# Photochemical Transformations. 22. Photo-Wagner–Meerwein Rearrangements and Photoreactions of Some Halogen Derivatives in Dibenzobicyclononatriene Systems[1]

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**Abstract:** Direct irradiations of 3,4-dichloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**1**) and *endo*-4,6-dichloro-2,3:-8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**2**) were studied in acetonitrile, tetrahydrofuran, and cyclohexane. Quantum efficiencies decreased as solvent polarity was lowered and product distributions were found to vary with solvent polarity. The allylic bromide **5** reacted photochemically in a manner similar to the allylic chloride **1**. A photochemical Ritter reaction producing the benzylic amides **10** and **11** occurred in water/acetonitrile solvents. Mechanisms involving radical and ionic intermediates are presented and discussed. Syntheses and reactions of related dibenzobicyclononatriene compounds are described.

Some years ago, it was reported from this laboratory[2] that irradiation of 3,4-dichloro-6,7:8,9-dibenzobicyclo[3.2.2]-nona-2,6,8-triene (**1**) in a variety of solvents led to the Wagner–Meerwein rearrangement products *endo*- and *exo*-4,6-dichloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**2** and **3**) as well as to minor amounts of 1,9-dichloro-3,4:6,7-dibenzotricyclo[3.3.1.0²,⁸]nona-3,6-diene (**4**). It was proposed
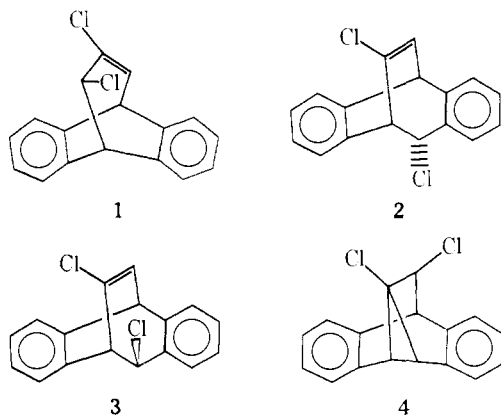


that ion pairs were produced photochemically from **1**, which combined (after cationic rearrangement) to give the thermodynamically less stable[3] isomers **2** and **3**. Since that time, a number of papers have appeared,[4] in which molecular rearrangements consistent with the intervention of carbocationic intermediates have been noted. We have investigated the system described earlier in somewhat more detail and wish now to report that extension as well as related work.

At the time of the preliminary report,[2] it was noted that irradiation of **1** in acetone, benzene, or benzonitrile led to substantial rearrangement to **2**, **3**, and **4**, while that in cyclohexane did not. From this it was concluded that the triplet state of **1** was involved in the observed photorearrangements. While it is true that the triplet state of **1** is photoreactive,[5] our present work shows that the earlier results are more likely attributable to solvent effects upon the ratio of heterolytic to homolytic processes, and that direct light absorption by **1** leads to the photoisomerization to **2** and to **3**.

When **1** was irradiated at 254 nm in acetonitrile, it was converted to a 1.8:1 mixture of **2** and **3**, with quantum yields of 0.17 and 0.09, respectively, and in a total chemical yield of **2** plus **3** of 50–55%. The quantum efficiency for loss of **1** was 0.50. No **4** was observed, and the remainder of **1** was converted to polar materials. As the irradiation continued, the amounts of **2** and **3** slowly declined, the maximum amounts of **2** and **3** being produced when about ⅔ of the **1** had been consumed. In

this experiment the ratio of **2** to **3** declined toward 1:1. In an independent experiment, an approximately equimolar solution of **2** and **3** was subjected to irradiation. No **1** was produced, but **2** and **3** were lost at approximately equal rates. When **2** was irradiated in acetonitrile, the quantum efficiency for its loss was about 0.25. Of this about one-fourth went to **3**; no **1** and little, if any, **4** were produced.

The efficiency for production of **2** and **3** from **1** was found to be solvent dependent. With tetrahydrofuran, the quantum yields for **2** and **3** production were 0.03 and 0.02, respectively, and, in cyclohexane, they were approximately 0.02 and 0.005, with loss of **1** quantum efficiencies somewhat greater than 0.1 in the two solvents. Similarly, the quantum efficiency of the **2 → 3** transformation was reduced to 0.001 in cyclohexane, although the loss had an efficiency of 0.09. With cyclohexane, substantial amounts of chlorohydrocarbons were produced, and their nature will be reported later.

