5**-OMs (or **3**-Cl, see below) can be ascribed to solvent participation in these ion-pair reactions.

The acetolyses of **4**-OMs was carried out under conditions where epimerization of the methanesulfonate would not have been observed, but where the formation of substantial amounts of **5**-OMs would have been detected. We did not observe return to **5**-OMs during the acetolyses.

To test whether a large fraction of the exo product from **5**-OMs came directly from the phenonium ion **14** rather than from the allylic ion **15**, we prepared deuterium-labeled compounds **16**. **16**-OH and **17**-OH were prepared by lithium alu-



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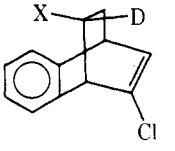

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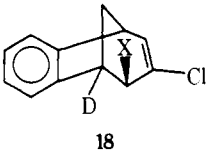

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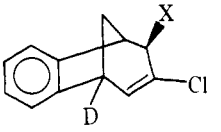

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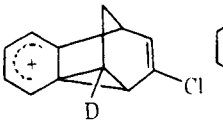

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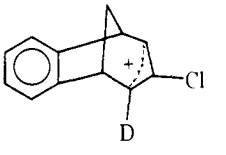

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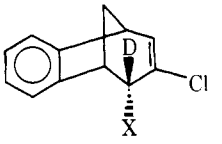

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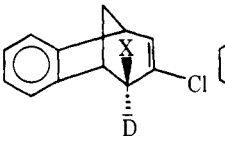

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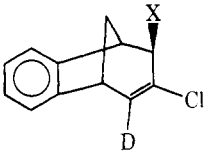


**24**

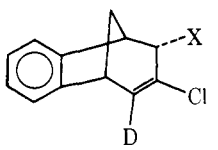
minum deuteride reduction of **10**. The mixture of methanesulfonates prepared from this alcohol mixture was subjected to controlled acetolysis, such that **16**-OMs reacted and **17**-OMs did not. The resulting acetate mixture was separated and the **3**-OAc-$d_1$ was methanolyzed. The resulting **3**-OH-$d_1$ was analyzed by $^2$H NMR procedures, using the lanthanide shift reagent Eu(FOD)$_3$.[14] This reagent separates the absorbances due to H-1 and H-5 (or D-1 and D-5) readily. Analysis showed 46% of **18**-OH and 54% of **19**-OH (equal amounts within our analytical errors). If a substantial amount of the exo product came from the ion **20** before equilibration with **21**, **18** should

have predominated over **19**. This is clearly not the case. Failure to find **5**-OMs in competition with solvolysis is also consistent with the idea that **14** is a higher energy species than is **15**.

It was also of interest to see whether **21** is the intermediate when this manifold was entered from the allylic side. For this reason **22**-OMs was prepared and acetolyzed in the presence of sodium acetate.

The product mixture contained more than 95% of exo acetates and less than 5% of endo acetates ($^1$H NMR analysis). $^2$H NMR analysis was not sensitive enough to allow estimation of the deuterium ratios in the endo isomer, but indicated that the exo acetate mixture was roughly 60% **23** and 40% **24**.

In order to learn whether the product spread was due to an unexpectedly high isotope effect or not, we prepared a sample of *endo*-methanesulfonate, all of whose deuterium label was on the ethylenic bond, i.e., **25**-OMs. This was prepared by conversion of the **23**-OAc–**24**-OAc mixture to alcohol, followed by oxidation to ketone. The ketone was a 60:40 mixture of **9** and **26**, and was converted to a similar mixture of **4**-OMs

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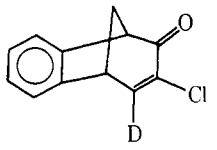


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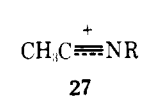


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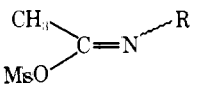



**28**

and **25**-OMs by reduction with lithium aluminum hydride and esterification. Although the mixture was largely **4**-OMs, the $^2$H NMR probe is, of course, blind to nuclei other than deuterium. The small sample size, however, made the analysis less precise. Nonetheless, the labeled acetate solvolysis product was now richer in **24**-OAc (64%) than in **23**-OAc (36%), a result inconsistent with the idea of an important isotope effect and consistent instead with some mechanistic phenomenon.

Product spreads, that is, the formation of different mixtures of isomeric allylic products from isomeric allylic reactants, were first studied by Young and his co-workers.[15] Young proposed that the product spreads were due to solvent participation, perhaps even of the direct displacement ($S_N2$) type. More recently Sneen and co-workers[16] suggested that solvolysis of allylic species leads to a tight ion pair in which the anion is closely associated with one of the two allylic centers, and that reaction with solvent (or other nucleophile) occurs at a rate competitive with anion migration to give the isomeric ion pair. Each ion pair reacts with solvent (or nucleophile) to give mixtures of products richer in unrearranged structure than the average composition of the two product mixtures. Our results on the excess of exo isomer from **4**-OMs and on the isotope distribution are consistent with Sneen's concept. We propose that endo ion pairs with **15** cations and methanesulfonate counterions are produced and that they react with acetic acid in the unsymmetrical way he describes.

**3**-Cl was also acetolyzed, at reflux, with silver acetate. It led to a 6:1 mixture of **3**-OAc and **4**-OAc, a mixture quite similar in composition to that from **5**-OMs. The ratio of **3**-OAc to **4**-OAc remained constant with time during the experiment.

Some work was also done on equilibration of the dichloroacetates of **3**, **4**, and **5**. A solution of **3**-$OCOCHCl_2$ in dichloroacetic acid was heated at 100°C until the $^1$H NMR spectrum no longer changed (3 days). Analysis indicated a mixture of 81% **5**-$OCOCHCl_2$, 14% **3**-$OCOCHCl_2$, and 5% **4**-$OCOCHCl_2$. These values are similar to those described above for the chlorides and acetates.

Ritter reactions[17] were also conducted in this system. Either **3**-OH or **5**-OH, treated with acetonitrile and sulfuric acid, gave the exo amide **3**-$NHCOCH_3$. The $^1$H NMR spectrum of the product indicated that significant amounts of endo amide **4**-$NHCOCH_3$ and [2.2.2] amide **5**-$NHCOCH_3$ were not present. When **3**-OMs was heated in 5% water–95% acetonitrile, a mixture of 65% of **3**-OH and 35% of **3**-$NHCOCH_3$ resulted. No **4**-OMs or **5**-OMs was observed in this reaction, although **5**-OMs (and **4**-OMs) would have been stable. Similarly when an aqueous acetonitrile solution of **3**-OMs was allowed to stand at room temperature for 51 days, the product mixture consisted ($^1$H NMR) of 44% **3**-OMs, 37% **3**-OH, and 19% **3**-$NHCOCH_3$.

Thus kinetically controlled capture by acetonitrile of the ions produced by solvolysis of the sulfonate esters and by acid-catalyzed reaction of the alcohol occurs preferentially from the exo side, just as does capture by other nucleophiles. Presumably the capture gives the nitrilium ion **27**, which, in the presence of water, is hydrated to give the conjugate acid of the imidol form of the amide, to which it is then converted by prototropy and proton loss. When water is absent, one might anticipate[18] that the imino anhydride **28** would form. With the excellent nucleofugal group methanesulfonate, and with a fairly stable $R^+$ cation, it seemed likely that the steps in the presumed formation of **28** would be reversible. In such a case, starting with **3**-OMs or **4**-OMs, one would anticipate not only the formation of the **3**-$NHCOCH_3$ precursor, but probably that of the **4**-$NHCOCH_3$ and **5**-$NHCOCH_3$ precursors, as well as, if the reactions were not carried out to completion, epimerization to the other allylic methanesulfonate and some isomerization to the [2.2.2] isomer **5**-OMs. Indeed, when such an experiment was conducted with **4**-OMs (**22**-OMs) (heating in dry acetonitrile), the principal products were **3**-OMs and **5**-OMs, and smaller amounts of **3**-$NHCOCH_3$ and **5**-$NHCOCH_3$ were produced, after addition of water.

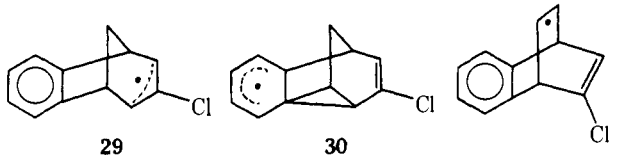
Let us summarize the ground-state behavior of the anti-allylic system. Kinetic control of carbenium ion reactions results largely in exo capture of nucleophile, that is, to give **3** isomers, with smaller, but generally measurable, amounts of endo capture to give **4** isomers. In the time required to equilibrate **3**, **4**, and **5**, experiment gives preponderant amounts of [2.2.2] isomers **5**, along with **3** and **4**, but no isomers in the syn-benzylic **6**–**8** (or cyclopropylcarbinyl, **11**) system. These results, plus those with deuterium-labeled compounds, indicate that the lowest lying (in energy) intermediate in this system is the allylic cation **15** (presumably initially produced, in the solvents we are using, as a member of an ion pair), and that the bridged phenonium ion **14** is a somewhat higher energy species, available in equilibration studies, but not to any measurable extent in kinetically controlled situations. The ions **12** and **13**, which would mix the two systems, are not available in high enough concentration in our experiments for mixing to be observed.

**The Allylic-Anti System. Photochemistry.** Our principal aim, as stated above, was to compare the intermediates produced in ground-state chemistry with those produced in photochemistry in what appear to be like reactions. To this end we have studied the photochemistry of a variety of **3**, **4**, and **5** species with various groups and under a variety of conditions.

