with dioxolane, formalin, and acetone. The mixture was irradiated with a 100-W Hanovia lamp at 30–35 °C for the required time and analyzed by GC. A representative example is shown in Table II, experiment 8.

Procedure (Reduction). 2 (10.3 g, >95% purity), distilled water (40 mL), and 5% Pd on C (2.0 g) were charged to a 100-cm^3 rocker autoclave and heated at 160 °C (2000 psig H_2) for 4 h. Analysis of the filtered reaction mixture showed 98.3% 2 conversion with 97.5% selectivity to ethylene glycol.

The above reaction was repeated except by using 2.0 g of 5% Pd on Al_2O_3. A 97.1% conversion of 2 was obtained with a 99.1% selectivity to ethylene glycol.

Registry No. 1, 4421-14-1; 2, 5694-68-8; 3, 141-46-8; 4a, 108665-17-4; 4b, 108665-18-5; 5, 107-21-1; 9, 109-94-4; 10, 628-35-3; 12, 39239-93-5; formaldehyde, 50-00-0.

Control by Pyridine Nitrogen of the Dual-Channeled Triplet-State Di-π-methane Photorearrangement of 5,8-Dihydro-5,8-methanoquinoline Systems

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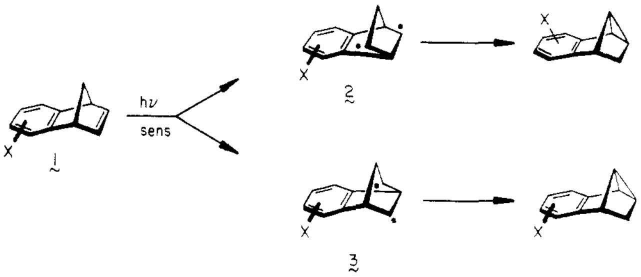
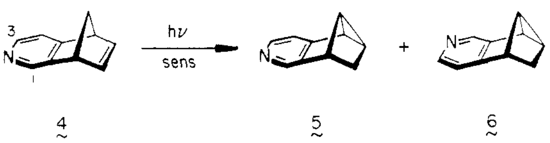
A series of five 5,8-dihydro-5,8-methanoquinolines has been synthesized and the triplet-state photoisomerization of these compounds investigated. In the case of the parent heterocycle, a 60:40 distribution of the two possible photoisomers was observed, with the major product arising by migration of the carbon atom ortho to nitrogen. Adoption of this pathway is notably enhanced (to the 83% level) when a chlorine is positioned at C-2 and becomes exclusive in the 2-methoxy example. The presence of a 4-chloro group reverses this trend (33:67), and the effect persists in the 4-methoxy example (25:75). The various regioselectivities are shown to conform to expectations which have their basis in molecular orbital theory.

In contrast to acyclic 1,4-dienes, which are so constructed as to engage in a single initial photoactivated "bridging step",[2] benzonorbornadienes have the latent ability to engage in two competitive excited-state 1,2-aryl-shift processes (viz., 1 → 2 and 1 → 3).[3] This dual-channel feature prompted us some time ago to undertake an extensive investigation of the controlling influence of substituents bonded to either of the two possible aryl sites,[4] to an olefinic center,[5] and to the bridgehead positions (singly[6] and doubly functionalized[7]). Internal competition experiments between various aryl/vinyl,[5b,c] bridgehead/vinyl,[8] and aryl/bridgehead substituent pairs[9] have also been performed, and the observed regiocontrol has proven highly revealing of detailed mechanism.[6-9]



More recently, we reported on the triplet-sensitized photorearrangement of several 5,8-dihydro-5,8-methanoisoquinolines,[10] the first heteroaromatics to be examined in this manner. For the parent heterocycle 4, the ring nitrogen atom was found to exert a directing influence favoring migration of C_{para} (75% of 5; 25% of 6). Attachment of chloro and methoxy groups at C-3 proved synergistic to the C_{para} 1,2-shift as expected. When the methoxy substituent was positioned at C-1 where it could operate in an antagonist fashion against nitrogen, OCH_3 totally controlled the regiochemical course of the di-π-methane rearrangement.[10]



In view of these developments, the scope of our investigations has now been expanded to include the isomeric 5,8-dihydro-5,8-methanoquinoline (7) and a number of its derivatives (8 and 9). Whereas the substitution plan in 4 is one that requires the sp^2-hybridized carbons positioned meta and para to the nitrogen center to vie for control of the rebonding pathways, the situation in 7 causes attention to be paid specifically to the C_{ortho}/C_{meta} pair. The ortho