When the allylic bromide **5** corresponding to **1** was irradiated in acetonitrile at 254 nm, **6** and **7** were produced in 41 and
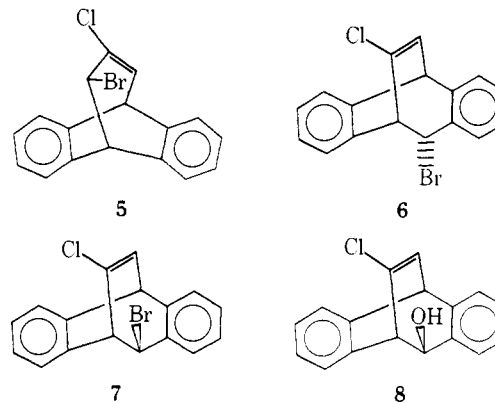


24% yield, respectively (ratio 1.7:1). Just as with the chloride, the remainder was a material which was absorbed strongly on silica gel. No reaction occurred in the dark in refluxing acetonitrile with either **1** or **5**.

The relative efficiencies of phototransformation among **1**, **2**, and **3** show that **1** is transformed directly to both **2** and **3**, rather than via the process **1 → 3 → 2** or **1 → 2 → 3**. The formation of both endo and exo isomers (with migration of chlorine to the more remote endo position favored) would appear to rule out any concerted rearrangement process to account for the reaction. We therefore assume, as did the earlier authors,[2] that the reaction path involves the intervention of intermediates in which the carbon–chlorine bond suffers cleavage, and rearrangement occurs, followed by recombination. The evidence which we have accumulated, and which is re-

ported now, indicates that the rearrangement of **1** to **2** and **3** in polar solvents involves ionic intermediates, as proposed earlier,[2] and that these reactions become less favored in nonpolar solvents. Preliminary results suggest that there is a competing homolytic cleavage into free radicals which predominates in nonpolar solvents. A portion of this evidence is indicated above, where the quantum yields for the formation of **2** and **3** from **1** fall off in the order acetonitrile > tetrahydrofuran > cyclohexane.

We were concerned by the relatively poor chemical yield of **2** and **3** in the photoreaction in acetonitrile, and speculated that it might be due to solvent capture of the cation to give an *N*-alkylnitrilium salt which would give the polar materials formed. Ratcliff and Kochi[6] have reported that the irradiation of dibenzyldimethylammonium chloride in acetonitrile does lead to Ritter reaction products via an *N*-benzylnitrilium salt, and we therefore decided to irradiate **1** in acetonitrile containing 5% water. Under these conditions, almost all of the **1** consumed could be accounted for, with about half of the **1** giving **2** and **3** (in the usual ratio) and about half being diverted to **8**[7] and **9**, with perhaps a trace of **10**. Similar results were
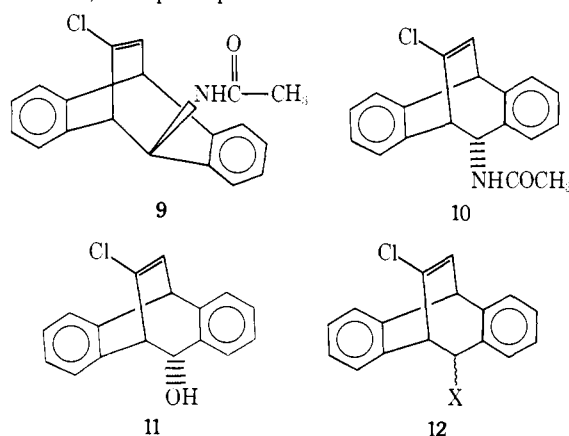


observed with the bromide **5**, which gave **6, 7, 8**, and **9**, and with the endo benzyl chloride **2**, which gave **3, 8**, and **9**. These new products are clearly those of heterolytic cleavage of the carbon–halogen bond, and offer support to the idea that ionic intermediates are involved in the **1, 2**, and **3** interconversions. Endo amide **10** was formed in amounts barely detectable by ^{1}H NMR analysis, and endo alcohol **11** was not detectable.

The exo amide **9** was prepared by a ground-state sulfuric acid catalyzed Ritter reaction in acetonitrile from the alcohol **8**. The crude reaction mixture also contained the endo amide **10** with a ratio of **9:10** of about 10:1, and we have evidence that this may be due to exo-endo interconversion. It would seem that the ion manifold produced by the ground-state reaction is very similar to, if not identical with, that of the photosolvolysis. A 1:1 mixture of the exo (**9**) and endo (**10**) amides was produced by acetylation of the mixture of amines obtained by lithium aluminum hydride reduction of the oxime of the ketone produced by oxidation of **8**, and **10** was isolated from that mixture.

