J. Org. Chem. 1984, 49, 625–630

dimethylhydrazone, 7422-90-4; 5-hexenal dimethylhydrazone, 88180-24-9; 2-bromobenzaldehyde ethylene acetal, 34824-58-3; allyl bromide, 106-95-6; 1-deuterio-5-hexenal, 88180-25-0; 1,3-propanedithiol, 109-80-8; 2-(4-pentenyl)-1,3-dithiane, 88180-26-1; 2-(4-pentenyl)-2-deuterio-1,3-dithiane, 88180-27-2; 5-hexenal, 764-59-0; 2-methylcyclopentanone, 1120-72-5; cyclopentane, 287-92-3; 4-bromobutene, 5162-44-7; 2-bromobenzaldehyde, 6630-33-7; pentene, 25377-72-4.

Thermal and Photochemical Reactions of 10-Oxabenzo-*syn*-sesquinorbornene (1,2,3,4,9,10-Hexahydro-9,10-*exo*-epoxy-1,4-*exo*-methanoanthracene)

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The chemical behavior of the title compound (5) is influenced both by the fused benzo group and by the oxa bridge. In thermal additions to the double bond 5 is from 1.3 to 13.7 times as reactive as the analogue 6 with CH_2 in place of the O bridge. Treatment of the oxa compound 5 with chloroform and 50% sodium hydroxide for 12 h yielded the crowded dichlorocarbene adduct to the double bond, while no way has been found to add dichlorocarbene to the methylene species 6. The photochemical behavior of 5 in acetone resembles that of the parent *syn*-sesquinorbornene, 1. The benzo group also enables 5 by direct photoexcitation to capture hydrogen from cyclohexane, which 1 cannot do without a sensitizer. As a consequence of this direct excitation, 5 undergoes rapid rearrangement which competes with its other photochemical reactions. X-ray crystallographic studies[9] of compound 5 and its dichlorocarbene adduct have been made and will be published separately.

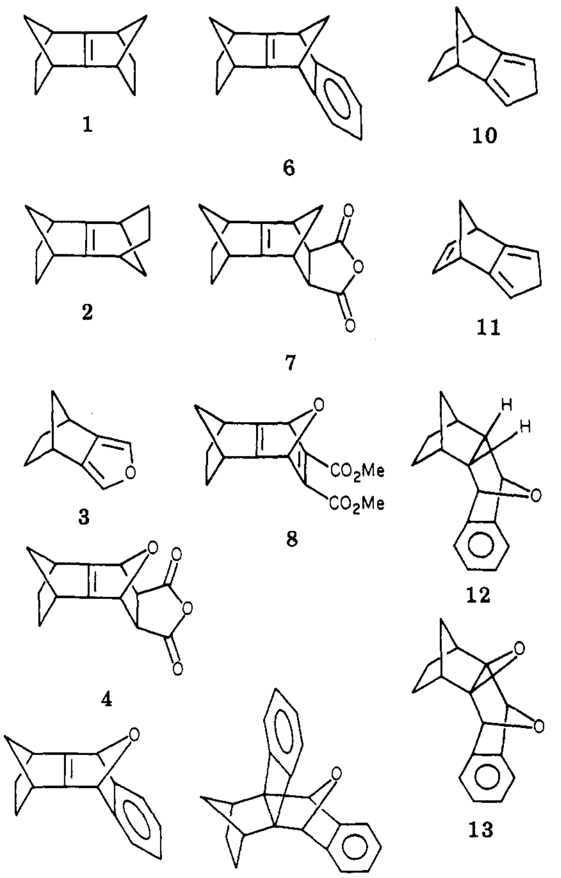
The reactivity of the carbon–carbon double bond responds to electronic effects of substituents in ways that are, in principle, fairly well understood. In addition, the double bond can be perturbed by geometric distortions of several kinds, each of which affects the chemical properties in particular ways. Incorporation in a small ring bends the system about the z axis (Figure 1); strained olefins with a double bond at a bridgehead exemplify, among other effects, torsion about the x axis.[1] Bending about the y axis is also enforced in 9,9′-dehydrodianthracene.[2]

The study of *syn*- and *anti*-sesquinorbornenes 1 and 2 (Chart I) has revealed a combination of some expected steric effects of the bridges[3] with newly discovered stereoelectronic properties of the π system. In the case of the syn isomer the double bond is bent like a hinge about the x axis 16–18° out of the normal planarity.[4] The readiness with which the sesquinorbornene system responds to small modifications of the environment of the double bond has prompted the present study[5] of some oxasesquinorbornenes in which the replacement of the CH_2 bridge by an oxygen atom has potential effects of both polar and steric kinds.

Vogel and co-workers[6] added maleic anhydride to norbornenofuran 3, obtaining a single product, shown by X-ray crystallography to be the *syn*-oxasesquinorbornene anhydride 4. We have compared furan with cyclopentadiene in addition to the dicarboxylic anhydrides of norbornene and norbornadiene.[7]

In this paper we report the preparation and properties of 10-oxabenzo-*syn*-sesquinorbornene (5) which proves to be a very favorable subject for X-ray crystallography and for comparisons of its chemical behavior with 4, 6, and 7.