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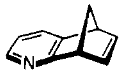
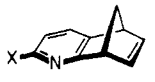
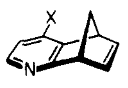


7



8a, X = Cl
b, X = OCH$_3$



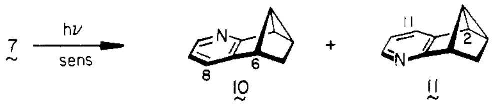
9a, X = Cl
b, X = OCH$_3$

site is recognized to be particularly conducive to neighboring group participation during solvolysis of homoortho sulfonate esters.[11]

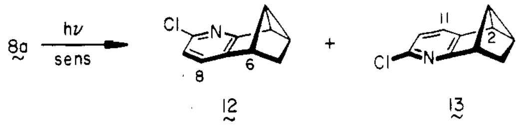
Results

The five heterocycles whose photochemical behavior was to be examined were prepared by the multistep route described elsewhere.[11] Their ^{1}H and ^{13}C NMR spectra are detailed in the Experimental Section. The triplet-sensitized photoisomerizations (acetophenone, E_T = 73.6 kcal/mol) were performed through Pyrex on dilute, deoxygenated benzene solutions at room temperature with 350-nm light (Rayonet reactor). Direct irradiation under otherwise identical conditions proved uniformly ineffective. Progress of the reactions was monitored by thin-layer chromatography or preferably capillary gas chromatography. Following consumption of starting material, the solvent was removed in vacuo and product separation/purification was achieved by medium-pressure liquid or preparative gas chromatography.

When photoexcited under the predescribed conditions, **7** was converted during 3 h to a 60:40 mixture of **10** and **11**. In line with the customarily distinctive 300- or 500-MHz ^{1}H NMR spectra of tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-trienes, the six aliphatic protons of each photoproduct appear at rather different chemical shifts, each with multiplicities unequivocally diagnostic of their specific position on the framework. Nonetheless, the finding that the pair of bridgehead protons in **10** (δ 3.36 and 2.67) differ only modestly in location from those in **11** (δ 3.40 and 2.48) did, by itself, not allow for convincing structural assignments to be made at this stage of the work (however, see below). On the other hand, more detailed spectral analysis disclosed that double irradiation of H-8 in **10** (δ 7.23) uniquely induces a 4% NOE enhancement of the H-6 absorption (δ 3.36), which must therefore reside in the immediate vicinity. In a complementary NOE study, irradiation of H-11 in **11** (δ 7.63) was seen to induce a somewhat larger effect (5% integral enhancement) only on H-2 (δ 2.48).

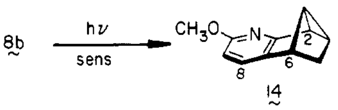


In a different context, the inductive and mesomeric contributions of an aryl-fused cyclopropane ring are recognized to shield ortho and para carbon atoms to a greater extent than the meta.[12] On this basis, C-7 in **11** (169.9 ppm) should appear downfield of C-1 in **10** (163.8 ppm), and this ordering is observed. As a consequence of these combined observations, the conclusion that **10** is the major photoproduct of **3** is considered secure.

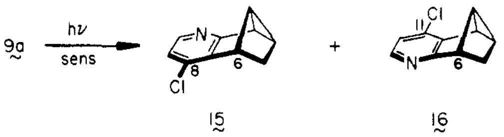


Our attention was next directed to **8a**, comparable triplet-sensitized irradiation of which proceeded to generate an 83:17 mixture of two di-π-methane regioisomers. The gross structures of these products were easily deduced to be **12** and **13**. The major constituent was identified specifically as **12** on the strength of chemical shift comparisons with **13**, as well as nuclear Overhauser experiments. The consequences of cyclopropane ring anisotropy[13] happen to be especially well defined in these compounds. For example, H-8 in **12** (δ 7.17) appears upfield of the deshielded H-11 in **13** (δ 7.61). Furthermore, in the case of **12**, separate irradiation of H-8 resulted in a 4.7% NOE enhancement in the integral attributable to H-6 (δ 3.33). Reciprocal effects were seen with H-6 of **12** and with H-2 of **13** (δ 2.51), the latter inducing a response in H-11 to the extent of 5.6%.

When photoexcited under comparable conditions, **8b** was rapidly transformed into a single tetracycloundecatriene (capillary gas chromatographic analysis). In the absence of a second regioisomer, comparative analysis of spectral data between two closely related molecules is, of course, not possible. Nonetheless, identification of the product as **14** was again made possible by informative NOE measurements. Most relevantly, double irradiation of H-8 (δ 7.15) induced a 6.4% NOE enhancement in the integral of the H-6 absorption (δ 3.27) but had no effect on H-2 δ 2.55).