In their interesting work on photosolvolysis of saturated alkyl iodides, Kropp and his co-workers[4b,c] have proposed that ionic intermediates intervene, but that they are not produced directly from the photoexcited state. They propose rather that the photoexcited state decays by homolysis to a radical pair, which may undergo radical reactions or may suffer intracomplex electron transfer to give an ion pair, which would then undergo carbenium-ion reactions. This is clearly an alternative to the idea that the homolyses and heterolyses are independent processes,[6,8] and, of course, different processes may obtain in different situations. However, McKenna and his co-workers[9a,b] have extended the Kropp hypothesis to benzyltrimethylammonium ion, benzyl chloride, and benzyl acetate, although

without evidence to distinguish seriatim from simultaneous processes, and it has been utilized by Hyömäki and Koskikallio[9c] for benzyl chloride solvolysis, again also without evidence. Unfortunately, solvent effects do not distinguish among the two processes; obviously change to polar solvents should favor electron transfer just as it favors heterolysis, and the nonpolar solvents we have used (tetrahydrofuran and cyclohexane) are good hydrogen donors as well, so they could react with chlorine atoms of the radical pairs to divert the intermediate from ion-pair formation. If the lifetime of the radical pair prior to electron transfer is very short, so that capture by radical trapping agents cannot occur, tests of this kind are of no use. We have added piperylene to the acetonitrile–**1** system and find that the quantum yields of **2** and **3** are not affected by 0.25 M diene, that is, either photochemical nor chemical quenching is observed. Such an experiment suggests that free radicals which recombine and then suffer electron transfer also do not play a significant part in these photorearrangements. Clearly, however, the amount of energy in the system is sufficient for either initial homolysis or heterolysis.

Some time ago, Walling and his co-workers[10] reported the results of their studies of the thermolysis of acyl peroxides, which leads, just as does the photochemistry we are discussing, to products of both radical and ionic processes. Their data prompted them to propose that their first intermediate was a species which they termed an "intimate ion-radical pair". They described this as an "intermediate in which electronic interaction between the fragments is still extensive and ionic and paired diradical formulations merely represent contributing structures of a resonance hybrid". They suggest that as the fragments become separated by solvent, or as conformational or rotational processes in solution occur, "ionic and radical structures become increasing distinct species". We feel that this concept is undoubtedly a very useful one, particularly if modified by the point of view that the "ion character" or polarity of that intermediate may vary from negligible to complete, depending upon the nature of the substrate itself or upon the environment, and we further suggest that it is applicable to intermediates produced as a result of photoexcitation as well as thermal excitation. If the Walling concept is accepted, the distinction between the seriatim and simultaneous processes blurs. We believe that acceptance of the Walling concept is the most conservative position to take at present. Indeed, Nozaki and co-workers[9d] have applied the Walling concept to the photolysis of benzhydryl esters in protic solvents and it has been considered as well by McKenna.[9a]

Recently Ullman and his co-workers[4f] proposed a mechanism for the photomethanolysis of certain benzyl alcohols containing an *N,N*-dimethylanilino group, in which intramolecular electron transfer from the "sensitizing" dimethylanilino group to the benzyl phenyl group was postulated. It was proposed that this was followed by cleavage of the carbon–oxygen bond to give hydroxide ion and an excited biradical cation which decayed to a benzyl cation. Their system, which demands the amino function to react, is considerably different from ours.

When the irradiation of **1** is carried out to exhaustion, or when **2** and **3** are irradiated, the "photostationary" state contains no measurable amounts of **1**, but only the **2–3** mixture. Available evidence[3,11] suggests that in the ground state the manifold of ions **13, 14, 15**, and **16** produced in solvolysis from **1, 2, 3**, or **4** has the classical benzylic ion **14** as its most stable component, and that kinetic capture by nucleophiles leads almost exclusively to mixtures of exo and endo **12** species. In this respect the cation manifold produced by irradiation of **1, 2**, and **5** is identical in nature with the ground-state manifold, and the photochemical process leads to a mixture of products similar to that of kinetic control. Our experiments are not precise enough to determine small differences, so that it is not

13 14

15 16
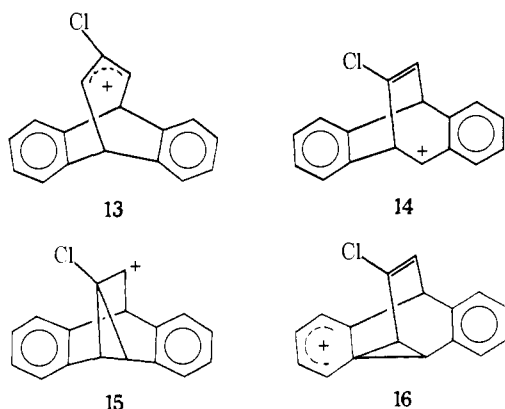
possible to state whether the two systems are in fact identical.

Treatment of **1** with lithium aluminum hydride reduced off the allylic chlorine atom and gave the unrearranged chlorohydrocarbon **17**. Similar reduction of **2** gave **18**. When **17** was treated with *N*-bromosuccinimide, **5** was produced. Treatment of **18** with *N*-bromosuccinimide gave a mixture of **5, 6,** and **7**. Unfortunately we do not have data to know whether the formation of **5** from **18** is due to radical rearrangement in the course of the reaction or is the result of subsequent rearrangement to the more stable[3] species. Clearly, however, the failure of the intermediate radical produced in the bromination of **17** to rearrange (that is, the failure to produce **6** or **7**) is further evidence that the photochemical reactions that we have observed to not involve radicals as product-determining intermediates.



