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$$CH_2{=}CHCH_2Ph \rightarrow CH_2{=}CH\cdot + \cdot CH_2Ph \quad (1)$$

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(27) D. R. Morton and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 3947 (1973), and references cited therein.
(28) (a) T. R. Fields and P. J. Kropp, *J. Am. Chem. Soc.*, **96**, 7559 (1974); (b) footnote 6 in ref 28a.
(29) As this paper was being revised, a communication [S. S. Hixson, *J. Am. Chem. Soc.*, **97**, 1981 (1975)] appeared in which the direct irradiation of 2-*tert*-butyl-1,1-diphenylethene, resulting in 2-benzhydryl-1,1-dimethylcyclopropane, was described. Labeling evidence suggested the intermediacy of the carbene resulting from the 1,2 migration of the ethylenic hydrogen atom. Although this case and those of Kropp and of ours have similar formal interpretations, i.e., carbene intermediates, experimental conditions are different in all three cases, so the remarks we have made regarding the relationship of our results to those of Kropp apply to those of Hixson as well.
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(31) Prepared by oxidation of 2-phenylcyclohexanol with potassium dichromate in sulfuric acid or chromic anhydride–pyridine in methylene chloride [R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970)]. The product was identical with that reported by C. C. Price and J. V. Karabinos, *J. Am. Chem. Soc.*, **62**, 1159 (1940).
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Stereoelectronic Control in the Photorearrangement of α-Chloro Ketones. Mechanistic Studies in Photochemistry. XIII[1,2]

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Abstract: The photorearrangement of *anti*- and *syn*-2-chlorobenzobicyclo[2.2.2]octadien-3-one (**1** and **2**) in methanol gave naphthalene, methyl 1-naphthylacetate (**6**) and 7-carbomethoxy-2,3-benzonorcaradiene (**5**). The photolysis of *anti*-2-chlorobicyclo[2.2.2]octen-3-one (**3**) gave the 7-carbomethoxynorcarene (**7**) in 55% yield. The corresponding *syn*-chloro ketone (**4**) did not rearrange to the norcarene product illustrating the stereospecificity of the rearrangement. The reactions were not quenched with piperylene nor sensitized with acetophenone or acetone establishing them as singlet rearrangements. Quantum yields for disappearance of ketone were measured: $\Phi_1 = 0.35$; $\Phi_2 = 0.33$; $\Phi_3 = 0.22$; $\Phi_4 = 0.44$. Finally, flash photolysis in the presence of iodide did not yield I_2^- transients, indicating an absence of free chlorine atoms in this reaction.

Our studies on the photochemistry of β,γ-unsaturated ketones[1,4-6] have been extended to investigate the effects of substituents on the course of the reaction. Direct comparisons of the relative photoreactivity of two competing reaction types has been the subject of numerous investigations in photochemistry (e.g., type I vs. type II reactivity in ketones,[7] etc.). The studies on the 1,3-acyl migration and oxa-di-π-methane rearrangement[1,8] have produced a very detailed understanding of β,γ-unsaturated ketone photochemistry. Likewise, α-halo ketone photochemistry has also been extensively studied and appears to be well understood.[9]

Our objective has been the study of interacting substituents in photochemical reactions, and the competition of α-chloro ketone and β,γ-unsaturated ketone photochemistry provides such a possibility. Also, a recent report of the photorearrangement of *exo*-2-chloronorbornenone (**9**)[10] suggested that all three substituents are involved. Our study deals with the β,γ-unsaturated α-chloro ketones **1–4** which are related to the corresponding unsubstituted β,γ-unsaturated ketones reported earlier.[4-6]

Results

The synthesis of chloro ketones **1–4** was accomplished by the addition of nitrosyl chloride to the corresponding olefin and acid hydrolysis of the resulting dimeric addition product as shown in Scheme I. In the benzobicyclic series, a single chloro ketone isomer was formed in 53% yield from the olefin. This could be equilibrated to a 1:2 epimeric mixture by a 10-min treatment of the chloro ketone with dimethylamine.

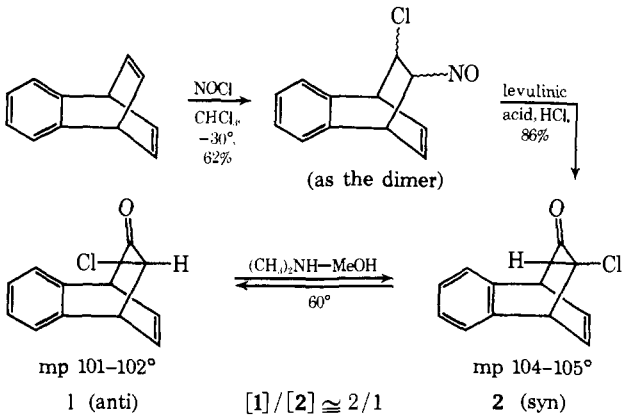
The assignment of the major isomer as *anti*-2-chlorobenzobicyclo[2.2.2]octadien-3-one (**1**) was made from the NMR chemical shifts of the C-2 protons for **1** [δ 4.14 (d)] and **2** [δ 3.87 (d)]. The greater shielding of the C-2 proton for **2** is in accord with the assignment of the proton above the shielding cone of the aromatic ring in other systems.[11]

The 2-chlorobicyclo[2.2.2]octen-3-ones (**3** and **4**) were synthesized by the same sequence. The hydrolysis of the nitroso chloride dimers gave a mixture of *syn*- and *anti*-2-chlorobicyclo[2.2.2]octen-3-ones which could be separated by silica gel chromatography.