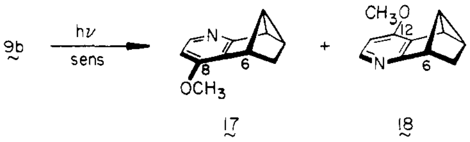


The acetophenone-sensitized irradiation of **9a** promoted efficient conversion to a 33:67 mixture of **15** and **16** (90% isolated). In this instance, the absence of spatially proximate aromatic and aliphatic hydrogens in either product did not allow for the implementation of NOE experiments.



Rather, chemical shift correlations were relied upon. First, the absorption of the chlorine-substituted carbon atom in the major photoproduct (138.9 ppm) appears downfield of that in the minor isomer (135.4 ppm). With **12** and **13** as reference compounds, the regioisomer having the more shielded para carbon was considered to be **16**. Secondly, while the chemical shift of H-6 at δ 3.46 in **16** is normal for the 11-aza series [compare **11** (δ 3.40) and **13** (δ 3.37)], that in **15** is downfield shifted to δ 3.62 as a consequence of carbon–chlorine bond anisotropy effects,[14] an indication that **15** belongs to the 8-aza class.

Photoisomerization of the 4-methoxy derivative **9b** ultimately led to the acquisition of spectral information needed to confirm the structural assignments to **15** and **16**. In this instance, the two photoproducts **17** and **18** were obtained in a 25:75 ratio. Following chromatographic



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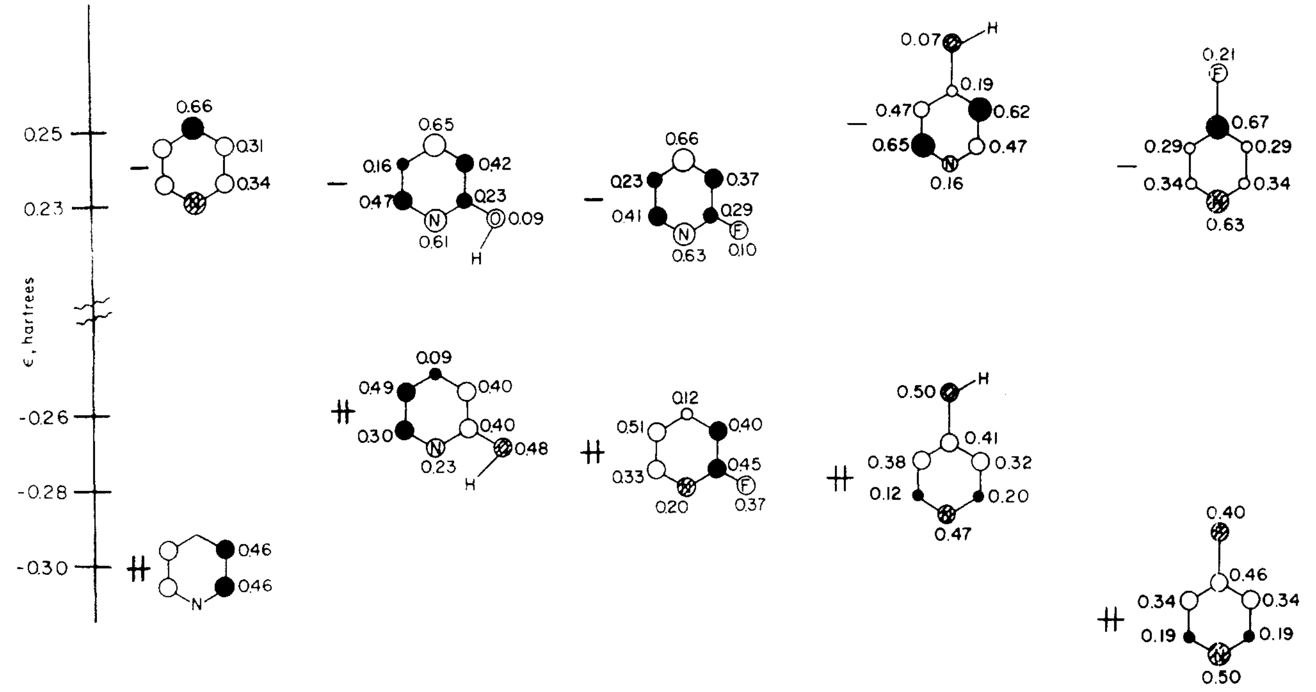