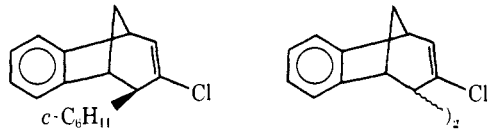
As our previous experience[2,3] with **1** indicated that those reactions which might be considered as "ionic", that is, photo-Wagner–Meerwein rearrangements and photosolvolyses, occurred readily in polar solvents such as acetonitrile, we began our study with the readily available[8] **3**-Cl in acetonitrile. Indeed, when **3**-Cl was subjected to direct irradiation at 254 nm in acetonitrile, a mixture of the three chlorides **3**-Cl, **4**-Cl, and **5**-Cl, in which the latter predominated, was formed. Although an apparently photostationary isomer composition resulted with approximately equal amounts of **3**-Cl and **4**-Cl

and double those amounts of **5**-Cl, irradiation of **5**-Cl gave little or no reaction. We conclude that adventitious impurities quenched (presumably by light absorption) the reactions of **3**-Cl and **4**-Cl, and that the "photostationary" state is largely **5**-Cl. When the irradiation mixture was treated with water, besides the chlorides **3**-Cl, **4**-Cl, and **5**-Cl, a substantial amount of **3**-$NHCOCH_3$ was formed. Thus photosolvolysis, presumably in this case to give the imidoyl chloride, competed with the photoepimerization and photoisomerization reactions. This result was then similar to that seen[3] with **1** and **2**, suggesting the intervention of carbocationic intermediates.

It seemed possible that the rearrangement of **3**-Cl to **5**-Cl could involve the radical pairs of chlorine atoms and carbon radicals **29, 30,** and **31** (or combinations of them), and we therefore undertook the tri-*n*-butyltin hydride reduction of **3**-Cl. This reaction, promoted by azobisisobutyronitrile, is a free-radical chain reaction[19] and undoubtedly produces the allylic radical **29** by chlorine atom abstraction from **3**-Cl with tributyltin radical. The only reduction product that we observed was **3**-H ($^1$H NMR analysis), so that rearrangement to **31** does not occur within the lifetime of the allylic radical **29**.




**29** **30** **31**



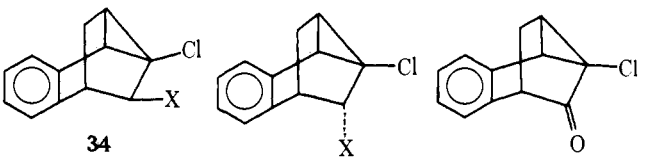

**32** **33**

An approximate lifetime for **29** can be calculated, by using the rate constant reported[20] for the hydrogen abstraction from tributyltin hydride by *tert*-butyl radical ($7 \times 10^5$ L/mol·s at 25 °C in cyclohexane). It would seem reasonable to assume that **29** is less reactive than *tert*-butyl radical and that this constant is an upper limit for that of **29**. With concentrations of hydride less than 0.1 M, the lifetime for capture of **29** by hydride should be greater than $1/7 \times 10^{-4}$ or greater than $1.5 \times 10^{-5}$ s at 25 °C. Our reduction was run at 60 °C, and one should be safe in assuming that, under reaction conditions, **29** has a lifetime no shorter than $10^{-6}$ s. This is surely a longer lifetime than that anticipated for collapse of a radical pair involving **29** (or one of its isomers) and a chlorine atom. Thus failure to see rearrangements in the reduction of **3**-Cl is evidence that a radical rearrangement from **29** to **31** is not involved in the **3**-Cl to **5**-Cl photorearrangement.

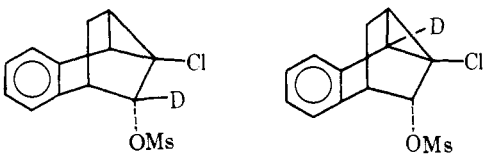
Irradiation of **1** in cyclohexane has been reported[3] to give very little Wagner–Meerwein reaction product **2**; we now report similar results with **3**-Cl. When a solution of **3**-Cl in cyclohexane was irradiated at 254 nm, no **5**-Cl could be observed ($^1$H NMR) and only a trace of **4**-Cl ($^1$H NMR) was noted. The principal products were **32** and a mixture of isomers represented by **33**. These products suggest that, in cyclohexane, irradiation of **3**-Cl leads to bond homolysis to **29** and a chlorine atom. Chlorine-atom attack on cyclohexane gives cyclohexyl radical, which on combination with **29** gives **32**. Reaction of two **29** radicals gives the various stereoisomers represented by **33**. Again no evidence was seen for rearrangement of **29** to **31**, as no materials with structure **5** were observed.

We then decided to study the possibility of rearrangement of **3**-X and **4**-X molecules containing carbon–oxygen bonds rather than carbon–chlorine bonds. It has previously been shown that certain allylic benzoates,[21,22] methanesulfonates,[7] *p*-toluenesulfonates,[7] phosphates,[23] and phosphites[23] undergo photosensitized allylic rearrangements. While the mechanistic paths for these rearrangements are not known, the photoactivities made it reasonable for us to study similar derivatives. It also seemed likely that labeling experiments would prove useful in elaborating the course of the photoreactions, and preparing specifically labeled alcohols offered considerable advantage over chlorides.[9]

Irradiation of **3**-OH or **3**-OAc at 254 nm in acetonitrile did not lead to any **4** or **5** derivative. Rather the di-$\pi$-methane products **34** were produced (see below for discussion). Concluding that these groups were not active enough leaving (nucleofugal) groups, we decided to look at dichloroacetates




**34** **35** **36**




**37** **38**

and methanesulfonates. Dichloroacetates have the advantage that they can be readily cleaved by alkaline hydrolysis or methanolysis to alcohols with retention of the carbon–oxygen bond, a cleavage not readily accomplished with sulfonate esters.[24]

When **3**-$OCOCHCl_2$ was irradiated in acetonitrile solvent, both **4**-$OCOCHCl_2$ and **5**-$OCOCHCl_2$ were formed rapidly, in an initial ratio of 1:4, respectively. Although the desired rearrangements occurred, there was an accompanying buildup of nonpolar materials, such that most of the dichloroacetates were destroyed after a short irradiation time. Whether this was due to some radical reaction, such as homolysis of the carbon–oxygen bond[25] or carbon–chlorine cleavage,[26] or had some other cause remains to be determined. In view of the complexity of the product mixtures, and in spite of the obvious advantages of the dichloroacetate system, we decided to leave this system and to go on to the methanesulfonates, which were observed to be separable by high-pressure liquid chromatography, to be identifiable by $^1$H NMR spectroscopy, and to photorearrange and photosolvolyze in high chemical yield.

Irradiation of **3**-OMs in acetonitrile at 254 nm for an extended period of time, followed by water treatment, gave a mixture which contained about 6% starting material, 60% **5**-OMs, and 34% **3**-$NHCOCH_3$. In an experiment carried only to about 10% completion, the approximate sum of quantum yields for the formation of **5**-OMs and **3**-$NHCOCH_3$ was 0.4.

A similar extended irradiation of **4**-OMs gave, besides 16% starting material, 26% **5**-OMs, 16% **3**-OMs, and 42% **3**-$NHCOCH_3$. The sum of quantum yields for the formation of **3**-OMs, **5**-OMs, and **3**-$NHCOCH_3$ was 0.5. Both **5**-OMs and **6**-OMs were photoinert in reasonable periods of irradiation.

**6**-OMs (or its benzylic congeners) was not observed in any of these photoreactions, and the only amide was **3**-$NHCOCH_3$. The endo amide and the [2.2.2] amide were absent, within our limits of detection.

When irradiation of **3**-OMs was carried out in 5% aqueous acetonitrile, the product mixture contained 50% **5**-OMs, 30% **3**-$NHCOCH_3$, and 20% **3**-OH. Obviously the intermediate(s) from both photoreactions (rearrangement and solvolysis) can be intercepted by water.

All of the reactions discussed thus far have been carried out under direct irradiation, but the question of multiplicity of the reactive excited state remains to be considered, particularly in view of the fact that certain photosolvolyses of halides occur from singlet excited states[3,5] and others from triplets.[27,28] We therefore decided to look briefly at the triplet-sensitized reactions of a number of **3** and **4** compounds, as well as the photoreaction of **9** in acetone. Irradiations of **3**-OH, **3**-OMs, and **4**-OMs were conducted in acetone at 300 nm. The photoreactions took an entirely different course from those of direct irradiation, leading to the di-$\pi$-methane[29] rearrangement products, rather than Wagner–Meerwein products. The reactions, as anticipated,[29] were stereospecific. Thus **3**-OH and **3**-OMs gave only the **34** compounds and **4**-OMs gave the epimeric **35** compound. **9** gave compound **36**. Similar results were seen in acetone–acetonitrile. Failure to see **5**-OMs from **3**-OMs or **4**-OMs in the sensitized reactions is convincing evidence that the Wagner–Meerwein reaction in these systems, like that of **1**, occur from the singlet excited state.

While formation of **34** and **35** is consistent with the di-$\pi$-methane formulation, it seemed[6] possible, though not likely, that they were formed by some convoluted set of carbenium ion rearrangements. We therefore decided to investigate the photoreaction of a deuterium-labeled compound. **22**-OMs was therefore studied in acetone with 300-nm irradiation. As some $\beta$-chloroallylic sulfonate esters have been shown to undergo allylic rearrangements, we considered the additional possibility of learning whether such a reaction occurred in the **22**–**25** system (the stereospecificity of the **3**-OMs to **34**-OMs and **4**-OMs to **35**-OMs rearrangements indicated that, if such a photorearrangement had occurred, it could not have been antarafacial). When **22**-OMs was irradiated in acetone, only **37** was produced (no **38** could be noted by $^1$H NMR analysis). The recovered **22**-OMs had no contamination with **25**-OMs. This experiment shows that allylic rearrangement does not occur in this system at a rate competitive with the di-$\pi$-methane rearrangement, and that the latter rearrangement is the mechanistic path for the **4**-OMs to **35**-OMs transformation.

Let us now return to the unsensitized (presumably singlet) reactions. Obviously the photosolvolysis reactions to give **3**-$NHCOCH_3$ (in acetonitrile) and **3**-OH (in wet acetonitrile), demonstrated with **3**-Cl, **3**-OMs, and **4**-OMs, involve cationic intermediates. There has been some discussion recently regarding the question of whether ion pairs produced photochemically are formed directly,[27,30] or whether the photoexcited state decays by homolysis to a radical pair which then suffers intracomplex electron transfer to give an ion pair,[31] although a position has been taken that this question is blurred in the real situation by resonance between "ionic" and "radical" pair structures.[3,32,33] With this concept the first intermediate is an "intimate ion–radical pair" whose continued separation leads, depending upon conditions, either to radicals or to ions or to mixtures of the two. Perhaps the photoinertness of **3**-OAc and **3**-OH to photosolvolysis and photo-Wagner–Meerwein rearrangement compared with the reactivity of **3**-OMs has a bearing on the homolysis–electron transfer proposal. Sulfate radical ion is known[34] to oxidize acetate ion and hydroxide ion to acetoxy and hydroxy radicals, respectively. This suggests that the latter two radicals are more stable with respect to their anions than is sulfate radical ion with respect to sulfate ion, and one may imply the same for acetoxy or hydroxy compared with methanesulfonoxy radical and anion. A similar conclusion may be drawn from the reactions of sulfonyl peroxides, which react with aromatics[35a] and with olefins[35b] by ionic rather than radical pathways. From this evidence it is possible to argue that it should be easier to form a geminate radical pair from **3**-OAc than from **3**-OMs. We observed the opposite in reactivity, from which we conclude that bond homolysis is not an important feature for these solvolyses or rearrangements.