Chart I



Results

The starting norbornenofuran 3 was prepared by the method of Vogel.[8] Treatment of 3 with a single equivalent

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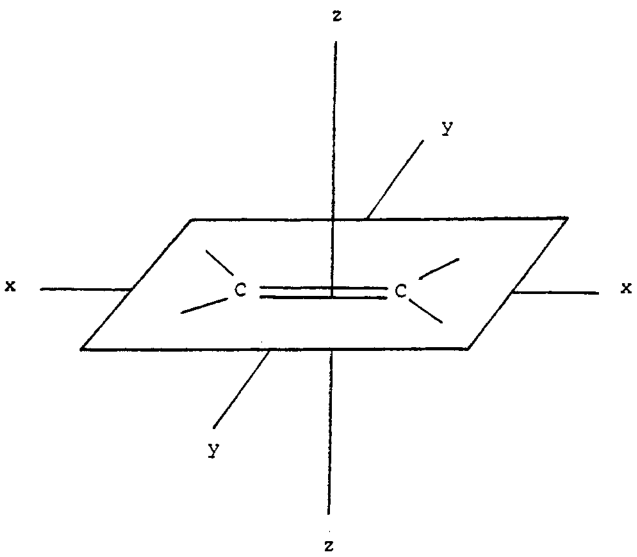


Figure 1.

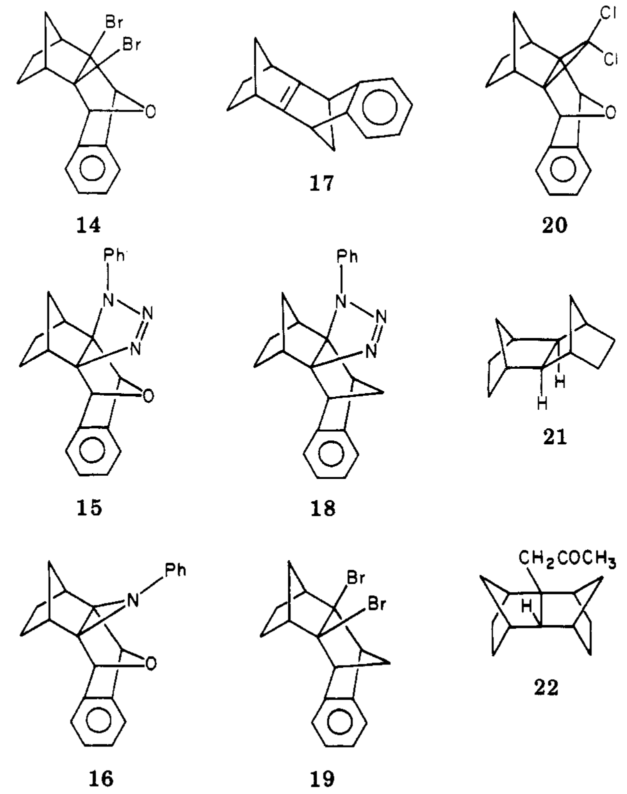
of benzyne from diazotized anthranilic acid led to a single adduct as evidenced by VPC analysis. By column chromatography (silica gel, hexane eluant) a yellow solid was isolated. Recrystallization from ethanol–water gave pale yellow platelets (mp 118–119.5 °C). The symmetry of the adduct was evidenced by the well-resolved eight-line ^{13}C NMR spectrum. Mass spectral analysis (70 eV) showed a molecular ion of m/e 210 and a prominent peak of m/e 118 (isobenzofuran fragment).

X-ray crystallographic analysis[9] demonstrated the expected[6] endo attack of benzyne on the furan **3**.

The C(4a)–C(8a) distance of 1.339 (3) Å in **5** is normal for an isolated double bond.[4] Also, the angles present in the sesquinorbornene framework correspond to the ring strain inherent in the norbornene[10] and 7-oxanorbornene[8,11] systems. However, the most interesting aspect of this molecule has to do with the large bend of the double bond about the x axis of Figure 1. This olefin **5** has the largest bending yet observed, with the dihedral angle being 157.9°. This represents a 22.1° deviation from the planarity generally associated with carbon–carbon double bonds and has earned for **5** the nickname "Big Bend" in this Texas laboratory.

Much attention has recently been given to molecular orbital interactions in relation to facial selectivity and dihedral angles in unsaturated polycyclic systems.[6,12-15] Whereas no one theoretical scheme has yet yielded quantitative predictions of all the effects of interest, the means are at hand for rationalizing the observations. From our present and previous[7] observations the enhanced bend in an oxanorbornene is consistent with a somewhat greater repulsive force exerted by a filled π orbital on an oxygen bridge compared to a methylene group. The most probable mechanisms for the origin of this force can account for the difference (CH_2 vs. O) as well as for the effect itself.

Chart II



Vogel and co-workers suggested that homoconjugation could be responsible for additional polarization of the double bond in **8**, resulting in a larger deviation from planarity and an attendant increase in reactivity.[6] This is in line with the author's report that compound **8** in fact undergoes spontaneous air epoxidation which precluded its isolation.

In all cases, there appears to be a relationship between degree of unsaturation in the molecule under consideration and its associated reactivity.[16]

Treatment of the furan **3** with excess benzyne led to a new product. This was found to be the result of [2 + 2] addition to the central double bond of **5**. Treatment of olefin **5** with benzyne under similar conditions yielded the same adduct **9**. ^{13}C NMR showed the presence of six different sp^2 carbons (including two different carbons without attached hydrogen), and ^{1}H NMR integration demonstrated the presence of eight aromatic protons, in agreement with the structure and symmetry of **9**. This result is similar to that which Paquette, Gleiter, and coworkers observed from the treatment of isodicyclopentadiene **10** or dehydroisodicyclopentadiene (**11**) with excess benzyne.[17]

In catalytic hydrogenation, bromination, and reaction with *m*-chloroperbenzoic acid (MCPBA) and with phenylazide, **5** resembles *syn*-sesquinorbornene (**1**) in its general reactivity and exclusive exo selectivity in all thermal additions. The reasons for this selectivity in **1**[3,4,18] are also present in **5**.