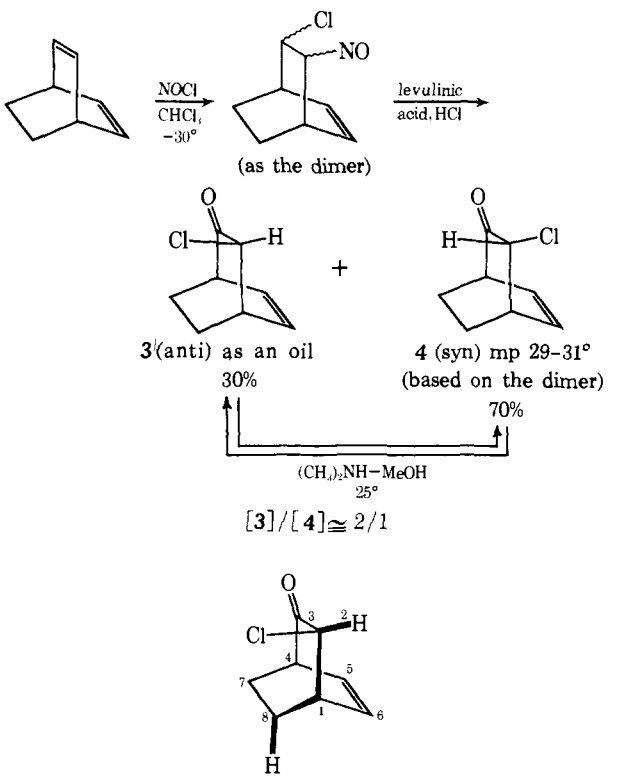
The assignment of the *syn*-2-chlorobicyclo[2.2.2]octen-3-one (**4**) to the solid product (mp 29–31°) was based on the comparison of its NMR spectrum with that of the epimeric product. Chloro ketone **4** displayed the C-2 proton doublet at δ 3.87 (J = 2.6 Hz) whereas the C-2 proton of chloro ketone **3**, having almost the identical chemical shift, appeared as a doublet of doublets at δ 3.92 (J = 1.4 and 3.5 Hz) due to the additional long range coupling of the C-8 anti proton. The W arrangement of the C-2 and C-8 protons gives rise to the 3.5 Hz coupling as shown by double irradiation experiments. When the bridgehead proton was irradiated at δ 3.08 ppm, the doublet of doublets collapsed to a doublet with a coupling constant of 3.5 Hz ($J_{H\text{-}2,anti\text{-}H\text{-}8}$).

Scheme I. Synthetic Routes to the Chloro Ketones 1–4

Benzobicyclo[2.2.2]octanone Series



Bicyclo[2.2.2]octanone Series

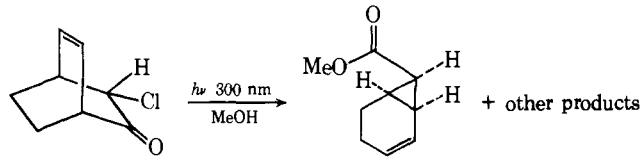


Likewise, irradiation at δ 3.88 ppm (H-2) led to a change in the complex multiplet centered at δ 1.8 ppm (anti-H-8) and no change in the olefinic multiplet or in the remaining aliphatic multiplet between δ 1.5 and 2.5 ppm.

Photochemical studies of each of the chloro ketones were carried out in methanol. Chloro ketones **1** and **2** gave a product mixture of naphthalene and benzonorcaradiene **5**[12] and methyl 1-naphthylacetate (**6**) as the only major products (Scheme II). Interestingly, the relative yields of the two rearrangement products differed significantly. In the case of the *syn*-chloro ketone **2**, the norcaradiene **5** was the major product while, for the *anti*-chloro ketone, both **5** and **6** were formed at approximately the same rate.

The results from the irradiation of *syn*- and *anti*-2-chlorobicyclo[2.2.2]octen-3-one (**3** and **4**) are even more striking. As shown in Scheme III, only the *syn*-chloro ketone **3**

Scheme III. Photorearrangement of *anti*-2-Chlorobicyclo[2.2.2]octen-3-one (**3**)

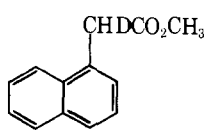


gave the norcarene **7**.[13] The *anti*-chloro ketone **4** gave 11 products, none major, and, although attempts were made to identify these, none were completely characterized; however, the norcarene **7** and its epimer **8** (synthesized by the thermal isomerization of **7**)[13] were shown *not* to be among the products. Likewise, for both **3** and **4**, cyclohexadiene was shown to be absent.

In an effort to provide a more quantitative measure of the reactivity differences, quantum yields were measured for the four ketones. As shown in Tables I and II, significant differences in the efficiency of reaction for each chloro ketone are readily apparent.

Sensitization experiments with acetophenone and quenching experiments employing piperylene for **1** and **2** were performed, and results are also reported in Table I. For both experiments, no new products were observed. The rearrangement to the norcardiene **5** could not be sensitized or quenched, indicating that its formation occurs via the singlet excited state.

In order to test for one of the mechanistic routes possible (see Discussion), experiments using methanol-*O*-*d* were carried out for **1** and **2**. Isolated norcaradiene ester **5** showed no incorporation of deuterium, while the naphthyl acetate **6′** showed incorporation of a single deuterium in the



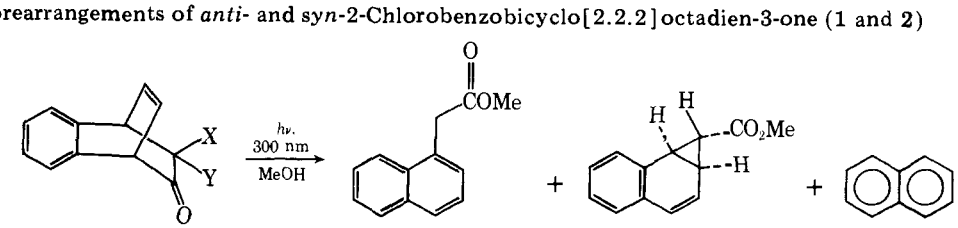
6′

methylene group. Comparison of the relative quantum yields for reaction in methanol and methanol-*O*-*d* show little effect due to the deuterated solvent (see Experimental Section).

Discussion

Generally, irradiation of α-halo ketones leads to photolysis of the carbon–halogen bond.[14,15] Two mechanistic rationales have been suggested: (1) homolytic cleavage produc-

Scheme II. Photorearrangements of *anti*- and *syn*-2-Chlorobenzobicyclo[2.2.2]octadien-3-one (1 and 2)



1 (anti), X = H; Y = Cl	**6** (3%)	**5** (60%)	(13%)
2 (syn), X = Cl; Y = H	(26%)	(34%)	(10%)

Table I. Quantum Yields for Direct, Quenched, and Sensitized Irradiations of 2-Chlorobenzobicyclo[2.2.2]octa-5,7-dien-3-ones (1 and 2)

Chloro-ketone	Conditions[a]	Φ_{dis}	Φ_{app} 5	Φ_{app} 6	Φ_{app} Naphthalene
1	Direct (300 nm)	0.35	0.21	0.01	0.04
	2.4 *M* piperylene (300 nm)	0.35	0.2	0.01	0.04
	0.5 *M* acetophenone (254 nm)	0.03	<0.01	<0.01	<0.01
2	Direct (300 nm)	0.32	0.11	0.09	0.04
	2.4 *M* piperylene (300 nm)	0.35	0.12	0.09	0.04
	Acetophenone (254 nm)	0.09	<0.01	<0.01	<0.01

[a] A methanol–ether solution of the ketone (0.25 mmol in 15 ml) was monitored, and the results were extrapolated to 0% conversion. Light output was 0.46 mEinstein/hr at 254 nm and 0.23 at 300 nm.