In any case, whatever the course by which ions are produced, it is clear that the photosolvolysis results we have observed in this system and those reported[3] in the **1** → **2** system involve cationic intermediates. The observation that **3**-$NHCOCH_3$ is obtained from both **3**-OMs and **4**-OMs suggests that the ionic species produced by photoexcitation and captured by acetonitrile is not substantially different from those produced in ground-state reactions. As in the ground state, kinetic control leads almost entirely to capture by nucleophile in the allylic position of the system and from the exo face. Thus it would seem plausible to simply consider ion pairs (or perhaps free ions) involving the allylic ion **15** as the substances responsible for the photosolvolysis results.

The pathways for the photochemical Wagner–Meerwein rearrangements are more difficult to tie down. There are a number of observations that must be rationalized. These include (a) photorearrangement of **1** gives both *endo*- and *exo*-**2** in substantial amounts (that is, the photorearrangement is not stereospecific); (b) unlike ground-state solvolysis, photoexcitation gives substantial conversion from the allylic (**3**-OMs or **4**-OMs) to anti (**5**) methanesulfonate (here one should note that photochemical experiments carried out to low conversions are like kinetically controlled experiments rather than equilibrations); (c) both **3**-OMs and **4**-OMs give **5**-OMs with appreciable quantum yields; (d) photoepimerization accompanies photo-Wagner–Meerwein rearrangement; (e) the allylic-anti system is insulated from the benzylic-syn system in photoreactions as well as in ground-state carbenium ion reactions; (f) neither the photosolvolysis nor the photo-Wagner–Meerwein rearrangement occurs with poor nucleofugal groups; (g) polar solvents favor photorearrangements; (h) radical intermediates are unattractive.

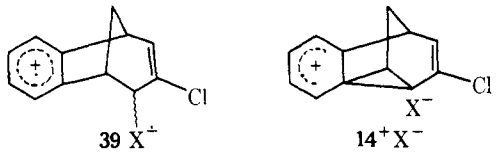
The possibility that the rearrangements are concerted excited-state ones must be considered. This would imply that the ionic photosolvolyses and the rearrangements are not related mechanistically. Certain features of the processes seem to us inconsistent with this idea. First the lack of stereospecificity (or even much stereoselectivity) is difficult to rationalize with a concerted reaction mechanism. The production[3] of about twice as much *endo*-**2** as *exo*-**2** from **1** and the fairly high quantum yields of formation of **5**-OMs from both **3**-OMs and **4**-OMs would require highly twisted transition states, particularly when the endo isomers are considered. This mechanism does not explain the nucleofugal effect, nor does it take into account the solvent effects observed in the two systems.

If the argument in the preceding paragraph is convincing to the idea that some intermediate or set of intermediates is involved in the photorearrangements, one might consider that bond heterolysis, ionic rearrangement, and ion-pair return together constitute an acceptable scheme. If, as we have concluded above, ion **15** is the kinetically capturable species in both ground state and photosolvolysis, can it also be the initially produced cation in the photo-Wagner–Meerwein rearrangement as well? We think not, for we believe that it could not return to **5**-OMs (presumably by geitonodesmic attack or by rearrangement to **14**) with as high a quantum efficiency as we have observed. It would, of course, accommodate the other observations listed above, but the efficient conversions with $Cl^-$, $OCOCHCl_2^-$, and $OMs^-$ to **5**-X compounds seem to us to make this intermediate unlikely.

Irradiation with 254-nm light involves the insertion of about 110 kcal/mol of light into the reacting molecules. Obviously such molecules have an excess of at least 75–80 kcal/mol over that required for bond heterolysis in a solvent of reasonable ionizing power, if one assumes that ground-state ions are produced. Photoexcited molecules therefore have reaction paths available which are different from the "best" path

available for ground-state reactions. One might therefore consider the possibility that an ion pair including the cation **14** is produced directly from the excited species, without the initial intervention of the allylic cation **15**. As we have noted above, **14** is somewhat above **15** in energy, but is accessible in ground-state equilibrations. We would propose that the $\mathbf{14}^+$, $X^-$ ion pair could collapse to **5**-X (and presumably to **3**-X as well) or could thermally relax to $\mathbf{15}^+$ $X^-$, whereupon the reactions of the latter (return to **3**-X or **4**-X or solvolysis to **3**-$NHCOCH_3$) could occur.

The difficulty with this proposal is the fact that ground-state Wagner-Meerwein rearrangements generally proceed with inversion at the carbon atom from which the nucleofuge departs. **14** could therefore not be expected to be formed directly from **4**-X species, if photochemical reactions follow the same symmetry requirements. It is possible of course that the stereochemical requirements are different in the excited-state decay, or that the barriers are not proscriptive, considering the large energy content of the excited state. It is of course possible that the reaction path does not lead to $\mathbf{14}^+$ $X^-$ directly, but rather that the $\pi$-$\pi^*$ excited state of **3**-X or **4**-X, in which radiation excitation must originally reside initially in the benzene ring, decays by intramolecular electron transfer to a state best represented by the zwitterion diradical **39**. The zwitterion **39**, like other ion radicals with carbon-halogen[36] or similar bonds, should be greatly unstable with respect to **14**-X and may have no (or only trivial) stereoelectronic requirements. Labeling experiments to test these proposals will be described later.




**39** $X^{\cdot}$ $\quad$ $\mathbf{14}^+X^-$

## Experimental Section

**General.** Commercially available reagents were used without purification unless otherwise noted. Dry acetonitrile was obtained by distilling Kodak spectrograde acetonitrile from calcium hydride prior to its use. Melting points were determined on a Thomas-Hoover Unimelt apparatus. Mass spectra were recorded with a Varian MAT Model CH5 mass spectrometer. Carbon-hydrogen analyses were performed by Galbraith Laboratories.

**Nuclear Magnetic Resonance Spectroscopy.** $^1H$ NMR spectra were obtained with either a Varian Associates A-60A, T-60, EM-390, or HA-100 spectrometer. Double irradiation experiments were carried out on a Varian Associates EM-390 spectrometer. Chemical shifts are relative to internal $Me_4Si$. $^2H$ NMR spectra were obtained with a JEOL JNM-PS-100 spectrometer. $^1H$ NMR product ratios were obtained by integration of a unique resonance for each component as described earlier.[9]

**High-Pressure Liquid Chromatography.** LC separations were carried out using two Waters Associates Model 6000A pumps controlled by a Waters Associates Model 660 solvent programmer. A Beckman Model 25 ultraviolet spectrometer equipped with a Waters Associates microcell apparatus was used for UV detection (254 nm). The stationary phase in all cases consisted of two Waters Associates 30 cm by 4 mm $\mu$-Porasil columns connected in series. Tetrahydrofuran-hexane mixed solvent systems were used as the mobile phase. LC samples for $^2H$ NMR analysis were obtained by repeated injection and collection of individual components.

**Photochemical Studies.** The following ultraviolet reactors were used in this study: Rayonet Type RS preparative photochemical reactor equipped with a merry-go-round apparatus (large Rayonet), Rayonet Srinivasan-Griffin photochemical reactor (small Rayonet), Ultraviolet Products Model PCOX1 photochemical reactor (Photoprep), and a water-jacketed immersion-well apparatus equipped with a 450-W high-pressure Hanovia lamp (Hanovia). Samples for quantum yield studies were deoxygenated by five freeze-pump-thaw cycles and sealed at pressures less than $2 \times 10^{-5}$ Torr. Cyclopentanone actinometry was used exclusively.[38] In all cases, substrate concentrations were set up in such a way that the substrate absorbed all of the incident light.

**3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-*endo*-2-ol Acetate (4-OAc).** A solution of 250 mg (1.2 mmol) of **4**-OH[9] in 5 mL of dry pyridine was cooled in an ice bath and 0.173 mL (2.4 mmol) of acetyl chloride was added slowly. The solution stood (room temperature) for 3 h. After dilution with water and extraction with ether, the ether extract was washed with water, 10% HCl, and water dried ($MgSO_4$). Evaporation of solvent and elution through a silica gel column (15% ether-hexane) gave 200 mg (67%) of **4**-OAc, mp 98–99 °C, after recrystallization from hexane-$CCl_4$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.2 (m, 4, aromatic H), 6.5 (d, 1, H-4, $J_{4,5}$ = 7 Hz), 5.7 (d, 1, H-2, $J_{2,1}$ = 5 Hz), 3.7 (m, 1, H-1), 3.4 (m, 1, H-5), 2.3 (m, 2, H-$8_{syn}$ and H-$8_{anti}$), 2.1 (s, 3, $-CH_3$). Anal. Calcd for $C_{14}H_{13}ClO_2$: C, 67.61; H, 5.27. Found: C, 67.35; H, 5.40.