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Table I. Effect of the Oxa Bridge: Competition between 5 and 6

reagent	k_5/k_6	reagent	k_5/k_6
diimide	13.7	*m*-chloroperbenzoic acid	1.3
phenyl azide	6.8	bromine	2.3

The dihydride **12**, epoxide **13**, and dibromide **14** (Chart II) were all identified by their well-resolved, symmetrical ^{1}H and ^{13}C NMR spectra. In the case of the triazoline **15**, structure proof was obtained by photochemical conversion[19] into the symmetrical aziridine **16**.

The effect of the oxygen bridge in **5** on the reactivity of this olefin could be determined by comparison with olefin **6**, first made by Paquette and co-workers.[17] This olefin is prepared by the addition of benzyne to isodicyclopentadiene (**10**). Although the Paquette group reported finding exclusive formation of the endo addition product, **6**, in the present study we found about an 80:20 mixture of **6** and the exo adduct **17**. The two adducts **6** and **17** can be separated cleanly by preparative HPLC (normal phase, hexane eluant).

It has already been shown that olefin **6** reacts readily with diimide[17] and MCPBA[16] to give exo hydrogenation and epoxidation, respectively. We found that, like olefin **5**, olefin **6** also reacts rapidly with phenyl azide and with bromine to give **18** and **19**, respectively.

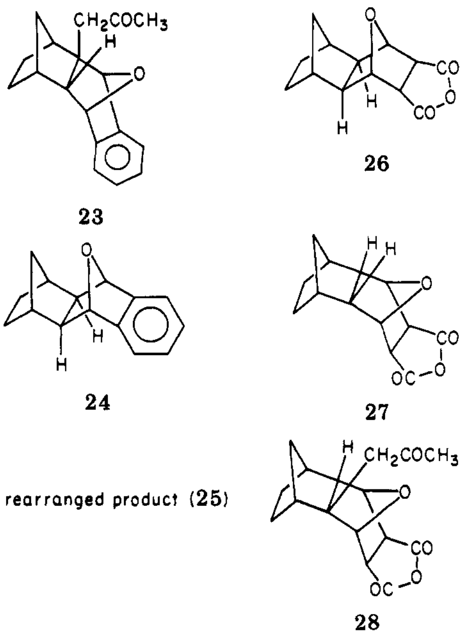
Competition between **5** and **6** toward diimide, phenyl azide, bromine, and *m*-chloroperbenzoic acid was followed kinetically, and the results are shown in Table I. In each case ln ([5]$_0$/[5]) was plotted against ln ([6]$_0$/[6]) at a series of times, and the slope of the plot was taken as the ratio k_5/k_6.

The concerted nature of attack on the double bond by diimide,[20] phenyl azide,[21] and MCPBA[22] is well established. The spread and magnitude of the rate differences in Table I suggests that, of the two expected effects of replacing CH$_2$ by O, the steric effect is favorable to reaction at the double bond while the polar effect is unfavorable, least so with diimide and most with MCPBA. Both of these effects are in line with previous experience.

The most striking difference in behavior between **5** and **6** was toward dichlorocarbene[23] (generated from chloroform and 50% NaOH). In the case of olefin **6**, treatment with an excess of dichlorocarbene for 24 h resulted in no reaction, returning only starting material.

However, treatment of olefin **5** under similar conditions resulted in the slow formation of a new product. Complete reaction at room temperature required ca. 12 h. ^{13}C NMR of the adduct revealed that a symmetrical addition had occurred to the central double bond of **5**. The structure **20** of the adduct was proved by X-ray crystallographic analysis.[9] This study shows that the chlorine–oxygen distance is only 2.57 Å, far less than the sum of the van der Waals radii for these two atoms (3.20 Å). Also, the corresponding chlorine–hydrogen distance of 2.14 Å (van der Waals 3.00 Å) indicates a high degree of steric compression present in this adduct, which would be aggravated if CCl$_2$ could add to **6**.

Chart III



Photochemical Behavior of Olefins 5 and 4 in the Presence of Acetone, Cyclohexane, and Benzene

We have found the hinge bending observed in derivatives of *syn*-sesquinorbornene (**1**)[4] to lead to some quite interesting consequences under photochemical conditions.[24] In all thermal reactions involving **1**, only exo addition has been found to occur to give exo,exo adducts. When photolyzed in the presence of acetone, **1**, like norbornene,[25] yields acetonyl addition products and hydrogenation products. However, the hydrogen addition was found to occur mainly on the endo face of the double bond to give *endo,endo*-dihydro adduct **21**.[24]

These results[24] were rationalized as being due to a conformation of the excited double bond in which the bend was in the opposite direction from that found in the ground state. Therefore, the conclusion was drawn that products arising from a free excited olefin molecule would be predominantly endo, while those arising from a ground-state-initiated sequence would be exo.[24] It was suggested that excited triplet acetone transfers its energy to *syn*-sesquinorbornene and that this excited olefin, in two successive captures of hydrogen from the solvent, is converted into the *endo,endo*-dihydride **21**. The acetonyl radicals formed in this process propagate a chain reaction with ground-state **1**, leading to the exo adduct **22**. The termination step of this chain reaction forms the coupling product 2,5-hexanedione.

Table II summarizes the results obtained from the photolysis of olefin **5**.