17 18

19 20
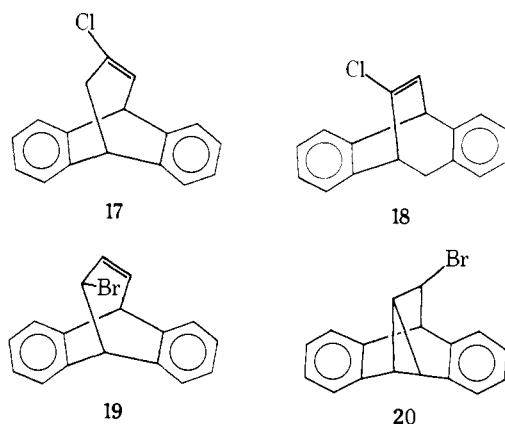
We have also done some preliminary work on the reactions of the dechloro analogue of **5**, that is, of **19**. When **19** was heated at 165 °C for 40 min, it was converted almost completely to the cyclopropylcarbinyl isomer **20**. Photoisomerization by direct irradiation also led to **20**. The thermal rearrangement undoubtedly involves ionic intermediates; labeling experiments are necessary to determine whether the phototransformation of **19** to **20** involves similar intermediates or whether a di-π-methane rearrangement[12] is involved.

## Experimental Section

**General.** Melting points were determined on a Thomas-Hoover apparatus. NMR spectra were recorded with Varian Associates A-60A and EM-390 spectrometers and a JEOL PS-100 spectrometer. Chemical shifts are in parts per million relative to tetramethylsilane. Mass spectra were obtained on a Varian MAT CH-5 spectrometer. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

**Direct Irradiation of 3,4-Dichloro-6,7:8,9-dibenzobicyclo[3.2.2]-nona-2,6,8-triene (1).** 3,4-Dichloro-6,7:8,9-dibenzobicyclo[3.2.2]-nona-2,6,8-triene (**1**) was irradiated at 254 nm in acetonitrile, tetrahydrofuran, and cyclohexane. Analysis was by LC using two Waters and Associates 4.0 mm × 30 cm μ-Porasil columns in series. The UV

detector response was measured with an Autolab 6300 electronic integrator which was calibrated.

**Acetonitrile.** Aliquots (2.6 mL) of a 0.06 M solution of **1** (135 mg of **1** in 7.8 mL of acetonitrile) were pipetted into three Vycor tubes (10 mm × 30 cm). The solutions were degassed on a vacuum line with five freeze-pump-thaw cycles and sealed at a pressure less than 2 × $10^{-5}$ Torr. Two tubes were masked to produce a 19-mm window circumscribing the tube. The third tube was completely masked. The solutions were irradiated in a Rayonet photochemical reactor (254 nm) for 15 min. Analysis by LC (elution with 0.25% THF/hexane) revealed the presence of 88% of **1** ($\Phi_{loss} = 0.50$), 4.1% of the endo chloride **2** ($\Phi_2 = 0.17$), and 2.2% of the exo chloride **3** ($\Phi_3 = 0.09$) in the irradiated solutions. The remainder of the product mixture did not elute from the μ-Porasil columns. The solution in the completely masked tube showed no loss of **1**.

**Tetrahydrofuran.** Aliquots (2.0 mL) of a 0.106 M solution of **1** (305 mg of **1** in 10 mL of tetrahydrofuran) were pipetted into three quartz tubes (10 mm × 30 cm). Each tube was prepared for irradiation in a manner identical with the acetonitrile irradiation (vide supra). The tetrahydrofuran solutions were irradiated in a Rayonet photochemical reactor (254 nm) for 90 min. Analysis by LC (elution with 0.25% THF/hexane) indicated 51% of **1** ($\Phi_{loss} = 0.15$), 9.8% of the endo chloride **2** ($\Phi_2 = 0.03$), and 6.5% of the exo chloride **3** ($\Phi_3 = 0.02$).

**Cyclohexane.** **1** (102 mg, 0.35 mmol) was dissolved in 12.6 mL of cyclohexane and placed in a quartz tube (10 mm × 30 cm). After deoxygenation with $N_2$, the tube was masked to produce a 95-mm window circumscribing the tube. The solution was irradiated in a Rayonet photochemical reactor for 1 h. Analysis by LC (elution with 0.25% THF/hexane) gave 27% of **1** ($\Phi_{loss} = 0.13$), 11% of the endo chloride **2** ($\Phi_2 = 0.02$), and 2.8% of the exo chloride **3** ($\Phi_3 = 0.005$). Substantial amounts of chlorohydrocarbons were found.