***anti*-2,6-Dichloro-7,8-benzobicyclo[2.2.2]octa-5,7-diene (5-Cl), Equilibration of 5-Cl, 3-Cl, and 4-Cl.** Neat **3**-Cl[8] (2.0 g, 8.9 mmol) was mixed with a trace of ferric chloride and heated at 140 °C for 0.5 h. The product was dissolved in ethyl ether, washed with water, and dried ($MgSO_4$). Evaporation of solvent left a yellow oil whose $^1H$ NMR spectrum indicated a mixture of **5**-Cl, **3**-Cl, and **4**-Cl in a ratio of 56:14:30, respectively (measured by the relative area of resonances for H-1 of **5**-Cl and H-2 of both **3**-Cl and **4**-Cl). Longer heating did not change the mixture composition. The mixture was dissolved in 50 mL of 85% acetone-water, and a saturated aqueous solution of silver perchlorate (1.03 g, 5.0 mmol) was added. The solution was stirred at room temperature for 15 days, followed by 2.5-h heating at 45 °C. Water was added, followed by ether extraction. The ethereal extract was washed with brine and dried ($MgSO_4$). Evaporation of solvent left 1.65 g of yellow oil which was dry packed onto silica and eluted with hexane. Evaporation of solvent and crystallization from hexane gave 450 mg (22%) of pure **5**-Cl: mp 83–84 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.2 (m, 4, aromatic H), 6.5 (dd, 1, H-5, $J_{5,4}$ = 7, $J_{5,1}$ = 2 Hz), 4.0 (m, 3, H-1, H-2, and H-4), 2.3 (ddd, 1, H-$3_{syn}$, $J_{3syn,3anti}$ = 12, $J_{3syn,2}$ = 8, $J_{3syn,4}$ = 3Hz), 1.9 (dt, 1, H-$3_{anti}$, $J_{3anti,3syn}$ = 12, $J_{3anti,4}$ = 3, $J_{3anti,2}$ = 3 Hz). Anal. Calcd for $C_{12}H_{10}Cl_2$: C, 64.02; H, 4.48. Found: C, 63.95; H, 4.42.

**6-Chloro-7,8-benzobicyclo[2.2.2]octa-5,7-dien-*anti*-2-ol Methanesulfonate (5-OMs).** To an ice-cold solution of 370 mg (1.8 mmol) of **5**-OH[9] in 10 mL of dry pyridine was added 0.28 mL (3.6 mmol) of methanesulfonyl chloride. The solution was allowed to warm to room temperature over a 2.5-h period, after which 10% HCl was added. The mixture was extracted several times with ether, and the ether extracts were washed with 10% HCl and water and then dried ($MgSO_4$). Filtration and solvent evaporation gave 450 mg of **5**-OMs, which, upon recrystallization from $CCl_4$, melted at 114–117 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 7.2 (m, 4, aromatic H), 6.6 (dd, 1, H-5, $J_{5,4}$ = 7, $J_{5,1}$ = 2 Hz), 5.0 (dt, 1, H-2, $J_{2,1}$ = 3, $J_{2,3syn}$ = 8, $J_{2,3anti}$ = 3 Hz), 4.4 (dd, 1, H-1, $J_{1,2}$ = 3, $J_{1,5}$ = 2 Hz), 3.9 (dt, 1, H-4, $J_{4,5}$ = 7, $J_{4,3syn}$ = 3, $J_{4,3anti}$ = 3 Hz), 3.0 (s, 3, $-CH_3$), 2.2 (ddd, 1, H-$3_{syn}$, $J_{3syn,3anti}$ = 13, $J_{3syn,2}$ = 8, $J_{3syn,4}$ = 3 Hz), 1.7 (dt, 1, H-$3_{anti}$, $J_{3anti,3syn}$ = 13, $J_{3anti,2}$ = 3, $J_{3anti,4}$ = 3 Hz). Anal. Calcd for $C_{13}H_{13}ClO_3S$: C, 54.83; H, 4.60. Found: C, 54.88; H, 4.72.

**3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-*exo*-2-ol Methanesulfonate (3-OMs).** A solution of the alcohol **3**-OH[9] (1.1 g, 6.4 mmol) was treated as above to give a yellow oil (1.4 g, 78%) whose $^1H$ NMR spectrum was consistent with that expected for **3**-OMs: ($CDCl_3$) $\delta$ 7.2 (m, 4, aromatic H), 6.6 (d, 1, H-4, $J_{4,5}$ = 7 Hz), 4.9 (d, 1, H-2, $J_{2,1}$ = 2 Hz), 3.8 (m, 1, H-1), 3.5 (m, 1, H-5), 3.1 (s, 3, $CH_3$), 2.3 (m, 2, H-$8_{syn}$ and H-$8_{anti}$). Crystallization from ethyl ether-hexane mixed solvent gave pure **3**-OMs, mp 90–92 °C. Anal. Calcd for $C_{13}H_{13}ClO_3S$: C, 54.83; H, 4.60. Found: C, 54.98; H, 4.70.

**3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-*endo*-2-ol Methanesulfonate (4-OMs) and the Corresponding Deuterium-Labeled Ester 22-OMs.** A solution of the alcohol **4**-OH[9] (or **22**-OH) (0.40 g, 1.9 mmol) was treated with methanesulfonyl chloride as above giving, after workup, white crystals (0.48 g, 89%) of **4**-OMs (or **22**-OMs, mp (after recrystallization from $CCl_4$) 128–130 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 7.3 (m, 4, aromatic H), 6.6 (d, 1, H-4, $J_{4,5}$ = 7 Hz), 5.5 (d, 1, H-2, $J_{2,1}$ = 5 Hz), 3.9 (t, 1, H-1, $J_{1,2}$ = 5, $J_{1,8syn}$ = 5 Hz), 3.5 (dd, 1, H-5, $J_{5,4}$ = 7, $J_{5,8syn}$ = 4 Hz), 3.1 (s, 3, $-CH_3$), 2.4 (2, m, H-$8_{syn}$ and H-$8_{anti}$). The spectrum of **22**-OMs was identical except that the H-2 resonance was not observed and H-1 was observed as a doublet. Anal. Calcd for $C_{13}H_{13}ClO_3S$: C, 54.83; H, 4.60. Found: C, 54.66; H, 4.70.

**6-Chloro-7,8-benzobicyclo[2.2.2]octa-5,7-dien-2-one (10).** A solution of 3.0 g (14 mmol) of **5**-OH[9] in 60 mL of acetone was titrated with 2.67 N Jones reagent[38] (ca. 5 mL) until a red tint persisted. The excess reagent was destroyed with isopropyl alcohol. The reaction mixture was then diluted with brine and extracted with four 30-mL portions of ether. The combined ether extracts were washed with water, aqueous sodium bicarbonate, and water and dried ($MgSO_4$). Filtration and evaporation of solvent yielded 2.38 g of light brown oil (83%) which appeared (NMR) to be quite pure. $^1H$ NMR ($CDCl_3$): $\delta$ 7.2 (m, 4, aromatic H), 6.6 (dd, 1, H-5, $J_{5,1}$ = 2, $J_{5,4}$ = 7 Hz), 4.4 (d, 1, H-1, $J_{1,5}$ = 2 Hz), 4.2 (dt, 1, H-4, $J_{4,5}$ = 7, $J_{4,3syn}$ = 3, $J_{4,3anti}$ = 3 Hz), 2.1 (ABX pattern, 2, H-$3_{syn}$ and H-$3_{anti}$). Pure **10** was obtained by vacuum distillation (84°C, 0.5 Torr). Anal. Calcd for $C_{12}H_9ClO$: C, 70.43; H, 4.43. Found: C, 70.50; H, 4.49.

**Reduction of 6-Chloro-7,8-benzobicyclo[2.2.2]octa-5,7-dien-2-one (10) with Lithium Aluminum Hydride (or Lithium Aluminum Deuteride).** A solution of 2.38 g (12.0 mmol) of **10** in 50 mL of anhydrous ether was slowly added to a solution of 0.50 g (13.0 mmol) of lithium aluminum hydride (lithium aluminum deuteride) in 50 mL of anhydrous ether. The reaction mixture was stirred for 1 h at room temperature. The excess $LiAlH_4$ was destroyed with a saturated aqueous solution of sodium potassium tartrate. The ethereal fraction was filtered and dried ($MgSO_4$). Evaporation of solvent left a white oil (2.02 g, 82%) whose $^1H$ NMR spectrum was consistent with a 1:1 mixture of **5**-OH and **6**-OH (**16**-OH and **17**-OH) measured by integration of the H-5 resonances for both **5**-OH ($\delta$ 6.6, $CDCl_3$) and **6**-OH ($\delta$ 6.4, $CDCl_3$). The stereochemistry at C-2 of **5**-OH and **6**-OH was determined by adding $Eu(FOD)_3$[14] to the mixture and observing that the H-5 resonance of **5**-OH moved downfield farther than the H-5 resonance of **6**-OH.

**6-Chloro-7,8-benzobicyclo[2.2.2]octa-5,7-dien-*syn*-2-ol Methanesulfonate (6-OMs).** A solution of the mixture of **5**-OH and **6**-OH (1:1) (2.02 g, 9.78 mmol) in 50 mL of dry pyridine was treated with 1.54 mL (19.8 mmol) of methanesulfonyl chloride to give 2.15 g (77%) of a pale yellow oil whose $^1H$ NMR spectrum was consistent with a 1:1 mixture of **5**-OMs and **6**-OMs. The oil was dissolved in 20 mL of 0.5 M sodium acetate in acetic acid and the solution was heated at 80 °C for 14 h. The solution was then diluted with water and extracted with three 25-mL portions of ethers. The ether extract was washed with water, saturated aqueous sodium bicarbonate, and brine and dried ($MgSO_4$). Filtration and evaporation of solvent left 1.98 g of a yellow oil whose $^1H$ NMR spectrum was consistent with a mixture of **6**-OMs, **3**-OAc, and **4**-OAc. The oil was added to ether whereupon a white precipitate formed. Recrystallization from ether gave 217 mg of pure **6**-OMs: mp 110.5–111.5 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.2 (m, 4, aromatic H), 6.5 (dd, 1, H-5, $J_{5,4}$ = 7, $J_{5,1}$ = 2 Hz), 5.2 (dt, 1, H-2, $J_{2,1}$ = 3, $J_{2,3syn}$ = 3, $J_{2,3anti}$ = 9 Hz), 4.3 (dd, 1, H-1, $J_{1,2}$ = 3, $J_{1,5}$ = 2 Hz), 4.0 (dt, 1, H-4, $J_{4,5}$ = 7, $J_{4,3syn}$ = 3, $J_{4,3anti}$ = 3 Hz), 2.9 (s, 3, $-CH_3$), 2.3 (ddd, 1, H-$3_{anti}$, $J_{3anti,3syn}$ = 13, $J_{3anti,4}$ = 3, $J_{3anti,2}$ = 9 Hz), 1.4 (dt, 1, H-$3_{syn}$, $J_{3syn,3anti}$ = 13, $J_{3syn,2}$ = 3, $J_{3syn,4}$ = 3 Hz). Anal. Calcd for $C_{13}H_{13}ClO_3S$: C, 54.83; H, 4.60. Found: C, 55.00; H, 4.72. The remaining oil was separated by preparative thick layer TLC (silica–10% ethyl ether–hexanes) giving, after recrystallization, an additional 211 mg of **6**-OMs.