Figure 1. SOMO/sub-SOMO orbitals and electron densities of pyridine and select derivatives.[16]

separation, the individual ^1H and ^{13}C chemical shift characteristics were seen to conform nicely to precedent. For example, C-12 in **18** (162.2 ppm) appears downfield of C-8 in **17** (158.5 ppm). Also, the H-6 absorptions follow the customary pattern; for **18** this signal appears at δ 3.38, whereas in **17** it is encountered at δ 3.54. Superimposed on this is the fact that double irradiation of the methoxy signal in the major photoproduct gave rise to a 2% enhancement in the integral of the H-2 absorption (δ 2.67). Comparable double irradiation of the OCH_3 singlet in the minor isomer did not elicit a measurable response in any aliphatic proton absorption. Consequently, photoexcited **9b** undergoes bond reorganization in that manner which leads predominantly to **18**.

Discussion

The response of **7** to triplet sensitization serves to reaffirm our awareness of the fact that pyridine nitrogen does not overwhelmingly direct the di-π-methane rebonding process. Preferred use of C_{ortho} in **7** by a factor of 1.5 can be compared directly with the threefold greater migratory ability of C_{para} in **4**.[10] When standardized against an assumedly constant C_{meta}, we see that C_{para}/C_{ortho} equals 2. The excited state regiochemical preferences for **4** and **7** thus conform remarkably closely in direction and magnitude to predictions based solely on the differences in electron densities present in the SOMO[15] of the pyridine molecule. Figure 1 displays in pictorial fashion data culled from the earlier molecular orbital study of Del Bene.[16] This model indicates clearly that the role of the nitrogen atom is to deliver approximately twice as much electron density to C_{para} than to C_{ortho}. Although proper account is not taken of the extent of donor–acceptor interaction[16] present in the relevant frontier orbitals of either **4** or **7**, these effects seemingly cancel when the two substrates are directly compared. It should be noted that the model suggests as well that C_{ortho} in **7** should migrate preferentially to C_{meta}. However, the theoretical bias is on the order of only 1.1, while the experimental value is appreciably higher (1.5). Some electronic perturbation probably emanates from the fused norbornyl ring and needs to be factored in to complete the overall orbital picture.

Del Bene did not give attention to 2- and 4-chloropyridine,[16] but did thoroughly examine the monofluorinated derivatives (Figure 1). Electronic perturbation in this manner is seen not to override the earlier pattern of higher electron density at C_{ortho} relative to C_{meta}. In fact, the situation in the 4-fluoro example hardly differs from that existing at these two centers in pyridine. The 2-fluoro isomer exhibits greater disparity in the relevant electron densities. Without making any allowance for the difference in halogens, **8a** would be expected on this basis to isomerize predominantly to **12**. Experimentally, regiocontrol in this direction is encountered to the extent of 83%. The photoisomerization of "meta-F" benzonorbornadiene has been earlier examined and a strong preference (91%) for migration of C_{meta} noted.[4] Consequently, the chlorine and nitrogen atoms in **8a** are working synergistically to bring about dominant conversion to **12**.

In contrast, the same two heteroatomic centers in **9a** are positioned to direct in antagonist fashion. The chlorine atom is expected to promote in a significant way the 1,2-shift of the proximal pyridyl ring carbon to give **16**;[4] in contrast, the ring nitrogen should modestly favor conversion to **15**. The high chlorine-directing influence is not reflected in the orbital densities of 4-fluoropyridine. This is not surprising, since chlorine substitution is recognized to offer greater regiocontrol in di-π-methane rearrangements than fluoro. In actuality, the fluorine atom in "ortho-F" benzonorbornadiene has been found to be regioneutral (50:50) in controlling aryl migration.[4]

The exceptionally high methoxy-directing influence in **8b** can equally well be ascribed to synergistic electronic factors. On the assumption that the OH for OCH_3 change is a minimal one,[17] **8b** should exhibit a strong tendency to

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(15) Herein, the term SOMO is used to denote the *highest* occupied molecular orbital in the excited state. By sub-SOMO is meant the equivalent orbital to the ground state HOMO.