**Direct Irradiation of *endo*-4,6-Dichloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (2) in Acetonitrile.** A 0.069 M solution of **2** (59 mg of **2** in 3 mL of acetonitrile) was placed in a Vycor tube (10 mm × 30 cm). The solution was degassed on a vacuum line with four freeze-pump-thaw cycles and sealed at a pressure less than 1 × $10^{-5}$ Torr. The tube was masked to produce a 10-mm window circumscribing the tube. The sample was irradiated in a Rayonet photochemical reactor (254 nm) for 30 min. Analysis by LC determined the product mixture to be 86% of the endo chloride **2** ($\Phi_{loss} = 0.24$) and 7% of the exo chloride **3** ($\Phi_3 = 0.12$).

**Direct Irradiation of 4-Bromo-3-chloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (5) in Acetonitrile.** A 0.036 M solution of **5** (299 mg of **5** in 25 mL of acetonitrile) was prepared and treated as described above for **1** in acetonitrile. After 105 min of irradiation (254 nm), analysis by LC indicated 41% of **5**, 24% of the endo bromide **6**, and 14% of the exo bromide **7**. The balance of the product mixture did not elute from the μ-Porasil columns.

**Direct Irradiation of 3,4-Dichloro-6,7:8,9-dibenzobicyclo[3.2.2]-nona-2,6,8-triene (1) in 5% Water/Acetonitrile.** **1** (269 mg, 0.94 mmol) was dissolved in 237.5 mL of acetonitrile and placed in a quartz reaction vessel. Water (12.5 mL) and 159 mg (1.5 mmol) of sodium carbonate were added to the solution. The solution was purged of oxygen by $N_2$ bubbling for 30 min prior to irradiation, then irradiated in a Rayonet photochemical reactor (254 nm) for 2 h with continuous $N_2$ bubbling. Water (100 mL) was added and the solution extracted with chloroform. The combined chloroform extracts were washed with 1 M hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride, and dried over anhydrous magnesium sulfate. Evaporation of the solvent left 301 mg of a dark brown oil. Preparative TLC on silica gel using chloroform provided three bands ($R_f$ 0.62, 0.13, 0.03). Band 1 ($R_f$ 0.62) consisted of 93 mg (35%) of 3,4-dichloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**1**), *endo*-4,6-dichloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**2**), and *exo*-4,6-dichloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**3**). Band 2 ($R_f$ 0.13) consisted of 38 mg (15%) of 6-chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*exo*-4-ol (**8**).[3] Band 3 ($R_f$ 0.03) consisted of 47 mg (16%) of 6-chloro-*N*-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*exo*-4-ylacetamide (**9**). A trace of 6-chloro-*N*-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*endo*-4-ylacetamide (**10**) was detectable by ¹H NMR analysis.

**Direct Irradiation of 4-Bromo-3-chloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (5) in 5% Water/Acetonitrile.** A 0.053 M solution of the bromide **5** (176 mg of **5** in 10 mL of 5% water/ acetonitrile) was treated in a manner similar to the procedure described above and irradiated for 100 min. Preparative TLC (silica gel

eluted with 10% THF/hexanes) and $^1$H NMR analysis established the presence of 30% of **5**, 10% of the endo bromide **6**, 10% of the exo bromide **7**, 25% of the exo alcohol **8**, and 10% of the exo amide **9**. The remainder consisted of minor products which were not investigated.

**Preparation of *N*-6-Chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*exo*-4-ylacetamide (9) Using the Ritter Reaction.** The alcohol **8** (100 mg, 0.37 mmol) was dissolved in 5 mL of acetonitrile. After the solution was cooled to 0 °C, 21 μL of concentrated sulfuric acid was added; the solution was stirred and allowed to stand for 100 h. The reaction mixture was poured into water, and the resulting slurry extracted with chloroform. The chloroform extracts were washed with saturated sodium carbonate and saturated sodium chloride, then dried over anhydrous magnesium sulfate. Removal of the solvent provided 76 mg (66%) of a white, crystalline solid, mp 188–193 °C. The $^1$H NMR spectrum of this solid indicated that both exo amide **9** and endo amide **10** were present in a ratio of 10:1. Recrystallization from 15% THF/hexane yielded the exo amide **9**: mp 193.5–194.5 °C; NMR (CDCl$_3$) δ 2.08 (3 H, s), 4.21 (1 H, dd, *J* = 2 and 4 Hz), 4.31 (1 H, d, *J* = 7 Hz), 5.21 (1 H, dd, *J* = 4 and 7 Hz), 5.92 (1 H, bd, *J* = 9 Hz), 6.85 (1 H, dd, *J* = 2 and 7 Hz), 6.99–7.53 (8 H, m).

Anal. Calcd for C$_{19}$H$_{16}$ONCl: C, 73.65; H, 5.22. Found: C, 73.59; H, 5.33.