**Preparation of a Mixture of 2-Deuterio-6-chloro-7,8-benzobicyclo[2.2.2]octa-5,7-dien-*syn*- and -*anti*-2-ol Methanesulfonates (16-OMs and 17-OMs).** A 1:1 mixture of **16**-OH and **17**-OH (304 mg, 1.46 mmol) was dissolved in 7 mL of dry pyridine and esterified as above to give 354 mg (85%) of a colorless oil which crystallized on standing. $^1H$ NMR analysis indicated a 1:1 mixture of **16**-OMs and **17**-OMs each with 1 g-atom of deuterium at C-2.

**3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-*exo*-2-ol Dichloroacetate (3-OCOCHCl$_2$).** To an ice-cold solution of 2.00 g (9.68 mmol) of **3**-OH[8] in 60 mL of dry pyridine was added 1.75 mL (17.3 mmol) of dichloroacetyl chloride. The reaction mixture was stirred for 0.5 h at 0 °C and was then diluted with water and extracted with four 50-mL portions of ether. The ether extract was washed with water and 10% HCl and dried ($MgSO_4$). Evaporation of solvent followed by elution through a silica gel column with 5% ethyl ether–hexanes gave 1.38 g of white solid, which after recrystallization from hexane gave 1.01 g (33%) of **3**-OCOCHCl$_2$, mp 89–90 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 7.2 (m, 4, aromatic H), 6.7 (d, 1, H-4, $J_{4,5}$ = 7 Hz), 6.0 (s, 1, $-CHCl_2$), 5.2 (d, 1, H-2, $J_{2,1}$ = 2 Hz), 3.5 (m, 2, H-1 and H-5), 2.3 (m, 2, H-$8_{syn}$ and H-$8_{anti}$). Anal. Calcd for $C_{14}H_{11}Cl_3O$: C, 52.94; H, 3.49. Found: C, 53.04; H, 3.50.

**6-Chloro-7,8-benzobicyclo[2.2.2]octa-5,7-dien-*anti*-2-ol dichloroacetate (5-OCOCHCl$_2$)** was prepared from 80 mg (0.39 mmol) of **5**-OH and 0.086 mL of dichloroacetyl chloride in 3 mL of pyridine: mp 100–102 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.2 (m, 4, aromatic H), 6.6 (dd, 1, H-5, $J_{5,4}$ = 7, $J_{5,1}$ = 2 Hz), 5.9 (s, 1, $-CHCl_2$), 5.1 (dt, 1, H-2, $J_{2,1}$ = 3, $J_{2,3syn}$ = 8, $J_{2,3anti}$ = 3 Hz), 4.3 (dd, 1, H-1, $J_{1,2}$ = 3, $J_{1,5}$ = 2 Hz), 3.9 (dt, 1, H-4, $J_{4,5}$ = 7, $J_{4,3syn}$ = 3, $J_{4,3anti}$ = 3 Hz), 2.2 (ddd, 1, H-$3_{syn}$, $J_{3syn,3anti}$ = 13, $J_{3syn,2}$ = 8, $J_{3syn,4}$ = 3 Hz), 1.6 (dt, 1, H-$3_{anti}$, $J_{3anti,3syn}$ = 13, $J_{3anti,2}$ = 3, $J_{3anti,4}$ = 3 Hz). Anal. Calcd for $C_{14}H_{11}Cl_3O$: C, 52.94; H, 3.49. Found: C, 53.00; H, 3.53.

**3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-*endo*-2-ol dichloroacetate (4-OCOCHCl$_2$)** was prepared from **4**-OH as above: $^1H$ NMR ($CDCl_3$) $\delta$ 7.2 (m, 4, aromatic H), 6.6 (dd, 1, H-4, $J_{4,5}$ = 7, $J_{4,2}$ = 1 Hz), 5.9 (s, 1, $-CHCl_2$), 5.8 (dd, 1, H-2, $J_{2,1}$ = 5, $J_{2,4}$ = 1 Hz), 3.8 (m, 1, H-1), 3.5 (m, 1, H-5), 2.4 (m, 2, H-$8_{syn}$ and H-$8_{anti}$).

**6-Chloro-7,8-benzobicyclo[2.2.2]octa-5,7-dien-*anti*-2-acetamide (5-NHCOCH$_3$).** The general method of Borch[39] was used with ketone **10**, followed by acylation, to prepare a mixture of the amides **5**-$NHCOCH_3$ and **6**-$NHCOCH_3$ ($^1H$ NMR). Crystallization of the mixture in THF–hexane followed by microdistillation of the mother liquors (ca. 160 °C, 0.06 Torr) afforded slightly impure **5**-$NHCOCH_3$: mp 70–80 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.1 (m, 4, aromatic H), 6.5 (dd, 1, H-5, $J_{5,4}$ = 7, $J_{5,1}$ = 2 Hz), 5.5 (m, 1, NH), 4.1 (m, 2, H-1 and H-2), 3.9 (m, 1, H-4), 1.9 (m, 4, H-$3_{syn}$ and $-CH_3$), 1.2 (m, 1, H-$3_{anti}$). Mass spectrum: *m/e* (rel intensity) M, 247 (14), M + 2, 249 (4.0), M − 85, 162 (100).

**7-Chloro-3,4-benzotricyclo[3.2.1.0$^{2,7}$]oct-3-en-*syn*-6-ol (35-OH).** A solution of 204 mg (1.00 mmol) of ketone **36** in 5 mL of anhydrous ether was reduced with 42 mg (1.1 mmol) of lithium aluminum hydride in 5 mL of ether as described above for the reduction of **10** to give 128 mg (62%) of **35**-OH which, after recrystallization from ether–hexane, melted at 72–72.5 °C: $^1H$ NMR ($CDCl_3$) $\delta$ 7.2 (m, 4, aromatic H), 4.3 (dd, 1, H-6, $J_{6,5}$ = 5, $J_{6,hydroxyl}$ = 9 Hz), 3.2 (t, 1, H-5, $J_{5,6}$ = 5, $J_{5,8anti}$ = 5 Hz), 2.7 (d, 1, H-2, $J_{2,1}$ = 8 Hz), 2.2 (ddd, 1, $H_{8anti}$, $J_{8anti,8syn}$ = 11, $J_{8anti,5}$ = 5, $J_{8anti,1}$ = 3 Hz), 2.1 (m, 1, H-1), 1.2 (d, 1, hydroxyl, $J_{hydroxyl,6}$ = 9 Hz), 1.0 (d, 1, H-$8_{syn}$, $J_{8syn,8anti}$ = 11 Hz). Anal. Calcd for $C_{12}H_{11}ClO$: C, 69.74; H, 5.36. Found: C, 69.85; H, 5.32.

**7-Chloro-3,4-benzotricyclo[3.2.1.0$^{2,7}$]oct-3-en-*syn*-6-ol Methanesulfonate (35-OMs).** A solution of the alcohol **35**-OH (1.0 g, 0.0048 mol) in 23 mL of dry pyridine was esterified in the usual fashion. Workup, followed by recrystallization from ether–hexane, gave 890 mg (65%) of **35**-OMs, mp 70.5–71.5 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 7.2 (m, 4, aromatic H), 5.2 (d, 1, H-6, $J_{6,5}$ = 5 Hz), 3.5 (t, 1, H-5, $J_{5,6}$ = 5, $J_{5,8anti}$ = 5 Hz), 2.9 (s, 3, $-CH_3$), 2.8 (d, 1, H-2, $J_{2,1}$ = 7 Hz), 2.3 (ddd, 1, H-$8_{anti}$, $J_{8anti,8syn}$ = 12, $J_{8anti,5}$ = 5, $J_{8anti,1}$ = 3 Hz), 2.1 (m, 1, H-1), 1.1 (d, 1, H-$8_{syn}$, $J_{8syn,8anti}$ = 12 Hz). Anal. Calcd for $C_{13}H_{13}ClSO_3$: C, 54.83; H, 4.60. Found: C, 55.00; H, 4.68.

**7-Chloro-3,4-benzotricyclo[3.2.1.0$^{2,7}$]oct-3-en-*anti*-6-ol Acetate (34-OAc).** A solution of **3**-OAc (200 mg, 0.80 mmol) in 85 mL of spectrograde acetone was placed in an immersion-well apparatus equipped with a Pyrex filter and irradiated with a 450-W high-pressure Hanovia lamp for 20 h. Evaporation of solvent left a dark brown oil which was eluted through a short silica gel column with carbon tetrachloride. Evaporation of solvent left a colorless oil (195 mg, 98%) whose $^1H$ NMR spectrum was consistent with that expected for **34**-OAc: ($CDCl_3$) $\delta$ 7.3 (m, 4, aromatic H), 4.9 (s, 1, H-6), 3.2 (d, 1, H-5, $J_{5,8anti}$ = 5 Hz), 2.8 (d, 1, H-2, $J_{2,1}$ = 8 Hz), 2.5 (ddd, 1, H-$8_{anti}$, $J_{8anti,8syn}$ = 12, $J_{8anti,5}$ = 5, $J_{8anti,1}$ = 2 Hz), 2.2 (m, 4, H-1 and $-CH_3$), 1.1 (d, 1, H-$8_{syn}$, $J_{8syn,8anti}$ = 12 Hz). The oil could be distilled (0.2 Torr) with an oil bath temperature of 130–150 °C. Mass spectrum: *m/e* (rel intensity) M, 248 (43.0); M + 2, 250 (14.0); M − 95, 153 (100). Anal. Calcd for $C_{14}H_{13}ClO_2$: C, 67.61; H, 5.27. Found: C, 67.73; H, 5.36.