Table II. Quantum Yields for the Direct Irradiations of 2-Chlorobicyclo[2.2.2]octa-5-en-3-ones

Chloro-ketone	Conditions[a]	Φ_{dis}	Φ_{app} of 7
3	Methanol (300 nm)	0.22	0.12
4	Methanol (300 nm)	0.44	<0.01

[a] A solution of 0.33 mmol of the ketone in 10 ml of methanol was monitored, and the results were extrapolated to 0% conversion. Light output was 0.46 mEinstein/hr at 300 nm.

ing a geminate radical pair[13,15] and (2) heterolytic cleavage giving the halide ion and an electron deficient carbon.[9,16] Generally, other possible competing pathways are not followed.

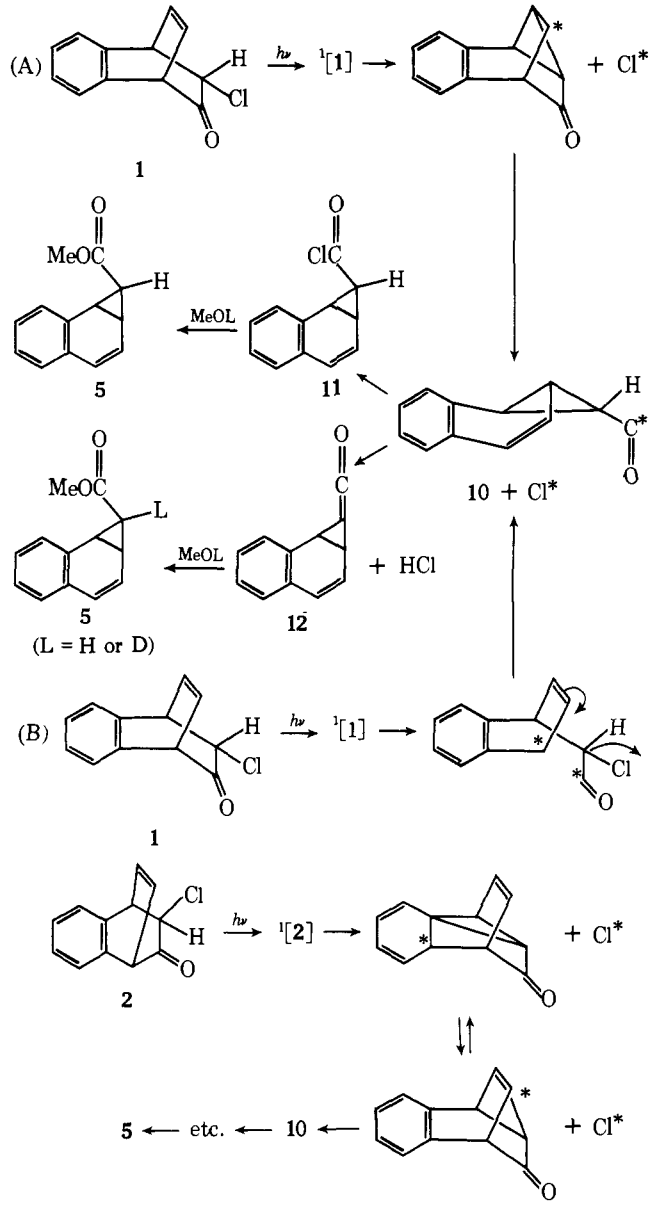
For ketones **1–3**, the presence of the α-chloro group suppresses the photochemical 1,3-acyl migration. It appears, from the nature of the products, that the reaction can also be viewed as either an acyl cleavage (type I) reaction or expulsion of a halide (either as a radical or anion). Although the differences between these two routes (A and B) can be viewed as essentially one of timing, each is given in Scheme IV. For ketone **2**, the aromatic ring may participate initially, then give way to the double bond, and from here follow the same route as **1**.

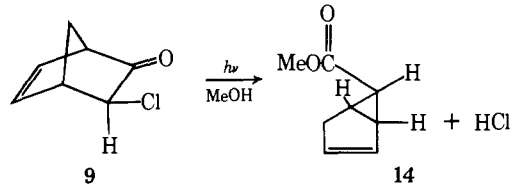
Two distinct possibilities are suggested for the conversion of **10** to product. Either the ketene **12** or the acid chloride (or acylium ion) **11** could be involved. To test for this, the irradiations were also performed in methanol-*O-d* where incorporation of deuterium would be expected from **12** while not expected from **11**. The total absence of deuterium in **5** thus rules out a ketene intermediate.

The possible stereospecificity for the rearrangement of *anti*- and *syn*-2-chloro ketones **1** and **2** was suggested by the product ratios obtained. Because the norcaradiene product isolated was the anti isomer from either chloro ketone[12] (the endo isomer is thermally unstable and isomerizes to the exo isomer[12]), no information can be deduced from the product structure; however, the fact that **2** gave almost twice as much of the ester **5** as did **1** implies stereoselectivity in the rearrangement.

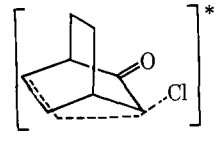
A better test of stereospecificity comes from the study of the two bicyclo[2.2.2]octenone derivatives **3** and **4** because, first, the saturated bridge does not participate in the rearrangement and, second, the product **7** is stable under these conditions [rearrangement to **8** occurs only at much higher temperatures (300°)[13]]. The *anti*-chloro ketone **3** gave only the *endo*-norcarene ester **7**, while the *syn*-chloro ketone **4** did not yield either **7** or **8**. These product studies clearly indicate the stereospecificity of this rearrangement as suggested earlier by Kaplan and Hartwig[10] for the photorearrangement of *exo*-2-chlorobicyclo[2.2.1]hepten-3-one (**9**)[17] which also gave only the endo isomer **14**.

Scheme IV. Possible Mechanisms for the Photorearrangement of Chloro Ketones 1 and 2





These results can be incorporated into a general picture for this rearrangement which involves backside bonding with the double bond as the halogen is expelled (as shown below for **3**).