Despite the complexity of the photochemical reactions of **5** in the three solvents examined, some general conclusions can be drawn from overall comparisons of the reactions in Table II with those previously observed for **1**. The total disappearance of starting material in all cases indicates considerable reactivity of this unsaturated system. In the acetone experiments, **5** is obviously an active target for the free radicals carrying the chain reaction leading to

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Table II. Photolysis of 10-Oxabenzo-*syn*-sesquinorbornene (5)[a] at 12 °C

			% yield of product				
[5], M	time,[d] h	solvent	*endo,endo*-dihydro (24)	*exo,exo*-dihydro (12)	*exo,exo*-acetonyl (23)	epoxide 13	rearranged product 25
0.0044	3	acetone[b]	5.4	0	87.6	7.0	0
0.0090	3	acetone	4.8	0	88.2	6.9	0
0.023	5	acetone	5.3	0	81.7	13.0	0
0.044	5	acetone	5.6	0	79.3	15.1	0
0.022	21	cyclohexane	28.6	1.0	0	0	51.0
0.030	23.5	cyclohexane	27.7	1.0	0	0	49.1
0.0094	1	cyclohexane[c]	14.6	1.5	0	0	28.6
0.020	23	benzene	9.6	1.5	0	0	81.2
0.025	21	benzene	11.6	trace	0	0	74.4
0.030	21	benzene	13.0	trace	0	0	68.4

[a] All yields are VPC yields. The light source was a 450-W medium-pressure Hanovia arc lamp. A Pyrex vessel was used unless otherwise noted. [b] In addition to these products, 2,5-hexanedione was also identified. [c] Quartz vessel used. [d] Starting material fully consumed in all cases.

Table III. Photolysis of 4[a] at 12 °C

			product composition,[c] %			
[4], M	time, h	solvent	4	*endo,endo*-dihydro (28)	*exo,exo*-dihydro (29)	*exo,exo*-acetonyl (30)
0.0098	22	acetone[b]	0	36.0	1.2	62.7
0.017	22	acetone	0	38.6	1.4	59.7
0.035	22	acetone	4.2	20.8	0.4	69.9
0.0088	24	cyclohexane	90	0	0	0
0.0088	24	benzene	97.2	0	0	0

[a] All yields are VPC yields. The light source was a 450-W medium-pressure Hanovia arc lamp. A Pyrex vessel was used in all cases. [b] In addition to these products, 2,5-hexanedione was also identified. [c] No epoxide formation was observed under any conditions employed.

the product **23** (Chart III). At the same time, the lesser production of dihydride **24** means that either the formation of excited **5** or its activity as an H abstractor cannot keep up with the competing chain reaction. The epoxide formation, evidently from stray oxygen sensitized by acetone, also speaks for the reactivity of the double bond in **5**.

In cyclohexane and in benzene, where there is no competition from the formation of **23**, these solvents appear as somewhat better hydrogen donors to excited **5** than is acetone. But the outstanding feature of the reactions in these hydrocarbon solvents is the formation of large amounts of the rearrangement product **25**, whose structure remains to be completely established. Work on this reaction is continuing.

The identity of the *exo,exo*-acetonyl adduct **23** came by isolation from the reaction mixture by chromatography and comparison spectroscopically with an authentic sample prepared by treatment of olefin **5** with di-*tert*-butyl diperoxyoxalate in acetone solvent.[24] This gave the expected *exo,exo*-acetonyl adduct (in competition with epoxide formation) in good yield. ^{1}H and ^{13}C spectra were identical in both cases. Also, comparison by VPC retention time and GC/MS showed identical properties.

The identity of the epoxide (**13**), formed in the runs in acetone solvent, was established by preparation of an authentic sample by MCPBA oxidation of olefin **5** as already described. VPC retention times and GC/MS data gave identical results for the two epoxide samples.

The identity of the *endo,endo*-dihydro product **24** rests on GC/MS data as obtained from the reaction mixture. Comparison of mass spectral data showed it to have the same molecular ion peak as an authentic sample of the *exo,exo*-dihydro compound **12**. Finally, proof that it was not the *exo,exo*-dihydro adduct came by simultaneous VPC injection of the reaction mixture with an authentic sample of **12** and observing a new peak at a slightly longer retention time. The authentic sample of *exo,exo*-dihydro adduct was prepared by catalytic hydrogenation as already described.

A comparison was made between **5** and the most available oxasesquinorbornene, **4**, lacking the benzo structural unit. Table III shows that the reactivity pattern of **4** on photochemical reaction with acetone yields chiefly chain addition to the double bond but much more H capture by the excited state than in the case of **5**. Neither of these reactions is seen for **4** in either cyclohexane or benzene, and in no solvent is there any of the rearrangement that is so important with **5** in the hydrocarbon solvents. Evidently sensitization by acetone is required by **4**, whereas **5**, on direct irradiation, yields an excited state capable of capturing hydrogen from a hydrocarbon solvent. It seems likely that the benzo group so lowers the energy of the excited state and prolongs its lifetime that an easy molecular rearrangement wins over the more energy-critical capture of hydrogen.

Experimental Section

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus or a Mel-temp capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 197 instrument and were calibrated with a polystyrene film. Mass spectra (MS) were obtained on a Finnigan OWA-1020 GC-MS-DS operating in the electron-impact mode with an ionizing energy of 70 eV. NMR spectra were obtained with JEOL-FX60 and Varian EM-390 NMR spectrometers with internal Me_4Si as a reference unless otherwise noted. Gas chromatographic analyses were performed on a Perkin-Elmer Sigma 3 gas chromatograph apparatus. High-pressure liquid chromatography was performed on a Waters Associates Model 204 liquid chromatograph equipped with UV detector (254 nm) and normal phase column. Ozonolyses were performed by using a Welsbach Ozonator Model T-23 which produces a steady stream of between 2% and 4% ozone in oxygen. The silica gel used for column chromatography separations was 60–200 mesh, obtained from Baker Chemical Co. The neutral aluminum oxide used was activity grade 1, manufactured for ICN Nutritional Biochemicals by Woelm Pharma. The silica gel used for thick-layer chromatography was Type 60 Pf-254 by EM Reagents and was obtained from Brinkman. Elemental analyses were performed by Micanal Organic Microanalysis, Tucson, AZ. All reagents and solvents were used as obtained from commercial sources.