**7-Chloro-3,4-benzotricyclo[3.2.1.0$^{2,7}$]oct-3-en-*anti*-6-ol (34-OH). Sensitized Irradiation of 3-OH.** A solution of **3**-OH[8] (2.0 g, 9.7 mmol) in 270 mL of spectrograde acetone was placed in an immersion-well apparatus equipped with a Pyrex filter and irradiated with the Hanovia lamp for 7 days. Evaporation of solvent left a brown oil which was packed onto 10 g of 60–200 mesh silica gel. This silica was placed in a column over an additional 10 g of silica gel. The column was then eluted with 25% ether in hexane. Evaporation of solvent left a pale yellow oil (1.56 g, 78%) whose $^1H$ NMR spectrum was consistent with that expected for **34**-OH: ($CDCl_3$) $\delta$ 7.2 (m, 4, aromatic H), 3.7 (s, 1, H-6), 3.2 (d, 1, H-5, $J_{5,8anti}$ = 5 Hz), 2.8 (d, 1, H-2, $J_{2,1}$ = 8 Hz), 2.6 (m, 2, H-$8_{anti}$ and hydroxyl), 2.1 (bd, 1, H-1, $J_{1,2}$ = 8 Hz), 1.1 (d, 1, H-$8_{syn}$, $J_{8syn,8anti}$ = 12 Hz). Mass spectrum: *m/e* (rel intensity) M,

206 (97.8); M + 2, 208 (33.5); M − 35, 171 (52.9); M − 65, 141 (100).

**7-Chloro-3,4-benzotricyclo[3.2.1.0$^{2,7}$]oct-3-en-*anti*-6-ol Methanesulfonate (34-OMs).** A solution of the alcohol **34**-OH (150 mg, 0.73 mmol) in 3.5 mL of dry pyridine was esterified in the usual fashion to give 185 mg (89%) of pale yellow oil whose $^1$H NMR was that expected for **34**-OMs: ($CDCl_3$) $\delta$ 7.3 (m, 4, aromatic H), 4.6 (s, 1, H-6), 3.4 (d, 1, H-5, $J_{5,8anti}$ = 5 Hz), 3.1 (s, 3, $-CH_3$), 2.8 (d, 1, H-2, $J_{2,1}$ = 8 Hz), 2.6 (ddd, 1, H-8$_{anti}$, $J_{8anti,8syn}$ = 12, $J_{8anti,5}$ = 5, $J_{8anti,1}$ = 2 Hz), 2.2 (m, 1, H-1), 1.1 (d, 1, H-8$_{syn}$, $J_{8syn,8anti}$ = 12 Hz). Mass spectrum: *m/e* (rel intensity) M, 284 (18.0); M + 2, 286 (6.6); M − 96, 188 (47.7); M − 143, 141 (100).

**7-Chloro-3,4-benzotricyclo[3.2.1.0$^{2,7}$]oct-3-en-6-one (36). Sensitized Irradiation of 9.** A solution of **9** (2.55 g, 12.5 mmol) in 270 mL of spectrograde acetone was placed in an immersion well equipped with a Pyrex filter. The solution was irradiated with the Hanovia for 21 h. Evaporation of solvent left 2.55 g (100%) of a pale brown oil whose $^1$H NMR spectrum was consistent with that expected for **36**: ($CDCl_3$) $\delta$ 7.3 (m, 4, aromatic H) 3.4 (dd, 1, H-5, $J_{5,8anti}$ = 5, $J_{5,1}$ = 1 Hz) 3.3 (d, 1, H-2, $J_{2,1}$ = 8 Hz), 2.7 (m, 2, H-1 and H-8$_{anti}$), 1.5 (d, 1, H$_{8syn}$, $J_{8syn,8anti}$ = 11 Hz). A small sample was distilled (86 °C, 0.2 Torr) and then crystallized from ether–hexane, mp 66–67 °C. Anal. Calcd for $C_{12}H_9ClO$: C, 70.43; H, 4.43. Found: C, 70.55; H, 4.43.

**Treatment of 3-OH with Aqueous Sulfuric Acid in Acetonitrile. Preparation of 3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-diene-*exo*-2-acetamide (3-NHCOCH$_3$).** To an ice-cold solution of 250 mg (1.2 mmol) of **3**-OH[8] in 1.5 mL of acetonitrile was added 90 $\mu$L of 95% sulfuric acid. The solution was stirred at room temperature for 7 days. Water was then added and the mixture was extracted with three portions of ether. The ether extract was washed with aqueous sodium bicarbonate and brine. The solution was dried ($Na_2SO_4$), filtered, and evaporated to dryness. This left 190 mg of white crystals whose $^1$H NMR spectrum indicated that the mixture comprised 85% **3**-NHCOCH$_3$ and 15% **3**-OH. Recrystallization from ether gave pure **3**-NHCOCH$_3$: mp 199–201 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.3 (m, 4, aromatic H), 6.5 (d, 1, H-4, $J_{4,5}$ = 7 Hz), 6.0 (m, 1, N-H), 4.5 (dd, 1, H-2, $J_{2,1}$ = 2, $J_{2,N-H}$ = 8 Hz), 3.5 (m, 2, H-1 and H-5), 2.0 (m, 5, H-8$_{syn}$, H-8$_{anti}$, and $-CH_3$). That H-2 is coupled to the NH proton was demonstrated by irradiating at $\delta$ 6.0 and observing the collapse of the H-2 doublet of doublets into a doublet with $J_{2,1}$ = 2 Hz. Anal. Calcd for $C_{14}H_{14}NClO$: C, 67.88; H, 5.70. Found: C, 67.66; H, 5.80.

**Treatment of 5-OH with Sulfuric Acid in Acetonitrile Solvent.** A solution of the alcohol **5**-OH (70 mg, 0.34 mmol) in 10 mL of acetonitrile was treated with 100 $\mu$L of sulfuric acid as above. After 65 h at room temperature the reaction mixture was worked up giving a slightly wet white solid (116 mg) whose $^1$H NMR spectrum was identical with that of **3**-NHCOCH$_3$.

**Treatment of 3-Cl with Tri-*n*-butyltin Hydride. Preparation of 3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-diene (3-H).** A solution of 300 mg (1.32 mmol) of **3**-Cl, 66 mg of azobisisobutyronitrile, and 777 mg (2.7 mmol) of tri-*n*-butyltin hydride in 30 mL of freshly distilled benzene was heated at 60 °C overnight. Carbon tetrachloride (1 mL) was added and the solution was stirred at room temperature for 2 days. The solvent was then removed and the oil was dry packed onto 10 g of silica gel. The silica was placed on a short column and eluted with hexane. The first 100 mL was collected. Evaporation of solvent and $^1$H NMR analysis indicated that the only product formed which contained aromatic protons was **3**-H. The oil was placed on a thick-layer silica gel plate and eluted with hexane. Removal of the major band ($R_f$ 0.21) left 220 mg (88%) of **3**-H: $^1$H NMR ($CDCl_3$) $\delta$ 7.1 (m, 4, aromatic H), 6.2 (broad d, 1, H-4, $J_{4,5}$ = 7 Hz), 3.3 (m, 2, H-1 and H-5), 2.8 (ddd, H-2$_{exo}$, $J_{2exo,2endo}$ = 17, $J_{2exo,1}$ = 5, $J_{2exo,4}$ = 2 Hz), 2.1 (m, 3, H-2$_{endo}$, H-8$_{syn}$, and H-8$_{anti}$). $^1$H NMR double irradiations (decoupling power of 0.4 mG): irradiation of the resonance H-4 at $\delta$ 6.2 caused collapse of the resonance at $\delta$ 3.3 to a broad singlet, as well as loss of the $J_{2exo,4}$ coupling at $\delta$ 2.8; irradiation of the H-1 and H-5 resonances at $\delta$ 3.3 caused the resonance at $\delta$ 6.2 (H-4) to collapse to a broad singlet. A small sample was crystallized from 90% ethanol–water, mp 42–43 °C. Anal. Calcd for $C_{12}H_{11}Cl$: C, 75.59; H, 5.81. Found: C, 75.70; H, 5.91.

**Acetolysis of 5-OMs.** A solution of 33 mg of **5**-OMs in 0.3 mL of 0.5 M sodium acetate in acetic acid was sealed in a 5-mm NMR tube and heated at 77 °C for 23 h. The reaction mixture was then diluted with water and extracted with ether. The ether extract was washed with water, aqueous sodium bicarbonate, and brine and dried ($MgSO_4$). Evaporation of solvent left 31.5 mg of a mixture whose $^1$H NMR spectrum was consistent with that anticipated for 15% **5**-OMs, 15% **4**-OAc, and 70% **3**-OAc. This gave a **3**-OAc to **4**-OAc ratio of 4.7. This ratio of acetate products was unchanged when the solution was heated for prolonged periods under identical conditions.

**Acetolysis of 6-OMs.** A solution of 30.8 mg of **6**-OMs in 0.3 mL of 0.5 M sodium acetate in acetic acid was sealed in a 5-mm NMR tube and heated at 77 °C for 10 days. The reaction mixture was worked up as above giving 27.5 mg of oil. $^1$H NMR analysis indicated 20% **6**-OMs. The remaining 80% was made up of a mixture of **7**-OAc and **8**-OAc in a ratio of 2.7:1, respectively.[10]

**Acetolysis of a Mixture of 16-OMs and 17-OMs.** A 1:1 mixture of **16**-OMs and **17**-OMs (96 mg, 0.34 mmol) was dissolved in 1 mL of 0.5 M sodium acetate–acetic acid and placed in a 5-mm NMR tube. The tube was sealed and heated to 73 °C for 16 h. Workup as above gave 87 mg of white oil which was placed on a thick-layer TLC plate (silica) and eluted with 10% ethyl ether–hexane. The nonmobile band (40 mg) was a mixture of **16**-OMs and **17**-OMs. The mobile band ($R_f$ 0.23) (28 mg) was a mixture of the deuterium-labeled acetates **3**-OAc-$d_1$ and **4**-OAc-$d_1$ (consisting predominantly of **3**-OAc-$d_1$. Failure to observe **7**-OAc-$d_1$ demonstrated that no acetolysis of **17**-OMs had occurred.) The acetate mixture was methanolyzed as above and the resulting deuterium-labeled **3**-OH and **4**-OH (26 mg) were separated by thick layer chromatography (silica–50% ethyl ether–hexane). The major band (lower mobility) was removed giving 13.4 mg of white solid whose $^1$H NMR spectrum was consistent with **3**-OH containing deuterium at both C-1 and C-5. Earlier work had demonstrated that addition of 23 mg of Eu(FOD)$_3$[14] to a solution of 23 mg of **3**-OH in 0.4 mL of $CDCl_3$ moved the H-1 resonance from $\delta$ 3.5 to 5.05 and the H-5 resonance from $\delta$ 3.5 to 4.05. Addition of Eu(FOD)$_3$ to the deuterium-labeled **3**-OH followed by $^2$H NMR analysis indicated that **18**-OH and **19**-OH were present in a ratio of 46:54.