3

The question remains, however, as to whether the β,γ-unsaturated ketone chromophore is actually expelling the

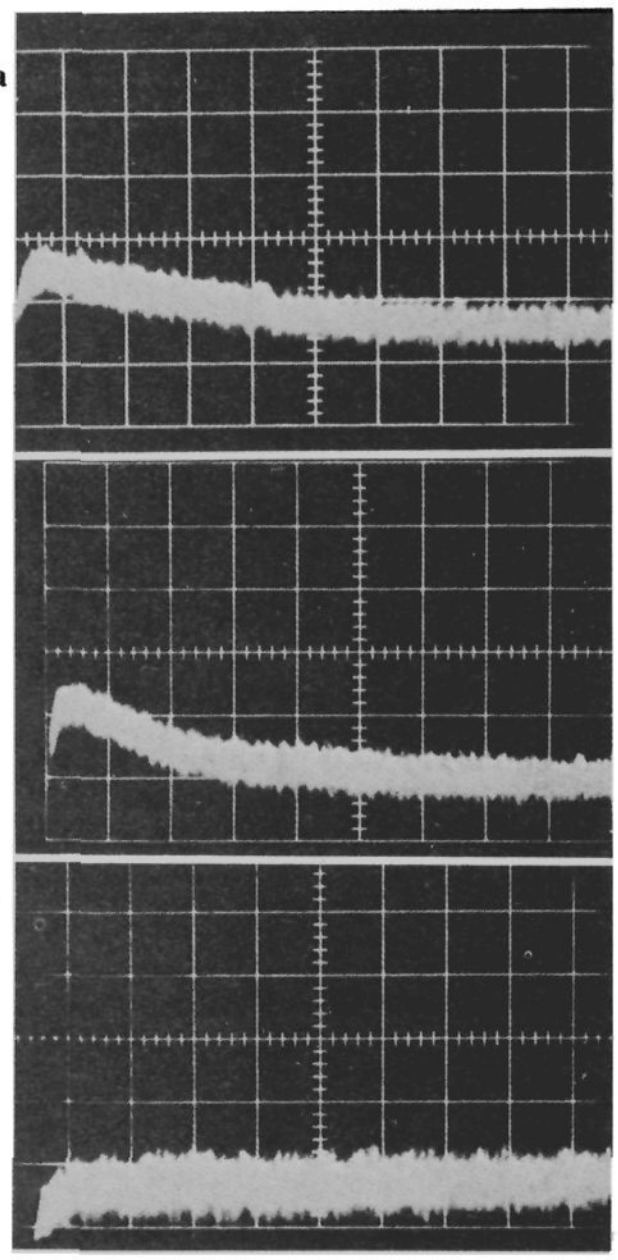


Figure 1. (a) Transient decay at 390 nm for 5.4×10^{-4} *M* KI in 90% H_2O–10% *tert*-butyl alcohol flashed at >250 nm. (b) Transient decay at 385 nm for 5.0×10^{-4} *M* phenacyl chloride and 6.0×10^{-3} *M* KI in 90% H_2O–10% *tert*-butyl alcohol at >300 nm. (c) Trace at 385 nm for 5×10^{-4} *M* **1** and 6.0×10^{-3} *M* KI in 90% H_2O–10% *tert*-butyl alcohol flashed at >300 nm. All scans are at 500 μsec/cm horizontal sweep and 0.02 V/cm vertical sweep. All studies were at ambient temperature in degassed solutions in a 20 × 2 cm cell. The duration of the photoflash was a few μsec.

chloride in the photochemical analog of a nucleophilic (or radical) substitution or whether the normal chloro ketone photofragmentation is internally trapped by the π system. Our quantitative studies (Tables I and II) indicate that the efficiencies of reaction for the four ketones are all about the same and do not show a particular pattern. This can be taken as evidence that the assistance by the double bond is not increasing the reactivity of the ketone, but rather that the double bond is playing a much more passive role in the rearrangement. Further evidence of the lack of double-bond participation can be seen in the complete supression of the 1,3-acyl migration.[18] For **3** and **4** and to a lesser extent for **1** and **2**, the acyl migration could have been anticipated as a major contributor to the photochemistry. Yet no products of 1,3-acyl migration were detected from these studies.[19] In fact, the normal photochemistry of β,γ-unsaturated ketones has been completely supressed as evidenced by the total lack of reactivity of the excited triplet states of **1–4** from the sensitization experiments. In the nonhalogenated analogs, the triplets rearrange quite efficiently ($\Phi_T = 0.1$–0.3) to the cyclopropyl ketones via the oxa-di-π-methane pathway.[1,4,6]

Finally, it is of interest to determine the nature of the bond cleavage step. As depicted in Scheme IV, the cleavage reaction could occur by either homolysis, leading to two radicals, or by heterolysis, leading to chloride ion and a cyclopropylcarbinylhomoallyl cation. In an effort to resolve this question, a flash trapping technique was developed using iodide ion [I^-] as the trapping agent.[20] The expulsion of chloride atom from phenacyl chloride[22] is demonstrated by this technique by observing the decay of the resultant I_2^- [23] shown in Figure 1. Under identical conditions, chloroketone **1** gave no observable transient (Figure 1c).

The absence of the I_2^- spectrum clearly demonstrates that chlorine atoms (or any other species capable of oxidizing I^-) are not available to iodide ion. The question of heterolysis vs. homolysis is narrowed, therefore, to the possibility of formation of either a tight radical pair which disproportionates before solvent separation or initial heterolysis directly to the ionic intermediates. We currently favor the tight radical pair mechanism based on our inability to trap any carbonium ion intermediates with external nucleophiles (e.g., methanol) and the lack of solvent effects on the reaction.[24]

Recent studies on a number of related photofragmentation[25] and photoextrusion[26] reactions support and often are explained best by the tight radical pair–ion pair hypothesis of Walling.[27]

Experimental Section[28]

Benzobarrelene. Benzobarrelene was synthesized in 15% yield by the method of Stiles, Burckhardt, and Freund.[29]

Addition of Nitrosyl Chloride to Benzobarrelene. Crude benzobarrelene (1.4 g, ca. 8.1 mmol) was dissolved in 50 ml of chloroform, and the resultant solution was cooled to −30° with Dry Ice–acetone. Gaseous nitrosyl chloride[30] (555 mg 8.5 mmol) was introduced over a period of 10 min above the surface of the stirred solution. Stirring was continued for an additional 20 min and the yellow-green reaction mixture was warmed to room temperature. Within 30 min, white, solid nitroso chloride dimer precipitated. This was collected, washed with chloroform, and dried in vacuo to give 820 mg of dimer, mp 182–184°. The chloroform solution and washings were combined and concentrated to 3 ml. After standing overnight at room temperature, the precipitated white solid was collected, yielding an additional 280 mg of dimer, mp 182–186°. The overall yield was 1.10 g (62%). Recrystallization from chloroform–hexane gave an analytically pure sample, mp 184–186°. The mass spectrum of the solid showed molecular ion peaks at *m/e* 219 and 221 with the relative intensity of 3:1 (monomer; one chlorine).