Preparation of 1,2,3,4,9,10-Hexahydro-9,10-*exo*-epoxy-1,4-*exo*-methanoanthracene (5) and 1,2,3,4,9,10-Hexahydro-9,10-*exo*-epoxy-4a,9a-*exo*-*o*-benzeno-1,4-*exo*-methanoanthracene (9). In a previously dried, 25-mL, round-bottomed flask equipped with a stir bar, nitrogen inlet, reflux condenser, and dropping funnel was placed the norbornenofuran **3** (1.18 g, 8.93 mmol) in 10 mL of dry dimethoxyethane (DME). To this solution was added the anthranilic acid (1.22 g, 8.94 mmol). The resulting solution was then heated to reflux under a nitrogen atmosphere, and isoamyl nitrite (1.0 mL) in ca. 5 mL of DME was added dropwise in 10 min. The solution was maintained at reflux for 15 min and cooled, and the solvent was removed (rotary evaporator). The black oil was diluted with ether, and the organics were washed several times with 5% sodium bicarbonate followed by brine. After drying (MgSO$_4$) of the mixture and removal of the ether (rotary evaporator), the resulting oil was chromatographed on a silica gel column and eluted first with hexane followed by hexane/methylene chloride (4:1) which gave relatively pure **5** (1.31 g, 70%). Recrystallization from ethanol/water gave pale yellow platelets: mp 118–119.5 °C; ^{1}H NMR (CDCl$_3$) δ 6.97 (AA′BB′ m, 4 H), 5.50 (s, 2 H), 3.09 (br s, 2 H), 0.8–1.7 (m, 6 H); ^{13}C NMR (CDCl$_3$) 159.7 (s), 147.7 (s), 125.1 (d), 120.1 (d), 81.9 (d), 48.5 (t), 42.5 (d), 23.8 (t) ppm; MS (70 eV), m/e 210 (relative intensity) (30.0), 181 (base) 165 (68.3), 153 (58.3), 118 (88.0).

Further elution with hexane/ether (1:1) gave the bis adduct **9**: white solid; mp 179–180 °C; yield (VPC) 22%; ^{1}H NMR (CDCl$_3$) δ 6.9–7.4 (m, 8 H), 5.10 (br s, 2 H), 2.40 (br s, 2 H), 0.6–1.7 (series of overlapping multiplets, 8 H); ^{13}C NMR (CDCl$_3$) 147.3, 146.2, 128.1, 126.1, 122.0, 119.6, 80.4, 63.8, 48.2, 37.9, 24.2 ppm; MS (70 eV), m/e (relative intensity) 286 (54.3), 258 (45.2), 257 (48.3), 229 (52.0), 220 (49.4), 219 (base), 202 (70.9), 189 (40.9), 165 (23.5), 152 (13.6); Anal. Calcd for C$_{21}$H$_{18}$O: C, 88.08; H, 6.34. Found: C, 87.81; H 6.39.

Preparation of 1,2,3,4,9,10-Hexahydro-1,4:9,10-*exo*,*exo*-dimethanoanthracene (6)[17] and 1,2,3,4,9,10-Hexahydro-1,4:9,10-*exo*,*endo*-dimethanoanthracene (17). A solution of **10** (3.00 g, 22.7 mmol) in anhydrous dimethoxyethane (25 mL) was heated to reflux while solutions of anthranilic acid (3.11 g, 22.7 mmol) in dimethoxyethane (5 mL) and isoamyl nitrite (3.8 mL) in the same solvent (5 mL) were added simultaneously from two dropping funnels over 30 min. The brown reaction mixture was stirred at the reflux temperature until gas evolution ceased. The solvent was removed and the residue chromatographed on neutral alumina (115 g) with hexane eluant. There was obtained a clear colorless liquid which solidified on cooling.

Analysis of the solid by ^{1}H NMR revealed the presence of two isomeric adducts in a ca. 4:1 ratio. The major product was found to be the syn isomer (**6**) as reported by Paquette et al.[17] The anti isomer (**17**) could be separated by HPLC (normal phase, hexane eluant).

17: ^{1}H NMR (CDCl$_3$) δ 6.9–7.4 (m, 4 H), 3.78 (br s, 2 H), 3.10 (br s, 2 H), 2.3–2.7 (m, 2 H), 1.6–1.9 (m, 2 H), 1.0–1.5 (m, 4 H); ^{13}C NMR (CDCl$_3$) 161.3, 153.3, 124.1, 121.0, 51.1, 48.7, 43.1, 26.2 ppm.

Preparation of 1,2,3,4,4a,9,9a,10-Octahydro-9,10-*exo*-epoxy-1,4-methanonaphthalene (12) (*exo*,*exo*-Dihydro Adduct of 5). Olefin **5** (105 mg, 0.50 mmol) was hydrogenated in a Parr shaker apparatus by using 5% Pd/charcoal catalyst and ethyl acetate as the solvent. The resulting solution was filtered through Celite and the solvent removed (rotary evaporator). Recrystallization from ethanol–water gave white crystals of **12**: mp 95–97 °C; yield 103 mg (97%); ^{1}H NMR (CDCl$_3$) δ 7.2 (m, 4 H), 5.05 (m, 2 H), 2.88 (m, 2 H), 2.6–0.4 (series of overlapping multiplets, 8 H); ^{13}C NMR (CDCl$_3$) 146.4 (s), 126.0 (d), 121.4 (d), 81.5 (d), 48.1 (d), 47.8 (t), 38.3 (d), 24.2 (t) ppm; MS (70 eV), m/e (relative intensity) 212 (12.1), 194 (20.7, 183 (16.1), 179 (12.2), 165 (74.2), 128 (21.7), 118 (base), 89 (17.9), 77 (16.9), 65 (11.6), 41 (57.4), 39 (72.6).