**Preparation of 6-Chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-4-one Oxime.** The oxime was prepared by the method of Hall.[13] 6-Chloro-2,3:8,9-dibenzobicyclo[3.2.2]nonatrien-4-one[3] (783 mg, 2.94 mmol) was dissolved in 75 mL of ethanol. Hydroxylamine hydrochloride (409 mg, 5.88 mmol) and 592 μL (7.35 mmol) of pyridine were added. The solution was heated at reflux for 12 h. The solution was allowed to cool, then poured into 125 mL of water. After standing for 3 h, the solution was filtered yielding 769 mg (93%) of 6-chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-4-one oxime, mp 213–216.5 °C dec. A portion of the oxime was recrystallized from methanol: mp 216 °C dec; NMR (CDCl$_3$) δ 2.98 (1 H, bs), 4.35 (1 H, d, *J* = 7 Hz), 5.76 (1 H, d, *J* = 2 Hz), 6.69 (1 H, dd, *J* = 2 and 7 Hz), 6.91–7.97 (8 H, m).

Anal. Calcd for C$_{17}$H$_{12}$ONCl: C, 72.50; H, 4.30. Found: C, 72.35; H, 4.22.

**Preparation of *N*-6-Chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*endo*-4-ylacetamide (10) from 6-Chloro-2,3:8,9-dibenzobicyclo3.2.2]nona-2,6,8-trien-4-one Oxime.** LiAlH$_4$ (206 mg, 5.43 mmol) was dissolved in 20 mL of absolute ether. A 20-mL solution of absolute ether containing 313 mg (1.11 mmol) of the oxime was injected into the hydride solution and refluxed for 32 h. The reaction mixture was quenched with a minimum amount of a saturated aqueous solution of sodium potassium tartrate, filtered, and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave 240 mg of an oil which, by $^1$H NMR analysis, contained at least four components. *N*-6-Chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*endo*-4-ylamine and *N*-6-chloro-2,3:8,9-dibenzobicyclo[3.2.2]-nona-2,6,8-trien-*exo*-4-ylamine were discernible in the $^1$H NMR spectrum.

The mixture of amines was acetylated without purification, using Harfenist and Magnien's procedure.[14] Acetic anhydride (3 mL) was added to the amines and allowed to stand for 1.5 h. Absolute ethanol (10 mL) was added and the solution heated at reflux for 10 min. After cooling, the reaction mixture was poured into 30 mL of water. The resultant slurry was extracted with ether. The ether extracts were washed with saturated sodium bicarbonate and saturated sodium chloride, then dried over anhydrous magnesium sulfate. Removal of the solvent yielded 257 mg of an impure solid. The $^1$H NMR spectrum indicated *N*-6-chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*endo*-4-ylacetamide (**10**) and *N*-6-chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*exo*-4-ylacetamide (**9**) in a ratio of 1:1 along with two other major products which were not identified. Preparative TLC (silica gel using 50% THF/hexanes) provided 90 mg of a pure mixture of the amides (as determined by $^1$H NMR). Selective recrystallization from 10% THF/hexanes yielded 41 mg of *N*-6-chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*endo*-4-ylacetamide (**10**): mp 262–264 °C; NMR (CDCl$_3$) δ 1.97 (3 H, s), 3.89 (1 H, dd, *J* = 2 and 4 Hz), 4.26 (1 H, d, *J* = 7 Hz), 5.29 (1 H, bd, *J* = 9 Hz), 5.58 (1 H, dd, *J* = 4 and 9 Hz), 6.78 (1 H, dd, *J* = 2 and 7 Hz), 6.98–7.38 (8 H, m).

Anal. Calcd for C$_{19}$H$_{16}$ONCl: C, 73.65; H, 5.22. Found: C, 73.57; H, 5.12.

**Ritter Reaction of 6-Chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-**

2,6,8-trien-*exo*-4-ol (8) to Low Conversion. The exo alcohol **8** (204 mg, 0.66 mmol) was dissolved in 10 mL of acetonitrile. The solution was cooled to 0 °C and 56 μL (1.0 mmol) of concentrated H$_2$SO$_4$ was added. The reaction mixture was warmed to room temperature and allowed to stand for 2.25 h. The solution was poured into water and the resultant mixture extracted with chloroform. The combined chloroform extracts were washed with saturated sodium bicarbonate and saturated sodium chloride, then dried over MgSO$_4$. Removal of the solvent left 203 mg of a white oil. $^1$H NMR analysis revealed 55% of the exo alcohol **8** and 45% of the exo amide **9** and endo amide **10**. The ratio of exo amide to endo amide was 18:1.