(16) Del Bene, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6184. We thank Dr. Del Bene for making available to us the entire output of her calculations from which the data in Figure 1 were culled.

proceed to **14** from its triplet state. The data in Figure 1 agree that a strong partiality should be shown for C_{ortho} migration. This analysis is directly relevant to MO calculations and photoelectron spectroscopy studies carried out earlier on both aryl-OCH_3-substituted benzonorbornadienes. Where the "meta-OCH_3" derivative is concerned, migration of C_{meta} is favored (89%)[4] and the SOMO orbital happens to be the discriminating regioselectivity factor.[18]

When "ortho-OCH_3" systems are involved, the situation is substantially different. Because of a significant enhancement in the contribution of the vinyl orbital to the dominant excited-state configuration, the sub-SOMO[15] now plays the central role in governing regioselectivity within the triplet manifold. Consequently, to the extent that **9b** undergoes photoisomerization under sub-SOMO control[15] (Figure 1), **18** should be preferred. This conclusion is consistent with the observation that **18** comprises 75% of the photoproduct mixture. Despite the internal consistency of this analysis, it must be realized that the multiconfigurational nature of excited triplet states makes it impossible to verify this hypothesis from inspection of ground-state orbitals.

In summary, the present findings provide additional confirmation of the assumption that triplet-excited benzonorbornadienes and their aza analogues usually enter into 1,2-aryl migration under essentially complete SOMO control[15] of the regioselectivity. The exception materializes when a meta-OCH_3 group is present. In these circumstances, the observed behavior conforms to expectations based upon sub-SOMO control.[15] Recent work has demonstrated that these relatively subtle effects can be overridden by the placement of a second substituent at either a bridgehead[9] or vinyl site.[5] These observations are taken to be a reflection of the operation of the "direct" 1,2-aryl shift mechanism, where 1,3-biradicals (and not bridged species) are the product-determining intermediates.

Experimental Section

General Dehydrogenation Procedure. A. 2-Chloro-5,8-dihydro-5,8-methanoquinoline (8a). A solution of freshly sublimed potassium *tert*-butoxide (160 mg, 1.4 mmol) in dry dimethyl sulfoxide (5 mL) was treated with the 6-exo-chloride[11] (140 mg, 0.654 mmol) and stirred at room temperature for 2 h. The reaction mixture was poured into ice–water and extracted with pentane (3×). The combined organic phases were dried and concentrated to give 100 mg (86%) of **8a**.

B. 2-Methoxy-5,8-dihydro-5,8-methanoquinoline (8b). Comparable treatment of the 6-exo-chloro-2-methoxy derivative (150 mg, 0.72 mmol) gave 98 mg (79%) of **8b**.

C. 4-Chloro-5,8-dihydro-5,8-methanoquinoline (9a). Comparable treatment of the appropriate 6-exo-chloride[11] (150 mg, 0.70 mmol) afforded 77 mg (62%) of **9a** after vacuum distillation in a Kugelrohr apparatus.

D. 4-Methoxy-5,8-dihydro-5,8-methanoquinoline (9b). A 150 mg (0.70 mmol) sample of the 6-exo-chloride wad dehydrochlorinated in analogous fashion to give 76 mg (61%) of **9b**.

^{1}H and ^{13}C NMR Spectra of the 5,8-Dihydro-5,8-methanoquinolines. 7: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (dd, J = 5.3, 1.4 Hz, 1 H), 7.29 (dd, J = 7.2, 1.2 Hz, 1 H), 6.75 (m, 3 H), 3.82 (m, 2 H), 2.39 (dt, J = 7.5, 1.6 Hz, 1 H), 2.30 (d, J = 7.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 174.9, 144.3, 143.2, 143.1, 142.3, 127.4, 118.6, 69.0, 51.8, 48.5.

8a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (dd, J = 7.6, 3.0 Hz, 1 H), 6.77 (m, 3 H), 3.84 (s, 1 H), 3.79 (s, 1 H), 2.38 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 176.5, 145.2, 143.54, 143.51, 142.1, 129.8, 118.3, 69.4, 51.8, 48.1.

8b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 1 H), 6.82 (t, J = 1.9 Hz, 2 H), 6.20 (d, J = 7.9 Hz, 1 H), 3.88 (s, 3 H), 3.80 (m, 2 H), 2.36 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 174.0, 161.4, 144.1, 142.0, 136.8, 130.4, 102.9, 69.9, 53.5, 52.1, 48.0.

9a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 5.6 Hz, 1 H), 6.83 (m, 2 H), 6.76 (d, J = 5.8 Hz, 1 H), 4.08 (m, 1 H), 3.89 (m, 1 H), 2.40 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 176.5, 144.4, 142.78, 142.74, 142.6, 135.8, 119.8, 68.4, 52.6, 47.1.