Preparation of 1,2,3,4,9,10-Hexahydro-4a,9a:9,10-*exo*,*exo*-diepoxy-1,4-*exo*-methanonaphthalene (13) (Epoxide of 5). Epoxide **13** was prepared as follows. A round-bottomed flask equipped with a stir bar and nitrogen inlet was charged with olefin **5** (100.4 mg, 0.478 mmol) and ca. 5 mL of dry methylene chloride. To this was added at 0 °C MCPBA (246 mg, 1.43 mmol, 3 equiv), and the reaction mixture was stirred overnight. An additional 10 mL of methylene chloride was added, and the resulting solution was washed with 10% sodium bisulfite (3×), 10% sodium bicarbonate (3×), the saturated brine (2×). Drying (MgSO$_4$) and removal of the solvent gave a white solid which was recrystallized twice from ether–hexane: yield 78 mg (72%); mp 168–170 °C; ^{1}H NMR (CDCl$_3$) δ 7.15 (m, 4 H), 5.13 (s, 2 H), 2.72 (br s, 2 H), 2.14 (d, J = 15 Hz, 1 H), 1.3–0.5 (series of overlapping multiplets, 5 H); ^{13}C NMR (CDCl$_3$) 147.8, 126.8, 121.8, 78.9, 63.2, 39.8, 39.0, 26.0 ppm; MS (70 eV), m/e (relative intensity) 226 (12.5), 198 (71.4), 169 (33.2), 165 (16.4), 157 (60.0), 153 (11.4), 141 (82.2), 128 (base), 115 (30.8), 77 (7.6), 41 (50.9), 39 (63.3). Anal. Calcd for C$_{15}$H$_{14}$O$_2$: C, 79.61; H, 6.25. Found: C, 79.11; H, 6.33.

Preparation of 1,2,3,4,9,10-Hexahydro-9-phenyl-4a,9a-azimino-1,4:9,10-*exo*,*exo*-dimethanoanthracene (18) (Phenyl Azide Adduct of Olefin 6). The triazoline **18** of olefin **6** was obtained as follows. A dried round-bottomed flask equipped with stir bar and nitrogen inlet was charged with **6** (396.2 mg, 1.90 mmol) and 2 equiv of phenyl azide in ca. 5 mL of dichloromethane. The resulting solution was stirred under nitrogen for 24 h. The solvent was removed, and the oil was chromatographed on a silica gel column with hexane eluant followed by dichloromethane eluant to give a white solid. Several attempts to purify this adduct further were unsuccessful: yield 290 mg (70%); ^{1}H NMR (CDCl$_3$) δ 6.6–7.5 (multiplets, 9 H), 3.80 (br s, 1 H), 3.58 (br s, 1 H), 2.86 (br s, 1 H), 2.64 (br s, 1 H), 0.5–2.5 (series of overlapping multiplets, 8 H); ^{13}C NMR (CDCl$_3$) 145.7, 145.3, 139.3, 129.3, 126.2, 126.1, 123.8, 123.4, 121.9, 114.7, 102.8, 77.2, 56.8, 50.3, (2 C), 44.4, 44.3, 42.9, 24.6, 23.7 ppm.

Preparation of 1,2,3,4,9,10-Hexahydro-9-phenyl-4a,9a-azimino-9,10-*exo*-epoxy-1,4-*exo*-methanoanthracene (15) (Phenyl Azide Adduct of Olefin 5) and Conversion to the Aziridine 16. Olefin **5** (100 mg, 0.48 mmol) was dissolved in 5 mL of CHCl$_3$ in a round-bottomed flask equipped with a stir bar. To this was added dropwise phenyl azide (71 mg, 0.60 mmol). An exothermic reaction ensued which subsided in less than 30 s. The resulting solution was stirred for 1 h and the ^{1}H NMR taken to reveal a single addition product, the triazoline **15**: mp (from anhydrous ether) 151–154 °C dec; ^{1}H NMR (acetone-d_6) δ 7.6–6.8 (m, 9 H), 5.49 (s, 1 H), 5.27 (s, 1 H), 2.86 (br s, 1 H), 2.62 (br s, 1 H), 1.8–0.6 (series of overlapping multiplets, 6 H); ^{13}C NMR (acetone-d_6) 144.9, 144.1, 139.3, 129.5, 127.3, 122.4, 122.3, 121.9, 115.0 (2 C), 104.2, 84.7, 83.8, 78.4, 44.3, 43.4, 42.6, 24.1 23.4 ppm.

Without further purification the triazoline **15** (83 mg, 0.25 mmol) was irradiated in acetone solvent with a Rayonet photochemical reactor apparatus for 8 h. Removal of the solvent (rotary evaporator) gave a brown solid (**16**) which was filtered through a silica gel column (2 g, 40% ethyl acetate–hexane) to give a pale yellow solid: yield 60 mg (79%); mp 179–180 °C dec; ^{1}H NMR (CDCl$_3$) δ 7.4–6.5 (overlapping multiplets, 9 H), 5.09 (s, 2 H), 2.74 (br s, 2 H), 2.47 (d, J = 10 Hz, 1 H), 2.2–0.6 (series of overlapping multiplets, 5 H); ^{13}C NMR (CDCl$_3$) 150.9, 149.0, 129.0, 126.1, 121.4, 118.5, 114.2, 79.1, 50.6, 43.5, 39.5, 25.9 ppm. Anal. Calcd for C$_{21}$H$_{19}$ON: C, 83.69; H, 6.35. Found: C, 83.33; H, 6.35.