**Reduction of 3,4-Dichloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (1).** The dichloride **1** (2.00 g, 7 mmol) was dissolved in 25 mL of dry THF. LiAlH$_4$ (0.38 mg, 10 mmol) was slowly added and the reaction mixture stirred at room temperature for 3 h. After being quenched with wet THF, the mixture was filtered through Celite. The filtrate was washed with 0.1 M hydrochloric acid and water, then dried over anhydrous magnesium sulfate. Evaporation of the solvent left a colorless oil which crystallized from 95% ethanol giving 1.6 g (90%) of 3-chloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**17**): mp 222–223 °C; NMR (CDCl$_3$) δ 2.75 (2 H, dd, *J* = 1.5 and 3.5 Hz), 4.14 (1 H, t, *J* = 3.5 Hz), 4.24 (1 H, d, *J* = 9.5 Hz), 6.47 (1 H, td, *J* = 1.5 and 9 Hz), 7.22 (8 H, m).

Anal. Calcd for C$_{17}$H$_{13}$Cl: C, 80.79; H, 5.18. Found: C, 80.53; H, 4.98.

**Reduction of *endo*-4,6-Dichloro-2,3:8,9-benzobicyclo[3.2.2]nona-2,6,8-triene (2).** The endo chloride **2** (510 mg, 1.8 mmol) was dissolved in 30 mL of dry THF. A 0.2 M LiAlH$_4$ solution (8 mL, 1.6 mmol) was injected into the reaction flask. The solution was heated at reflux for 5 h and worked up as described above. A colorless oil (340 mg, 76%) was crystallized from hexanes yielding 290 mg (65%) of 6-chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**18**): mp 142–144.5 °C; NMR (CDCl$_3$) δ 2.92 (1 H, dd, *J* = 3.2 and 17 Hz), 3.37 (1 H, dd, *J* = 3 and 17 Hz), 3.77 (1 H, ddd, *J* = 1.75, 3, and 3.2 Hz), 4.26 (1 H, d, *J* = 7 Hz), 6.68 (1 H, dd, *J* = 1.8 and 7 Hz), 6.8–7.5 (8 H, m).

Anal. Calcd for C$_{17}$H$_{13}$Cl: C, 80.79; H, 5.18. Found: C, 80.63; H, 5.18.

**Preparation of 4-Bromo-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (19).** 6,7:8,9-Dibenzobicyclo[3.2.2]nona-2,6,8-triene (214 mg, 0.98 mmol) was dissolved in 20 mL of carbon tetrachloride. *N*-Bromosuccimide (210 mg, 1.2 mmol) was added and the reaction mixture was irradiated at reflux with an incandescent light. After 2.5 h, the solution was cooled and filtered. Removal of the solvent gave a yellow oil. Purification by preparative LC provided 100 mg (30%) of a clear oil which was crystallized from hexane yielding **19**: mp 118–119.5 °C; NMR (CDCl$_3$) δ 4.09 (1 H, d, *J* = 8.5 Hz), 4.28 (1 H, dd, *J* = 1.5 and 3.7 Hz), 4.93 (1 H, ddd, *J* = 1.4, 3.5, and 3.7 Hz), 5.09 (1 H, ddd, *J* = 1.5, 3.5, and 11 Hz), 6.21 (1 H, ddd, *J* = 1.4, 8.5, and 11 Hz), 6.93–7.43 (8 H, m).

Anal. Calcd for C$_{17}$H$_{13}$Br: C, 68.73; H, 4.41. Found: C, 68.56; H, 4.52.

**NBS Bromination of 3-Chloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (17).** **17** (1.00 g, 4 mmol) was dissolved in 25 mL of carbon tetrachloride. *N*-Bromosuccimide (0.85 g, 4 mmol) was added and the reaction mixture was irradiated at reflux with a 750-W incandescent light. After 2.5 h, the solution was cooled and filtered through Celite. Removal of the solvent left an oil which was crystallized from carbon tetrachloride yielding 1.1 g (90%) of 4-bromo-3-chloro-6,7:-8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**5**): mp 165.5–168 °C; NMR (CDCl$_3$) δ 4.35 (1 H, d, *J* = 9 Hz), 4.54 (1 H, d, *J* = 4.2 Hz), 4.96 (1 H, d, *J* = 4.2 Hz), 6.71 (1 H, d, *J* = 9 Hz), 6.73–7.60 (8 H, m); mass spectrum *m/e* (rel intensity) 330 (M$^+$·, 78), 332 (M$^+$· + 2, 100), 334 (M$^+$· + 4, 25). Calcd for C$_{17}$H$_2$ClBr: M$^+$·, 330.