Anal. Calcd for $C_{12}H_{10}ClNO$: C, 65.60; H, 4.58; N, 6.38. Found: C, 65.75; H, 4.45; N, 6.53.

Levulinic Acid Hydrolysis of the Benzobarrelene Nitrosochloride Dimer. The mixture of 1.2 g (5.5 mmol) of benzobarrelene nitrosochloride dimer, 40 g of freshly distilled levulinic acid, and 3 ml of 2 *N* HCl was stirred at 75° for 20 hr. The clear solution was cooled to room temperature and diluted with 200 ml of water. The resulting mixture was extracted (4×) with 150-ml portions of pentane. The pentane extract was concentrated to 150 ml and cooled, yielding crystalline *syn*-2-chlorobenzobicyclo[2.2.2]octa-5,7-dien-3-one (**2**). Recrystallization from hexane afforded 0.965 g (80%) of analytically pure **2**, mp 104–105°.

The infrared spectrum ($CHCl_3$) showed bands at 5.75 (C=O), 7.49 8.87, 9.35, two weak bands at 9.77 and 9.90, and 10.44 μ; NMR ($CDCl_3$) δ 7.4–7.1 (m, 4 H, aromatic), 6.85–6.45 (m, 2 H, vinyl), 4.55–4.25 (m, 2 H, bridgeheads), 3.87 (d, 1 H, α to Cl); the mass spectrum showed a molecular ion of *m/e* 204 and 206 (relative intensity 3:1) and *m/e* 128 (naphthalene) as the base peak; uv (cyclohexane) λ_{max} 268.5 nm (ε 909), 274.5 (871), 309.5 (256), 319.5 (249); uv (methanol), 274.0 (1180) and 310 (300).

Anal. Calcd for $C_{12}H_9ClO$: C, 70.41; H, 4.43. Found: C, 70.25; H, 4.26.

The syn assignment was based on the upfield shift of the methine proton (α to chlorine) relative to the stereoisomer produced by equilibration with dimethylamine (see Results).

***anti*-2-Chlorobenzobicyclo[2.2.2]octa-5,7-dien-3-one (1).** A solution of 0.530 g of *syn*-2-chlorobenzobicyclo[2.2.2]octa-5,7-dien-3-one (**2**), 25 ml of methanol, and 25 ml of 25% aqueous dimethylamine was heated to 60° for 10 min. The yellowish solution was evaporated to dryness under reduced pressure, and 20 ml of ethyl

ether was added to the crystalline residue. Filtration of the resulting solution from insoluble material (about 20 mg) followed by evaporation of the solvent and recrystallization from hexane afforded 0.314 g (59%) of analytically pure anti isomer (**1**), mp 101–102°. Since the equilibrium mixtuc contained 67% of the anti isomer (by NMR), the yield was 88% based on consumed syn isomer.

The infrared spectrum ($CHCl_3$) showed bands at 5.74 (C=O), 7.52, 8.87, 9.33, 10.12, 10.30, and 10.47 μ; NMR ($CDCl_3$) δ 7.45–7.15 (m, 4 H, aromatic), 6.8–6.6 (m, 2 H, vinyl), 4.55–4.18 (m, 2 H, bridgeheads), 4.14 (d, 1 H, α to Cl); uv (cyclohexane) λ_{max} 267 nm (ϵ 450), 274.5 (373), 307 (325), 317.5 (319); uv (methanol) 268 (623), 274.5 (566), 307.0 (358); the mass spectrum showed molecular ion of *m/e* 204 and 206 (relative intensity 3:1) and *m/e* 128 (naphthalene) as the base peak.

Anal. Calcd for $C_{12}H_9ClO$: C, 70.41; H, 4.43. Found: C, 70.61; H, 4.18.

***trans*-Bicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Acid.** This compound was obtained using a modification of the method of Adler and Stein.[31] A methanol solution of bicyclo[2.2.2]oct-2-ene-5,6-carboxanhydride (1.78 g, 0.01 mol) and sodium methoxide (2.16 g, 0.04 mol) was heated at reflux for 1 hr, the solvent was removed in vacuo, and the residue was added to 30 ml of water and heated at reflux for an additional 20 min. The solution was cooled, acidified with HCl, and the precipitate was collected and dried to give 1.8 g (92%) of the trans diacid, mp 212–212.5° (reported[31] mp 211°).

Bicyclo[2.2.2]octa-2,5-diene. Electrolysis of *cis*-bicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic acid or its anhydride did not give reproducible results, and generally the yields were much lower from that reported.[32] The compound was obtained by electrolysis of *trans*-bicyclo[2.2.2]octa-2-ene-5,6-dicarboxylic acid.

In a typical run, 2 g (10 mmol) of the trans diacid dissolved in 110 ml of a standard pyridine–water–triethylamine solution[33] (90/10/1.25, v/v/v) was electrolyzed between platinum gauze electrodes under a nitrogen atmosphere. The cell was cooled externally to maintain an internal temperature of about 20°. The initial current of 0.9 A was maintained during the electrolysis by increasing voltage from about 30 V at the beginning to about 120 V at the end of the electrolysis. Water (150 ml) was added to the resultant dark solution, and the mixture was extracted with three 120-ml portions of pentane. The pentane solution was washed with dilute hydrochloric acid and with water, dried over sodium sulfate, and fractionally distilled. From a total of 10.3 g of the diacid (five runs), 2.05 g (37%) of bicyclo[2.2.2]octa-2,5-diene was obtained: bp 120–126°; mp 54–56° (lit.[34] mp 57°).

Addition of Nitrosyl Chloride to Bicyclo[2.2.2]octa-2,5-diene. The reaction of bicyclo[2.2.2]octa-2,5-diene (1.8 g, 17 mmol) with nitrosyl chloride (1.11 g, 17 mmol) in the manner described before afforded only a little precipitate. Evaporation of the solvent under reduced pressure gave 2.85 g of a partly crystalline slurry. Ether was added, and the crystalline material was filtered and washed, yield 0.50 g, mp 164–180°. Several crystallizations from chloroform–hexane mixture did not affect the melting point range since the product was a mixture of syn and anti isomers.

Anal. Calcd. for $C_8H_{10}ClNO$: C, 56.00; H, 5.84; N, 8.16. Found: C, 55.89; H, 5.89; N, 8.33.

The mass spectrum of the solid showed peaks of *m/e* 341 and 343 with the relative intensity of 1:0.65 (two chlorine atoms) and fragmentation to monomers (*m/e* 171 and 173 with the relative intensity of 1:0.32—one chlorine atom).