Preparation of 1,2,3,4,9,10-Hexahydro-9,10-*exo*-epoxy-4a,9a-*exo*,*exo*-dibromo-1,4-*exo*-methanoanthracene (14) (Dibromide of Olefin 5). To a methylene chloride solution containing olefin **5** (55.3 mg, 0.263 mmol) at 0 °C was added bromine dropwise. After the reddish color was imparted to the solution, the solvent was removed (rotary evaporator) and ether added to give a white solid: 58 mg (60%); mp 73.5–74.0 °C dec. This compound decomposes upon standing: ^{1}H NMR (CDCl$_3$) δ 7.6–7.1 (series of multiplets, 4 H), 5.52 (s, 2 H), 2.87 (br s, 2 H), 2.1–0.6 (series of overlapping multiplets, 6 H); ^{13}C NMR (CDCl$_3$) 144.6, 127.6, 122.4, 91.5, 86.1, 53.1, 48.3 25.1 ppm.

Preparation of 1,2,3,4,9,10-Hexahydro-4a,9a-*exo*,*exo*-dibromo-1,4:9,10-dimethanoanthracene (19) (Dibromide of Olefin 6). The olefin **6** (80.5 mg, 0.387 mmol) was taken up in dichloromethane and cooled to 0 °C in a round-bottomed flask. Bromine in dichloromethane was added until the red-brown color persisted. The solvent was removed (rotary evaporator) and the resulting solid filtered through a short column of silica gel with ether as the eluant. A white, waxy solid (**19**) was obtained which was recrystallized from ether/hexane: mp 107.5–110 °C dec; yield (after purification) 56.3 mg (39.5%); ^{1}H NMR (CDCl$_3$) δ 7.1 (m, 4 H), 3.85 (br s, 2 H), 3.39 (d, 1 H, J = 10 Hz), 2.96 (overlapping peaks, 3 H), 2.37 (d, 1 H, J = 10 Hz), 1.48 (d, 1 H, J = 10 Hz), 0.87 (br s, 4 H); ^{13}C NMR (CDCl$_3$) 145.5, 126.4, 123.6, 88.0, 62.9, 59.6, 55.0, 47.4, 25.4 ppm. Anal. Calcd for C$_{16}$H$_{16}$Br$_2$: C, 52.21; H, 4.38. Found: C, 52.26; H, 4.47.

Preparation of 1,2,3,4,4a,9,9a,10-Octahydro-9,10-*exo*-epoxy-4a,9a-*exo*-(dichloromethano)-1,4-*exo*-methanoanthracene (20). To a previously dried round-bottomed flask equipped with a stir bar and nitrogen inlet were added olefin **5** (98.5 mg, 0.469 mmol), chloroform (120 mg, 0.938 mmol), ca. 3 mL of methylene chloride, and 1.5 mg of triethylbenzylammonium chloride. To this solution was added ca. 100 mg of 50% sodium hydroxide solution, and the mixture was stirred vigorously under nitrogen overnight. Filtration followed by extraction with ether, washing of the organic layer with saturated NaCl solution, drying of the mixture (MgSO$_4$), and the removal of the solvents (rotary evaporator) resulted in a viscous oil. Addition of absolute ethanol gave a white solid: 101 mg (74%); mp 138–141 °C; ^{1}H NMR (CDCl$_3$) δ 6.8–7.5 (4 H, overlapping multiplets), 5.24 (br s, 2 H), 3.87 (d, 1 H, J = 13 Hz), 2.68 (br s, 2 H), 0.8–1.7 (series of overlapping multiplets, 5 H); ^{13}C NMR (acetone-d_6) 151.3, 126.6, 122.7, 81.2, 46.9, 40.2, 29.2 ppm. The observed ^{13}C spectrum of **20** lacks two of the expected nine peaks. In our experience in this series, it is frequently seen that the signals of quaternary carbon atoms in three-membered rings are greatly weakened and even indistinguishable from the background, presumably because of exceptional nuclear relaxation times.

Attempted Addition of Dichlorocarbene to Olefin 6. To a dry round-bottomed flask equipped with stir bar and nitrogen inlet was added the olefin **6** (89.6 mg, 0.431 mmol) along with chloroform (120 mg, 1.0 mmol) and ca.1.5 mg of triethylbenzylammonium chloride. This was taken up in ca. 3 mL of methylene chloride. To this was added ca. 100 mg of 50% NaOH solution, and the two-phase reaction mixture was stirred vigorously for 24 h. A workup as described for the reaction of **5** followed by ^{1}H NMR showed mostly starting olefin and no evidence of any addition to the double bond.

General Procedure for the Photolysis of 1,2,3,4,9,10-Hexahydro-9,10-*exo*-epoxy-1,4-*exo*-methanoanthracene (5) and 3a,4,5,6,7,8,9,9a-Octahydro-4,9-*exo*-epoxy-5,6-*exo*-methanonaphthalene[2,3-*c*]furan-1,3-dione (4). In typical runs, the olefin (**5** or **4**) was dissolved in 10.0 mL of previously nitrogen-purged solvent and placed in either Pyrex or quartz test tubes, depending upon the particular conditions. The tubes were then fitted with rubber septa and further purged with nitrogen before irradiation. The light in all cases was unfiltered from a 450-W medium-pressure Hanovia arc lamp. Irradiation times are indicated in Tables II and III. The temperature of the cooling bath was maintained by a Neslab-Coolflow recirculator. The reactons were followed by VPC.