**NBS Bromination of 6-Chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (18).** **18** (50 mg, 0.20 mmol) was dissolved in 0.5 mL of carbon tetrachloride. *N*-Bromosuccimide (40 mg, 0.22 mmol) was added and the reaction mixture treated as described above excepting the reaction time which was 5 h. TLC analysis of the crude product mixture revealed three compounds ($R_f$ 0.36, 0.32, 0.28). Chromatography over silica gel gave 44 mg (88%) of a pale yellow oil. The $^1$H NMR spectrum indicated 4-bromo-3-chloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**5**), *endo*-4-bromo-6-chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**6**), and *exo*-4-bromo-6-chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**7**) in a ratio of 1:2:2. These compounds were not isolated and the analysis was

computed assuming that the NMR spectra of **6** and **7** are similar to those of the analogous chlorides.

**Thermal Isomerization of 4-Bromo-6,7:8,9-dibenzobicyclo[3.2.2]-nona-2,6,8-triene (19).** The bromide **19** (122 mg, 0.4 mmol) was weighed into a Pyrex tube. The sealed tube was heated at 165 °C for 40 min, cooled, and opened. TLC (silica gel using 10% ether/hexanes) indicated two major components. Preparative separation by LC (0.5 cm × 25 cm silica gel column eluted with hexanes) gave the following: fraction 1, 109 mg (90%) of a pale yellow oil. Crystallization from hexanes yielded 1-bromo-3,4:6,7-dibenzotricyclo[3.3.1.0$^{2,8}$]nona-3,6-diene (**20**): mp 143–144 °C; NMR (CDCl$_3$) δ 2.56–2.9 (3 H, m), 4.13 (1 H, dd, $J$ = 1.5 and 3.5 Hz), 4.64 (1 H, dd, $J$ = 3 and 3.5 Hz), 7.05–7.35 (8 H, m); mass spectrum molecular ion $m/e$ 296 (calcd, 296).

Anal. Calcd for C$_{17}$H$_{13}$Br: C, 68.73; H, 4.38. Found: C, 68.90; H, 4.46.

Fraction 2, 6 mg (5%) of a colorless oil, was shown by $^1$H NMR to be **19**.

**Direct Irradiation of 4-Bromo-6,7:8,9-dibenzobicyclo[3,2,2]nona-2,6,8-triene (19).** A 0.14 M solution of the bromide **19** (32 mg of **19** in 0.8 mL of acetonitrile-$d_3$) was placed in a 5-mm quartz NMR tube. The solution was deoxygenated with N$_2$ and irradiated in a Rayonet photochemical reactor (254 nm) for 90 min. The solution was concentrated by evaporation. The $^1$H NMR spectrum indicated equal amounts of **19** and **20**. LC analysis (4 mm × 30 cm column eluted with hexane) revealed two major components. Preparative separation by LC and subsequent $^1$H NMR analysis of the two major components confirmed the presence of 40% of **19** and 40% of **20**. The remaining 20% consisted of minor products which were not studied.

**Attempted Quenching of 3,4-Dichloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene in Acetonitrile.** Aliquots (3.0 mL) of a 0.01 M solution of **1** (75 mg of **1** in 25 mL of acetonitrile) were pipetted into six quartz tubes. To these tubes were added respectively 0, 10, 20, 40, 100, and 100 μL of 1,3-pentadiene (cis and trans). Five tubes were masked to allow equal amounts of light flux; the sixth tube was completely masked. The solutions were deoxygenated by N$_2$ bubbling, then irradiated in a Rayonet photochemical reactor (254 nm) for 30 min. Analysis by LC (elution with 0.25% THF/hexane) gave the following results: [diene] = 0.0 M, endo chloride **2** ($\Phi_0/\Phi_q$ = 1.0), exo chloride **3** ($\Phi_0/\Phi_q$ = 1.0); [diene] = 2.5 × 10$^{-2}$ M, endo chloride **2** ($\Phi_0/\Phi_q$ = 1.1), exo chloride **3** ($\Phi_0/\Phi_q$ = 0.93); [diene] = 5.1 × 10$^{-2}$ M, endo chloride **2** ($\Phi_0/\Phi_q$ = 1.0), exo chloride **3** ($\Phi_0/\Phi_q$ = 0.93); [diene] = 9.9 × 10$^{-2}$ M, endo chloride **2** ($\Phi_0/\Phi_Q$ = 1.0), exo chloride **3** ($\Phi_0/\Phi_q$ = 0.72); [diene] = 2.45 × 10$^{-1}$ M, endo chloride **2** ($\Phi_0/\Phi_q$ = 1.0), exo chloride **3** ($\Phi_0/\Phi_q$ = 1.0). The completely masked tube showed no loss of **1**.

**Quantum Yields.** Cyclopentanone actinometry[15] was used exclusively. Actinometry solutions were irradiated simultaneously with sample solutions. Actinometry and sample solutions were degassed on a vacuum line with at least five freeze–pump–thaw cycles and sealed at a pressure less than 2 × 10$^{-5}$ Torr. Actinometry solutions were analyzed by GC (5% Carbowax 20M). Sample solutions were analyzed by LC (UV detector response was calibrated against standard solutions of the respective compounds).

## References and Notes

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