The mother liquor and washings were combined and concentrated in vacuo, yielding green thick oil presumably containing monomeric nitroso chloride adduct.

***syn*-2-Chlorobicyclo[2.2.2]oct-5-en-3-one (4).** Levulinic acid hydrolysis of the previously obtained oil gave chloro ketone (mainly *syn*-chloro ketone **4**) by the following procedure. A solution prepared from 2.3 g of the oil, 60 g of freshly distilled levulinic acid, and 4.5 ml of 2 *N* hydrochloric acid was heated to 60° for 10 hr. After that time, green color disappeared and the solution became yellow. The reaction mixture was cooled to room temperature, diluted with 250 ml of water, and extracted three times with 100-ml portions of ethyl ether. The ether extract was washed successively with cold 5% sodium bicarbonate solution and water, and dried over 4A molecular sieves, and the solvent was removed in vacuo. The residue (1.8 g) was chromatographed on a 1 × 70 cm silica gel column (Davison, grade 950, 60–200 mesh) slurry packed in 3% ether–hexane (20-ml fractions taken): fractions 1–5, 3% ether–hexane, nil; fractions 6–20, 5% ether–hexane, nil; fractions 21–23, 8% ether–hexane, the *anti*-chloro ketone **3** (traces); fractions 24–30, 8% ether–hexane, the *syn*-chloro ketone **4**; fractions 31–40, 10% ether–hexane, the *syn*-chloro ketone **4**. Fractions 24–40 were combined, and the solvent was removed in vacuo, yielding 1.18 g of the product as a colorless oil, which crystallized on cooling, mp 29–31°. Distillation of the product [90° (2 mmHg)] did not change the melting point range.

The infrared spectrum (neat) of *syn*-2-chlorobicyclo[2.2.2]octen-3-one (**4**) showed bands at 3.27, several peaks from 3.37 to 3.44, 3.48, 5.75, 6.21, 6.67, 7.36, 9.13, 9.55, 10.42, 10.89, 11.59, 11.83, 12.50, 12.99, 14.18, and 15.58 μ; NMR (CCl_4) δ 6.60–6.10 (m, 2 H, vinyl), 3.87 (d, 1 H, J = 2.6 Hz, α to Cl), 3.30–3.05 (m, 2 H, bridgeheads), 2.15–1.35 (m, 4 H, methylenes); uv (cyclohexane) λ_{max} 266 nm (ϵ 105, sh), 272 (137) 278 (145), 282 (115), 311 (94); uv (methanol) 278 (142) and 306 (124); the mass spectrum showed molecular ion peaks at *m/e* 156 and 158 (relative intensity of 3:1) and the base peak at *m/e* 80 (cyclohexadiene).

Anal. Calcd for C_8H_9OCl: C, 61.30; H, 5.75. Found: C, 61.39; H, 5.83.

***anti*-2-Chlorobicyclo[2.2.2]oct-5-en-3-one (3).** Levulinic acid hydrolysis of the crystalline nitrosyl chloride adducts gave a mixture of two isomeric chloro ketones. A mixture of 0.433 g (2.54 mmol) of the adducts, 20 g of freshly distilled levulinic acid, and 1.5 ml of 2 *N* hydrochloric acid was stirred at 70° until a clear solution was formed (40 hr). After cooling to room temperature, the solution was diluted with 80 ml of water and extracted with 100-ml portions of pentane (×4). The pentane extracts were dried, and the solvent was removed in vacuo to yield 0.398 g (2.54 mmol, 100%) of two chloro ketones. The NMR spectrum of the mixture showed two pairs of peaks corresponding to ClC-H at δ 3.87 (*syn*-**4**, 70%) and 3.92 (*anti*-**3**, 30%). The same ratio of isomers was obtained from VPC analysis.

In order to obtain anti isomer, the mixture was equilibrated with dimethylamine. A solution prepared from 0.660 g of the chloro ketones, 10 ml of methanol, and 6 ml of 25% dimethylamine was allowed to stand for 1 hr at room temperature; then 20 ml of brine was added, and the resultant mixture was extracted with 25-ml portions of ethyl ether (×4). The ether extracts were washed with diluted hydrochloric acid, water, dried, and evaporated in vacuo to afford 0.659 g of a clear oil. The NMR spectrum and VPC analysis indicated the presence of 64 and 36% of *anti*-**3** and *syn*-**4** isomers, respectively.

The oil was chromatographed on a 1 × 60 cm silica gel column (Davison, 60–200 mesh) slurry packed in ether–benzene–hexane (2:15:83). Fractions of 30 ml were taken: fractions 1–15, ether–benzene–hexane (2:15:83), nil; fractions 16–20, ether–benzene–hexane (4:15:81), the *anti*-chloro ketone **3**; fractions 21–30, ether–benzene–hexane (4:15:81), the *syn*-chloro ketone **4** with a small amount of the anti isomer. Evaporation of solvent from fractions 16–20 afforded 0.413 g (63%) of *anti*-2-chlorobicyclo[2.2.2]octen-3-one (**3**) as a clear oil which crystallized below 0°. The VPC analysis (15% UCON UCW 98, 5 ft, 0.125 in., 170°) showed only one peak.

The infrared spectrum (neat) showed bands at 3.27, several peaks from 3.34 to 3.44, 3.48, 5.73, 6.21, 6.84, 6.92, 7.37, 8.91, 9.26, 9.45, 9.57, 10.30, 10.50, 11.52, 12.00, 12.31, 13.16, 13.93, and 15.87 μ; NMR (CCl_4) δ 6.70–6.15 (m, 2 H, vinyl), 3.92 (two d, 1 H, J_1 = 1.4, J_2 = 3.5 Hz, α to Cl), 3.25–3.00 (m, 2 H, bridgeheads), 2.50–1.20 (m, 4 H, methylenes) (for double irradiation experiment, see text); uv (cyclohexane) λ_{max} 299 nm (ϵ 84, sh), 3.07 (99), 316 (89, sh), 330 (46, sh); uv (methanol) 306 (112); the mass spectrum (88°, 70 eV) showed base peak at *m/e* 80 (cyclohexadiene) and molecular ion peak at *m/e* 156 and 158 with the relative intensity of 3:1.

Anal. Calcd for C_8H_9OCl: C, 61.30; H, 5.75. Found: C, 61.27; H, 5.74.