Preparation of the *exo*,*exo*-Acetonyl Adduct (23) of Olefin 5.[24] Olefin **5** (64.5 mg, 0.310 mmoles) was placed in a dry 10-mL round-bottomed flask equipped with a stir bar. To this was added 5 mL of nitrogen-purged acetone. This solution was then placed in a nitrogen glovebag and stirred for 30 min. To this was added di-*tert*-butyl diperoxyoxalate (36.8 mg, 0.157 mmol) in one portion. The resulting solution was stirred for 2 h, after which VPC analysis indicated complete reaction (yield 95% by VPC). Recrystallization from ether/hexane gave a white solid: 62.1 mg (75%); mp 121–122 °C; ^{1}H NMR (CDCl$_3$) δ 7.0–7.4 (m, 4 H), 5.03 (m, 2 H), 3.00 (m, 2 H), 0.8–2.5 (series of overlapping multiplets, 12 H); ^{13}C NMR (CDCl$_3$) 208.6, 146.7, 146.6, 126.0 (two C), 122.4, 120.9, 85.3, 81.4, 55.6, 55.1, 53.7, 46.0, 43.1, 38.5, 31.1, 25.1, 23.4 ppm; IR (CDCl$_3$) 3050, 2950, 1708, 1360, 1175, 690 cm^{-1}; MS (70 eV), m/e (relative intensity) 268 (51.1), 250 (13.5), 222 (5.6), 207 (63.5), 199 (70.5), 179 (76.6), 165 (27.0), 157 (17.1), 141 (12.2), 128 (11.1), 115 (10.7), 91 (4.1), 77 (6.7), 67 (11.8), 43 (base). Anal. Calcd for C$_{18}$H$_{20}$O$_2$: C, 80.56; H, 7.51. Found: C, 80.85; H, 7.49.

Characterization of Dihydro Adducts 12 and 24 Obtained from the Photolysis of 5. The *exo,exo*-dihydro adduct **12** was prepared for reference as previously described. Characterization of the *endo,endo*-dihydro adduct **24** is based upon comparison of mass spectral data and VPC retention times with those of the *exo,exo*-dihydro adduct **12**. For **24**: MS, m/e (relative intensity) 212 (1.12), 179 (1.4), 165 (7.1), 128 (4.3), 118 (base), 90 (7.1), 77 (4.6), 63 (4.3), 51 (4.3), 41 (12.1), 39 (23.5). The mass spectral data of **12** are reported with its preparation (above).

Characterization of Rearranged Product 25. Attempts to purify the rearranged product **25** by column chromatography (SiO$_2$, chloroform eluant) resulted in decomposition of the product to give a red-purple, viscous oil. Also, attempts to crystallize the rearranged product from the reaction mixture were unsuccessful. For **25**: MS (70 eV), m/e (relative intensity) 210 (55.6), 195 (13.8), 181 (base), 165 (15.6), 152 (31.4), 91 (2.1), 76 (5.9), 63 (3.4), 39 (12.6).

Preparation of the *exo*,*exo*-Acetonyl Adduct (28) of Olefin 4. A 25-mL round-bottomed flask was dried and charged with **4** (79.0 mg, 0.340 mmol) and 10.0 mL of dry acetone which had been previously purged with nitrogen. This solution was placed in a glovebag with a nitrogen atmosphere and stirred for 30 min. To this was added in one portion the di-*tert*-butyl diperoxyoxalate (41.1 mg, 0.176 mmol). This was stirred for 4 h at 25 °C and the solvent removed. VPC analysis showed a mixture of several products, with the acetonyl adduct being formed in 79.0% yield. Column chromatography (SiO$_2$, ether eluant) gave a white solid: 58 mg (59%); mp 165–166 °C; ^{1}H NMR (CDCl$_3$) δ 4.8 (br m, 3 H), 3.08 (br s, 2 H), 2.40 (br s, 2 H), 2.21 (br s, 2 H), 2.05 (s, 3 H), 0.8–2.0 (series of overlapping multiplets, 6 H); ^{13}C NMR (CDCl$_3$) 207.7, 173.7, 172.5, 87.2, 83.6, 56.1, 54.8, 48.5, 47.8, 46.8, 44.0, 38.8, 31.2, 29.2, 25.6, 23.6 ppm; MS (70 eV), m/e (relative intensity) 290 (1.8), 272 (3.7), 244 (3.6), 234 (9.4), 220 (10.9), 202 (19.3), 174 (38.0), 160 (24.7), 149 (26.0), 135 (40.5), 132 (70.4), 117 (29.0), 91 (97.3), 79 (88.4), 77 (base), 65 (44.5), 53 (50.1). Anal. Calcd for C$_{16}$H$_{18}$O$_5$: C, 66.20; H, 6.25. Found: C, 65.98; H, 6.37. This product was identical in all respects with that formed under photochemical reaction of **4** in acetone.

Characterization of Dihydro Adducts 26 and 28 from the Photolysis of Olefin 4. The olefin **4** was catalytically reduced with hydrogen to give the reference sample of *exo,exo*-dihydro adduct **27** as reported by Vogel.[6] The *endo,endo*-dihydro adduct **28** was characterized by comparison of VPC and mass spectral data with those of the *exo,exo*-dihydro adduct **27**. For **26**: MS (70 eV), m/e (relative intensity) 234 (.02), 205 (4), 188 (5), 162 (19), 133 (20), 119 (5), 105 (12), 91 (28), 79 (36), 66 (50), 53 (16), 39 (base). For **27**: MS (70 eV), m/e (relative intensity) 234 (3), 205 (0.3), 190 (2), 162 (4), 149 (2), 136 (63), 133 (8), 118 (5), 107 (10), 95 (19), 91 (23), 82 (25), 77 (28), 66 (53), 53 (16), 51 (17), 41 (65), 39 (base).

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Registry No. **3**, 71065-24-2; **4**, 75813-98-8; **5**, 88230-07-3; **6**, 73321-29-6; **9**, 88230-08-4; **10**, 6675-72-5; **12**, 88270-77-3; **13**, 88230-09-5; **14**, 88230-13-1; **15**, 88230-11-9; **16**, 88230-12-0; **17**, 88270-76-2; **18**, 88230-10-8; **19**, 88230-14-2; **20**, 88230-15-3; **23**, 88230-16-4; **24**, 77341-77-6; **26**, 88270-78-4; **27**, 75847-81-3; **28**, 88230-17-5.