**Acetolysis of 22-OMs and Preparation of 25-OMs.** A solution of 1.86 g (6.51 mmol) of deuterium-labeled methanesulfonate ester **22**-OMs in 25 mL of 0.5 M sodium acetate–acetic acid was heated at 60 °C for 6 days. The solution was diluted with brine and extracted with three 25-mL portions of ether. The combined ether extracts were washed with water and dried ($MgSO_4$). Evaporation of solvent left 1.40 g (86%) of a pale yellow oil whose $^1$H NMR spectrum was consistent with a mixture of **3**-OAc-$d_1$ and **4**-OAc-$d_1$ in a ratio greater than 15:1, respectively (approximate areas obtained by the integration of H-1 for both **3**-OAc-$d_1$ and **4**-OAc-$d_1$ and the assumption that deuterium is scrambled to an equal extent in both compounds). $^2$H NMR analysis indicated that the acetate **3**-OAc-$d_1$ contained 60% deuterium at C-2 and 40% deuterium at C-4. A solution of 1.35 g (5.41 mmol) of the oil in 100 mL of 0.1 M sodium methoxide in methanol was heated at reflux for 15 min, cooled, diluted with brine, and extracted with ether. The ether extract was washed with brine and dried ($MgSO_4$). Evaporation of solvent left 980 mg (87%) of a white solid whose $^1$H NMR spectrum was consistent with that expected for ca. 95% **3**-OH-$d_1$. This solid was dissolved in 20 mL of acetone and titrated with 2.67 N Jones reagent[38] until a red tint remained. The solution was diluted with brine and extracted with three 30-mL portions of ether. The ether extract was washed with brine, saturated aqueous sodium bicarbonate, and brine and dried ($MgSO_4$). Evaporation of solvent left a solid (0.86 g) which was dissolved in 20 mL of anhydrous ether and slowly injected into a precharged flask containing lithium aluminum hydride (160 mg, 4.2 mmol), in 10 mL of ethyl ether. The reaction mixture was stirred at room temperature for 2 h. Excess hydride was destroyed with saturated aqueous sodium potassium tartrate. The solution was filtered and dried ($MgSO_4$). Evaporation of solvent left a white solid whose $^1$H NMR spectrum was consistent with that of **4**-OH containing some deuterium at C-4. The alcohol (470 mg) was esterfied as above with methanesulfonyl chloride giving 590 mg of white crystals. Recrystallization from carbon tetrachloride gave 380 mg (22% overall yield from **22**-OMs) of pure **4**-OMs whose $^1$H and $^2$H NMR spectra were consistent with **4**-OMs which contained 60% protium and 40% deuterium at C-4 (i.e., 40% **25**-OMs and 60% **4**-OMs).

**Acetolysis of 25-OMs.** A solution of 78.4 mg of the **25**-OMs mixture described above in 1.0 mL of 0.5 M sodium acetate in acetic acid was heated at 46 °C for 2 days. The mixture was worked up as above giving 73 mg of white oil whose $^1$H NMR spectrum was consistent with ca. 25% starting material and >70% deuterated **3**-OAc. The mixture was separated by preparative TLC (silica–10% ether–hexane). $^2$H NMR

analysis of the acetate mixture revealed that the deuterium-containing **3**-OAc was a 66:34 mixture of **25**-OAc and **24**-OAc, respectively.

**Silver-Assisted Acetolysis of 3-Cl.** A solution of 2.0 g (8.9 mmol) of **3**-Cl[8] in 15 mL of glacial acetic acid and 3.0 g (18 mmol) of silver acetate was heated at reflux for 2 h. The reaction mixture was cooled, diluted with water, and extracted with 25-mL portions of ether. The ether extract was washed with water, aqueous sodium bicarbonate, water, and brine and dried ($MgSO_4$). Evaporation of solvent left 2.2 g of white solid whose $^1H$ NMR spectrum was consistent with that anticipated for a 6.1:1 mixture of **3**-OAc and **4**-OAc, respectively (obtained by the relative areas of resonances for H-2 of **3**-OAc vs. H-2 of **4**-OAc).

**Thermolysis of 3-OCOCHCl$_2$.** A solution of 75 mg (0.24 mmol) of **3**-OCOCHCl$_2$ in 0.5 mL of dichloroacetic acid was sealed in a 5-mm NMR tube and heated at 100 °C until no further change was observed ($^1H$ NMR) (3 days). The sample was then diluted with water and extracted with four 10-mL portions of ether. The ether extract was washed with water, aqueous sodium bicarbonate, and water and dried ($MgSO_4$). Evaporation of solvent followed by methanolysis as above left 34 mg (71%) of oil. LC analysis indicated the following ratio of alcohols: 81% **5**-OH, 14% **3**-OH, and 5% **4**-OH.

**Thermolysis of 3-OMs in Wet Acetonitrile.** A solution of 41 mg (0.14 mmol) of **3**-OMs in 0.4 mL of 5% water-acetonitrile-$d_3$ in a 5-mm NMR tube was heated at 79 °C for 4 days. The reaction mixture was then diluted with water and extracted with ether. The ether extract was washed with brine and dried ($MgSO_4$). Evaporation of solvent left 30 mg of oil. LC analysis indicated the presence of only **3**-OH and **3**-NHCOCH$_3$, in a ratio of 65:35, respectively.

**Room Temperature Thermolysis of 3-OMs in Wet Acetonitrile.** A solution of 39 mg (0.13 mmol) of **3**-OMs in 0.4 mL of aqueous deuterated acetonitrile prepared as above was allowed to stand at room temperature for 51 days. The solution was then worked up as above and analyzed by $^1H$ NMR. The product mixture contained 44% **3**-OMs, 37% **3**-OH, and 19% 3-NHCOCD$_3$ (obtained by the relative areas of resonances for the H-2 protons of each compound).

**Thermolysis of 22-OMs.** A solution of 148 mg (0.52 mmol) of **22**-OMs in 1.5 mL of dry acetonitrile was heated at 77 °C for 28 days. Aqueous workup gave 146 mg of a yellow oil. LC analysis gave the following product ratios: 41:15:39:1.6:3.1 of **4**-OMs-$d_1$, **3**-OMs-$d_1$, **5**-OMs-$d_1$, **3**-NHCOCH$_3$-$d_1$, and **5**-NHCOCH$_3$-$d_1$, respectively. (The deuterium ratios in these products will be reported in another paper.)

**Thermolysis of 3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-*exo*-2-ol Acetate (3-OAc) in Perchloric–Acetic Acids.** A solution of 34 mg (0.14 mmol) of **3**-OAc in 0.4 mL of 0.03 M perchloric acid–acetic-$d_3$ acid-$d_1$ was sealed in a 5-mm NMR tube, heated at 75 °C, and then analyzed by $^1H$ NMR. The ratios were obtained by measuring ($^1H$ NMR) the relative area of resonances for H-2 of **3**-OAc, H-2 of **4**-OAc, and H-2 of **5**-OAc. These ratios are (listed as time, % **3**-OAc:% **4**-OAc:% **5**-OAc) 0 h, 100:0:0; 13.5 h, 31:24:45; 37 h, 26:19:55; 62 h, 13:7:80; 113 h, 11:9:80.

**Direct Irradiation of 3-Cl in Acetonitrile.** A solution of 204 mg (0.91 mmol) of **3**-Cl in 2 mL of acetonitrile was placed in a quartz tube. The tube was sealed with a rubber septum and the solution was deoxygenated by bubbling dry nitrogen gas through it. The solution was then irradiated (254 nm) in a "Photoprep" apparatus. Aliquots (0.1 mL) were withdrawn after 24, 31, and 45 h followed by LC analysis. The following ratios were obtained (**3**-Cl, **4**-Cl, and **5**-Cl, respectively): 24 h, 36:20:44; 31 h, 27:20:53; 45 h, 24:24:52.

**Identification of *endo*-3,4-Dichloro-6,7-benzobicyclo[3.2.1]octa-3,6-diene (4-Cl).** A solution of 0.81 g (3.6 mmol) of **3**-Cl in 8 mL of acetonitrile was placed in a quartz tube and irradiated with a high-pressure Hanovia lamp. The resulting solution was evaporated to dryness and eluted through a short silica gel column with hexanes. The solvent was removed and the resulting oil was separated by LC. Using hexane mobile phase, retention volumes were as follows: **3**-Cl, 9 mL; **5**-Cl, 11 mL; **4**-Cl, 13 mL. Compound **4**-Cl was collected. $^1H$ NMR ($CDCl_3$): $\delta$ 7.2 (m, 4, aromatic H), 6.4 (dd, 1, H-4, $J_{4,5}$ = 7, $J_{4,2}$ = 1 Hz), 4.8 (dd, 1, H-2, $J_{2,1}$ = 5, $J_{2,4}$ = 1 Hz), 3.5 (m, 2, H-1 and H-5), 2.2 (m, 2, H-8$_{syn}$ and H-8$_{anti}$). Mass spectrum: *m/e* (rel intensity) $M^+$, 225 (44.0); $M^+ + 2$, 227 (27.2); $M^+ - 35$, 190 (85.6); $M^+ - 72$, 153 (100).

**Direct Irradiation of 3-Cl in Dry Acetonitrile Followed by an Aqueous Workup.** A solution of 70 mg (0.31 mmol) of **3**-Cl in 0.85 mL of acetonitrile-$d_3$ was placed in a 5-mm quartz NMR tube and deoxygenated as above. The solution was irradiated (254 nm) in the "small Rayonet" reactor (ten lamps) until no further change (followed by $^1H$ NMR) was detected. The brown solution was then diluted with water and extracted with three 10-mL portions of ether. The ether extract was washed with water and brine and dried ($MgSO_4$). Evaporation of solvent left a brown oil (67 mg) whose $^1H$ NMR spectrum indicated that, in addition to the chloride mixture, a substantial amount of **3**-NHCOCD$_3$ was also present.