Photolysis of *syn*-2-Chlorobenzobicyclo[2.2.2]octa-5,7-dien-3-one (2). A. In Methanol. A solution of 0.204 g (1.0 mmol) of the *syn*-chloro ketone **2** dissolved in 15 ml of methanol in a Pyrex tube was degassed for 20 min with purified nitrogen and irradiated with RPR 300-nm lamps in a merry-go-round apparatus for 5 hr. After that time, a VPC analysis showed more than 98% conversion of the starting chloro ketone and appearance of three products. The solvent was removed under reduced pressure and the residue chroma-

tographed on a 1 × 45 cm silica gel column slurry packed in 1.5% ether–hexane (15 ml fractions): fractions 1–10, 1.5% ether–hexane, nil; fractions 11–15, 1.5% ether–hexane, naphthalene; fractions 16–26, 4% ether–hexane, nil; fractions 27–35, 4% ether–hexane, 66 mg (0.33 mmol, 34%) of methyl 1*H*-cyclopropa[α]naphthalene-1a,7b-dihydro-1-carboxylate (**15**); fractions 36–38, 4% ether–hexane, nil; fractions 39–52, 4% ether–hexane, 50 mg (0.24 mmol, 26%) of methyl 1-naphthylacetate (**6**).

B. In Methanol-*O*-*d*. A solution prepared from 0.204 g (1 mmol) of the *syn*-chloro ketone **2**, 13 ml of anhydrous ether, and 2 ml of methanol-*O*-*d* was degassed for 20 min and irradiated as described above for 2 hr (VPC analysis indicated about 50% conversion). Work-up and silica gel chromatography as above gave the following results: fractions 11–15, naphthalene; fractions 27–35, 127 mg of a mixture of the starting chloro ketone and methyl 1*H*-cyclopropa[α]naphthalene-1a,7b-dihydro-1-carboxylate (**5**); fractions 39–52, 30 mg of methyl 1-naphthylacetate-1′-*d* (**6′**). The NMR spectrum (CCl_4) of the mixture indicated no deuterium incorporation in the starting chloroketone nor in **5**.

Isolated methyl 1-naphthylacetate-1′-*d* (**6′**) gave the following spectral results: NMR ($CDCl_3$) δ 8.1–7.2 (m, 7 H, aromatic), 4.1–4.0 (broad s, 1 H, $CHDCO_2Me$), 3.66 (s, 3 H, methyl); mass spec (113°, 70 eV), 57 (10), 71 (8), 115 (13), 116 (18), 127 (3), 128 (7, naphthalene), 139 (4), 140 (8), 141 (17), 142 (100, loss of CO_2 and CH_3), 143 (15), 200 (5), 201 (33, molecular ion), and 202 (3).

Photolysis of *anti*-2-Chlorobenzobicyclo[2.2.2]octa-5,7-dien-3-one (1). A. In Methanol. A degassed solution of 0.102 g (0.5 mmol) of the *anti*-chloro ketone **1** in 15 ml of methanol was irradiated in a Pyrex tube with RPR 300-nm lamps in a merry-go-round apparatus for 3 hr. After that time, no starting material could be detected by VPC analysis. Work-up and chromatography as described previously gave 9 mg (0.07 mmol, 13%) of naphthalene, 59 mg (0.30 mmol, 60%) of methyl 1*H*-cyclopropa[α]naphthalene-1a,7b-dihydro-1-carboxylate (**5**), and 4 mg (0.02 mmol, 3%) of methyl 1-naphthylacetate (**6**).

B. In Methanol-*O*-*d*. Using the standard conditions, a degassed solution prepared from 56 mg (0.275 mmol) of *anti*-chloro ketone **1**, 10 ml of dry ether, and 1 ml of methanol-*d* was irradiated for 1.5 hr (about 60% conversion by VPC). The concentrated reaction mixture was chromatographed on a 1 × 45 cm silica gel column slurry packed in 2% ether–hexane, (15 ml fractions): fractions 1–4, 2% ether–hexane, nil; fractions 5–10, 2% ether–hexane, naphthalene; fractions 11–19, 3% ether–hexane, nil; fractions 20–36, 3% ether–hexane, 21 mg (0.105 mmol) of methyl 1*H*-cyclopropa[α]naphthalene-1a,7b-dihydro-1-carboxylate (**5**); fractions 37–38, 4% ether–hexane, about 2 mg (0.01 mmol) of methyl 1-naphthylacetate-1-*d* (**6′**); fractions 49–55, 4% ether–hexane, nil; fractions 56–63, 20% ether–hexane; 22 mg (0.108 mmol) of the starting chloro ketone.

The NMR spectra gave no deuterium incorporation in the starting chloro ketone nor in methyl 1*H*-cyclopropa[α]naphthalene-1a,7b-dihydro-1-carboxylate (**5**).

Photolysis of *anti*- and *syn*-2-Chlorobenzobicyclo[2.2.2]octa-5,7-dien-3-ones in Pentane and Ether. A degassed solution of 20 mg (0.1 mmol) of the corresponding chloro ketone in 5 ml of dry ether or pentane was irradiated at 300 nm in a merry-go-round apparatus for 1 hr. A VPC analysis showed the presence of naphthalene and the corresponding chloro ketone only. After addition of methanol to the photomixture, the peaks corresponding to methyl 1*H*-cyclopropa[α]naphthalene-1a,7b-dihydro-1-carboxylate and methyl 1-naphthylacetate could be seen. The ratio of the products was identical with that for irradiation experiments in the presence of methanol.

Photolysis of *anti*-2-Chlorobicyclo[2.2.2]oct-5-en-3-one (3). A. In Methanol. 213 mg (1.36 mmol) of *anti*-chloro ketone (**3**) was dissolved in 10 ml of methanol in a Pyrex tube, and the solution was degassed with nitrogen for 20 min. Irradiation was carried out with RPR 300-nm lamps in a merry-go-round apparatus for 6 hr. At the end of irradiation, VPC analysis showed about 90% conversion of the starting chloro ketone and appearance of one major and three minor products. Examination of the photoreaction mixture during photolysis revealed that two of the minor products were unstable and decomposed with time. VPC analysis of the photomixture on a Porapak Q column at 200° indicated the presence of less than 1% of cyclohexadiene.

Table III. Ratio of the Product in MeOH to that in MeOD

Ketone	5	6
2	1.03 ± 0.05	0.99 ± 0.05
1	1.01 ± 0.03	1.02 ± 0.04

Irradiated solution was concentrated to 0.5 ml under reduced pressure and chromatographed on a 1 × 60 cm silica gel column slurry packed in 3% ether–pentane (20 ml fractions taken): fractions 1–10, 3% ether–pentane, nil; fractions 11–16, 5% ether–pentane, nil; fractions 17–25, 5% ether–pentane, 80 mg (0.53 mmol, 39%) of *endo*-7-carbomethoxy-Δ²-norcarene (**7**).[13] The ir (neat) and NMR (CCl_4) spectra of the product were identical with those reported.[13]

Equilibration of *endo*-7-Carbomethoxy-Δ²-norcarene (7). According to the reported procedure,[13] 10 mg of *endo*-7-carbomethoxy-Δ²-norcarene was pyrolyzed at 310° for 5 min in a sealed tube under nitrogen. The exo isomer **8** obtained had an identical ir spectrum with that reported. A VPC coinjection experiment of the product with the photomixture revealed that none of the photoproducts corresponded to *exo*-7-carbomethoxy-Δ²-norcarene (**8**).

B. In Pentane. A degassed solution made from 20 mg of *anti*-chloro ketone and 5 ml of dry pentane was irradiated at the above conditions for 1 hr. VPC analysis indicated peaks corresponding to the starting chloro ketone and to the stable minor product from the previous experiment. After addition of methanol to the irradiated solution, a peak corresponding to *endo*-7-carbomethoxy-Δ²-norcarene could be seen and was the major product obtained. Work-up of the resulting solution afforded an oil which gave the ir spectrum identical with that of original *endo*-7-carbomethoxy-Δ²-norcarene.[13]

Photolysis of *syn*-2-Chlorobicyclo[2.2.2]oct-5-en-3-one (4) in Methanol. A degassed solution of 100 mg (0.64 mmol) of the *syn*-chloro ketone **4** in 10 ml of methanol was irradiated with RPR 300-nm lamps in a merry-go-round apparatus for 1 hr (about 95% conversion). VPC analysis showed formation of at least eight products, none in greater than 10% yield. However, the mixture contained only 1–2% of *endo*-7-carbomethoxy-Δ²-norcarene (by coinjection). None of the exo isomer was observed. A VPC analysis of the photomixture on a Porapak Q column (200°) indicated less than 1% of cyclohexadiene. None of the products were identified.

Isotope Effect Determinations. Isotope effects on the photoreactions of *anti*- and *syn*-chlorobenzobicyclo[2.2.2]octa-5,7-dien-3-ones (**1** and **2**) were studied using the following procedure. The chloro ketone (100 mg, 0.49 mmol) and 11 mg of eicosane were dissolved in 25 ml of ether. This was divided into two 10-ml samples and placed in Pyrex tubes. After addition of 1 ml of methanol to the first and 1 ml of methanol-*O*-*d* to the second sample, they were degassed with purified nitrogen and irradiated together to about 40% conversion with RPR 300-nm lamps in a merry-go-round apparatus. The product yields were determined directly by VPC analysis, using eicosane as the internal standard. The results are summarized in Table III.

Quantum Yield Determinations. Quantum yield determinations were performed in the following general procedures.

Direct Irradiations. A solution of 0.35 mmol of the chloroketone and eicosane (as the internal standard) in 10 ml of solvent (methanol or 6% methanol–ether) in a Pyrex tube was degassed with purified nitrogen and placed in a merry-go-round apparatus. Irradiation was carried out with the RPR 300-nm lamps. Light output was measured using ferrioxalate actinometry according to the method of Hatchard and Parker.[35]

Samples were removed and the contents determined directly by VPC employing a ⅛ in. × 5 ft 15% Ucon UCW98 on Chromosorb W column. The results are given in Table I.

Acetone-Sensitized Irradiations. A solution of 0.08 mmol of the chloro ketone and eicosane (internal standard) was dissolved in 5 ml of acetone in a quartz tube; 1 ml of methanol was added and then degassed with nitrogen for 0.5 hr. Irradiation was carried out with RPR 254-nm lamps in a merry-go-round apparatus for 0.5–1 hr, depending on the compound being studied. The solutions were analyzed directly by VPC. The results are given in Table I.

Acetophenone-Sensitized Irradiations. Acetophenone was purified before use. Samples of 0.25 mmol in 15 ml of methanol with sufficient acetophenone to capture >99% incident light were de-

gassed with nitrogen for 0.5 hr, irradiated with RPR 254-nm lamps, and analyzed directly by VPC using an internal standard. The results are recorded in Table I.

Quenching Experiments. *trans*-Piperylene was purified before use. The chloro ketone (0.3 mmol) was dissolved in 10 ml of ether divided into two 4-ml samples and placed in Pyrex tubes. After addition of 2 ml of methanol and 2 ml of ether to the first and 2 ml of methanol and 2 ml of *trans*-piperylene to the second sample, these were degassed with nitrogen and irradiated together to about 40% conversion with RPR 300-nm lamps in a merry-go-round apparatus. The irradiated samples were analyzed directly by VPC using an internal standard. The results are given in Table I.

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A New Stereocontrolled Approach to Spirosesquiterpenes. Synthesis of Acorenone B

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Abstract: The total synthesis of acorenone B illustrates a new approach to secoalkylation and 1,2-alkylative carbonyl transposition. Spiroannelation of 2-isopropyl-5-methylcyclopentanone with cyclopropyldiphenylsulfonium fluoroborate, followed by rearrangement of the oxaspiropentane, gives stereohomogeneous (*Z,Z*)-5-isopropyl-8-methylspiro[3.4]octan-1-one. Formylation followed by acidic treatment effects cyclobutyl ring cleavage to an enol lactone which constitutes a net stereocontrolled geminal alkylation with introduction of a one-carbon and a three-carbon chain differentially functionalized. Standard methods converted the enol lactone to 1-isopropyl-4-methylspiro[4.5]dec-6-en-8-one. Sulfenylation α to the ketone, addition of methyllithium to the carbonyl group, dehydration to the enol thioether, and hydrolysis to the enone complete the synthesis.

The development of synthetic approaches for the generation of a quaternary carbon atom, especially a spiro center, in a stereochemically defined fashion continues to be a major challenge. Among spiro compounds, the spiro[4.5]decane system has attracted the most attention because sesquiterpenes of this ring type are important as biosynthetic intermediates in terpene biogenesis, constituents of essential oils, antifungal agents, and stress metabolites.[1,2] The acoranes form one subset of this class of spirosesquiterpenes for which completely stereocontrolled syntheses are lacking.[3,4] Our recent developments in spiroannelations offer a potential solution to this stereochemical question.[5] In this paper, we report the first stereocontrolled approach to an acorane, acorenone B (**1**).[4,6] The scheme illustrates a new approach to secoalkylation[5] and 1,2-alkylative carbonyl transposition[7] under development in our laboratories.