**Direct Irradiation of 3-OMs.** A solution of 29 mg (0.11 mmol) of **3**-OMs in 0.3 mL of acetonitrile-$d_3$ was placed in a 5-mm quartz NMR tube, deoxygenated, and irradiated for 42 h as above. The deep brown solution was then diluted with water and extracted with ether. The ether extract was dried ($MgSO_4$) and then evaporated to dryness, leaving 19 mg of yellow oil. $^1H$ NMR analysis indicated a 60:34:6 ratio of **5**-OMs, **3**-NHCOCH$_3$, and **3**-OMs, respectively.

**Direct Irradiation of 5-OMs.** A solution of 30 mg (0.10 mmol) of **5**-OMs in 0.3 mL of acetonitrile-$d_3$ was deoxygenated and irradiated for 6 days as above. No change could be detected ($^1H$ NMR) except for the trace formation of methanesulfonic acid.

**Direct Irradiation of 6-OMs.** A solution of 40 mg (0.14 mmol) of **6**-OMs in 0.4 mL of acetonitrile-$d_3$ was irradiated as described above. After 90 h, no change could be detected ($^1H$ NMR) except for the trace formation of methanesulfonic acid.

**Direct Irradiation of 3-OAc in Acetonitrile Solvent.** A solution of 32 mg (0.13 mmol) of **3**-OAc in 0.4 mL of acetonitrile-$d_3$ was irradiated as above. After 43 h, $^1H$ NMR analysis indicated that the **3**-OAc:**34**-OAc ratio was 7:3 (measured by the relative area of resonances of H-2 of **3**-OAc and H-6 of **34**-OAc).

**Direct Irradiation of 3-OH in Acetonitrile Solvent.** A solution of 26 mg (0.13 mmol) of **3**-OH in 0.4 mL of acetonitrile-$d_3$ was irradiated as above. After 20 h of irradiation, $^1H$ NMR analysis indicated that the **3**-OH:**34**-OH ratio was 8:3, respectively (measured by the relative area of resonances of H-2 of **3**-OH and H-5 of **34**-OH).

**Direct Irradiation of 5-Cl in Acetonitrile Solvent.** A solution of 41 mg (0.18 mmol) of **5**-Cl in 0.5 mL of acetonitrile-$d_3$ was irradiated as described above. Periodic analysis ($^1H$ NMR) showed no change in composition. After 7 days of irradiation, some small, unidentifiable $^1H$ NMR resonances were observed. However, resonances corresponding to either **3**-Cl or **4**-Cl were not detected.

**Direct Irradiation of 3-Cl in Cyclohexane Solvent.** A solution of 110 mg (0.49 mmol) of **3**-Cl in 10 mL of spectrograde cyclohexane was placed in a 10-mm quartz tube. Deoxygenation followed by irradiation (254 nm) in the "Photoprep" apparatus for 17 h, followed by evaporation of solvent, left 138 mg of yellow oil which was placed on a thick-layer silica plate and eluted with hexane. Three bands were observed after development, with $R_f$ values of 0.14, 0.23, and 0.32. The band with a $R_f$ of 0.32 (25 mg, 19%) was identified by $^1H$ NMR as **3**-c-C$_6$H$_{11}$: ($CDCl_3$) $\delta$ 7.1 (m, 4, aromatic H), 6.3 (d, 1, H-4, $J_{4,5}$ = 7 Hz), 3.3 (m, 2, H-1 and H-5), 2.1 (m, 3, H-2$_{endo}$, H-8$_{syn}$, and H-8$_{anti}$), 1.5 (m, 11, cyclohexyl H). That the stereochemistry at C-2 is exo cyclohexyl was realized from the chemical shifts of H-2$_{exo}$ and H-2$_{endo}$ of **3**-H ($\delta$ 2.8, H-2$_{exo}$, and $\delta$ 2.1, H-2$_{endo}$). Since the H-2 resonance of this product is at $\delta$ 2.1, the C-2 cyclohexyl group is exo and the C-2 proton is endo. In all $^1H$ NMR spectra studied, the C-2 exo proton (in **4**-X) was downfield of the corresponding C-2 endo proton (in **3**-X). Recrystallization from an ethanol–water mixed solvent afforded pure **3**-c-C$_6$H$_{11}$, mp 86–87 °C. Anal. Calcd for C$_{18}$H$_{21}$Cl: C, 79.25; H, 7.76. Found: C, 79.07; H, 7.92. The band with a $R_f$ of 0.23 (35.5 mg, 32%) was identified by $^1H$ NMR analysis as **3**-Cl with a trace of **3**-c-C$_6$H$_{11}$. The band with a $R_f$ of 0.14 (23 mg, 12%) was identified by mass spectrometry as a C$_{24}$H$_{20}$Cl$_2$ radical dimer. Mass spectrum: *m/e* (rel intensity) M, 378 (25.0); M + 2, 380 (17); M − 189, 189 (100). ($^1H$ NMR analysis of similar irradiations indicated the presence of a trace of **4**-Cl in the product as well, but no **5**-Cl.)

**Direct Irradiation of 3-OCOCHCl$_2$.** Six 4-mm quartz tubes were each charged with a solution of 15 mg (0.047 mmol) of **3**-OCOCHCl$_2$ in 1.5 mL of acetonitrile. Each tube was sealed and the solutions were deoxygenated with dry nitrogen as above. The solutions were irradiated (254 nm) in the "small Rayonet" (15 lamps). One tube each was removed after 0.25, 0.5, 1, 2, and 3 h. The reaction mixtures were then each methanolyzed in 0.1 M NaOCH$_3$–CH$_3$OH. LC analysis indicated the following ratios of the known isomers (**3**-OH:**4**-OH:**5**-OH): 0.25 h, 69:6:25; 0.5 h, 44:11:45; 1 h, 24:10:66; 2 h, 14:8:78; 3 h, 14:5:81. After 3 h, the buildup of unidentified nonpolar (small retention volume) products made analysis impossible.

**Direct Irradiation of 4-OMs.** A solution of 187 mg (0.66 mmol) of **4**-OMs in 4.5 mL of acetonitrile was placed in a quartz tube which

was sealed with a rubber septum. The solution was deoxygenated as above and irradiated (254 nm) in the "small Rayonet" (11 lamps) for 6.33 h. The solution was then diluted with water and extracted with ether. The ether extract was washed with brine and dried ($MgSO_4$). Evaporation of solvent left 159 mg of brown oil whose $^1H$ NMR spectrum was consistent with that anticipated for a 26:16:16:42 ratio of **5**-OMs, **3**-OMs, **4**-OMs, and **3**-$NHCOCH_3$, respectively.

**Direct Irradiation of 3-OMs in Wet Acetonitrile.** A solution of 24 mg (0.084 mmol) of **3**-OMs in 0.3 mL of wet acetonitrile-$d_3$ (5% $H_2O$-$CD_3CN$) was deoxygenated and irradiated as above. The brown solution was then diluted with water and extracted with ether. The ether extract was washed with water and dried ($MgSO_4$). Evaporation of solvent left 40 mg of yellow oil whose $^1H$ NMR spectrum was consistent with a 5:3:2 mixture of **5**-OMs, **3**-$NHCOCH_3$, and **3**-OH, respectively.

**Sensitized Irradiation of 22-OMs.** A solution of 43.5 mg (0.152 mmol) of **22**-OMs in 0.4 mL of acetone-$d_6$ was placed in a 5-mm Pyrex NMR tube and deoxygenated as above. The solution was then irradiated (300 nm) in the "small Rayonet" (ten lamps). $^1H$ NMR analysis indicated the slow formation of **37**. No resonance for H-6 of **38** was detected.

**Sensitized Irradiation of 3-OMs.** A solution of **3**-OMs (63 mg, 0.22 mmol) in 0.4 mL of acetone-$d_6$ (containing a trace of water was sealed and deoxygenated as above. Irradiation (300 nm) in the "small Rayonet" followed by $^1H$ NMR analysis indicated the formation of both **34**-OMs and **3**-OH. Prolonged irradiation (224 h) followed by an aqueous workup (as above) and $^1H$ NMR analysis indicated ca. 5:3:2 of **3**-OMs, **34**-OMs, and **3**-OH, respectively. No **35**-OMs could be observed.

**Sensitized Irradiation of 4-OMs.** A solution of **4**-OMs (46 mg, 0.16 mmol) in 0.5 mL of acetone-$d_6$ was placed in a 5-mm Pyrex NMR tube, sealed, and deoxygenated as above. The solution was irradiated (300 nm) in the "small Rayonet" (ten lamps) for ca. 8 days. $^1H$ NMR analysis indicated a 18:5 ratio of **35**-OMs to **4**-OMs, respectively. No **3**-OMs or **34**-OMs was observed.

**Quantum Yield Measurements for 3-OMs and 4-OMs.** The quantum yield of formation for **3**-$NHCOCH_3$ was obtained by LC using **3**-$NHCOCH_3$ as an external standard. That is, the area response (254 nm) of **3**-$NHCOCH_3$ was obtained by measuring the area response of known concentrations of **3**-$NHCOCH_3$. Other product quantum yields were then obtained by measuring the extinction coefficients of the individual components and relating them to the extinction coefficient of **3**-$NHCOCH_3$ (Owing to the high degree of error associated with this method, only the sum of product quantum yields is reported.) A LC step gradient was used to ensure that the mobile phase used in the chromatographic separation was identical with that used in the measurement of extinction coefficients. The following extinction coefficients ($M^{-1}$ $cm^{-1}$) were obtained: **5**-OMs in 40% THF-hexane, 217; **3**-OMs in 10% THF-hexane, 441; **4**-OMs in 10% THF-hexane, 338; **3**-$NHCOCH_3$ in 40% THF-hexane, 176.

Solutions of **3**-OMs (32.0 mg) and **4**-OMs (32.2 mg) in 3.0 mL each of dry acetonitrile were placed in identical Vycor tubes. The solutions were subjected to five freeze-pump-thaw cycles and sealed at less than $1 \times 10^{-5}$ Torr. The samples were then irradiated (254 nm) in the "large Rayonet". Earlier experiments using cyclopentanone actinometry[37] indicated a light flux of $4.0 \times 10^{-6}$ einsteins lamp-$h^{-1}$ $tube^{-1}$. LC analysis indicated the following sums of product ratios: from **3**-OMs (sum of quantum yields of formation for **5**-OMs and **3**-$NHCOCH_3$), approximately 0.4; from **4**-OMs (sum of quantum yields of formation for **3**-OMs, **5**-OMs, and **3**-$NHCOCH_3$), approximately 0.5.

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