9b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 6.0 Hz, 1 H), 6.77 (br s, 1 H), 6.36 (d, J = 6.0 Hz, 1 H), 4.06 (s, 1 H), 3.80 (s, 1 H), 3.75 (s, 3 H), 2.29 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 177.0, 158.4, 145.7, 143.0, 142.5, 130.3, 104.3, 69.3, 55.0, 52.3, 45.0.

General Photoisomerization Procedure. 5,8-Dihydro-5,8-methanoquinoline (7). A solution of **7** (80 mg) and acetophenone (50 μL) in dry benzene (50 mL) was placed in a Pyrex tube and purged with a slow stream of nitrogen for 30 min. The vessel was stoppered and irradiated in a Rayonet reactor fitted with 3500-Å lamps for 3 h. The reaction mixture was concentrated under reduced pressure, and purification was achieved by MPLC on silica gel (elution with 35% ethyl acetate in petroleum ether) using peak-shaving techniques. There was isolated 21 mg of pure **10**, 35 mg of a mixed fraction, and 10 mg of pure **11**.

10: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 5.1 Hz, 1 H), 7.23 (d, J = 7.3 Hz, 1 H), 6.93 (dd, J = 7.3, 5.1 Hz, 1 H), 3.36 (m, 2 H), 2.95 (m, 1 H), 2.67 (t, J = 5.1 Hz, 1 H), 2.11 (m, 1 H), 0.84 (dd, J = 9.0, 2.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 163.8, 146.1, 141.4, 126.9, 119.7, 45.2, 41.1, 30.7, 29.4, 19.4; MS, m/z (M^+) calcd 143.0735, obsd 143.0747.

11: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (dd, J = 5.2, 1.3 Hz, 1 H), 7.63 (dd, J = 7.4, 1.4 Hz, 1 H), 6.97 (dd, J = 7.4, 5.2 Hz), 3.40 (dt, J = 7.8, 2.7 Hz, 1 H), 3.27 (m, 1 H), 2.95 (ddd, J = 9.3, 7.8, 3.2 Hz, 1 H), 2.48 (t, J = 5.2 Hz, 1 H), 2.07 (m, 1 H), 0.85 (dd, J = 9.3, 2.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 169.9, 144.8, 135.4, 130.3, 120.3, 44.4, 43.8, 28.4, 27.0, 20.2; MS, m/z (M^+) calcd 143.0735, obsd 143.0729.

Photoisomerization of 2-Chloro-5,8-dihydro-5,8-methanoquinoline (8a). A solution of **8a** (87 mg) and acetophenone (50 μL) in benzene (30 mL) was irradiated in the predescribed manner for 30 min. Solvent removal and purification of the residue by MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether) resulted in the separation of **12** from **13**, although both were contaminated with acetophenone. Final purification was achieved by preparative VPC.

12: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, J 7.7 Hz, 1 H), 6.95 (d, J = 7.7 Hz, 1 H), 3.38 (m, 1 H), 3.33 (m, 1 H), 2.94 (m, 1 H), 2.64 (t, J = 5.2 Hz, 1 H), 2.12 (m, 1 H), 0.80 (dd, J = 9.3, 2.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) 164.9, 147.9, 140.2, 129.5, 119.5, 46.2, 40.6, 30.6, 29.2, 19.7; MS, m/z (M^+) calcd 177.0345, obsd 177.0343.

13: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 1 H), 7.04 (d, J = 7.8 Hz, 1 H), 3.41 (m, 1 H), 3.33 (m, 1 H), 2.99 (m, 1 H), 2.51 (t, J = 5.2 Hz, 1 H), 2.12 (m, 1 H), 0.89 (dd, J = 9.5, 2.2 Hz, 1 H); MS, m/z (M^+) calcd 177.0345, obsd 177.0330.

Photoisomerization of 2-Methoxy-5,8-dihydro-5,8-methanoquinoline (8b). A benzene solution (30 mL) of **8b** (78 mg) and acetophenone (50 μL) was irradiated in the predescribed manner for 1 h and 20 min. The single product was purified by preparative VPC to give 44 mg (56%) of **14**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, J = 8.0 Hz, 1 H), 6.37 (d, J = 8.0 Hz, 1 H), 3.95 (s, 3 H), 3.32 (m, 1 H), 3.27 (m, 1 H), 2.87 (m, 1 H), 2.55 (t, J = 5.2 Hz, 1 H), 2.06 (m, 1 H), 0.76 (dd, J = 9.0, 2.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) 163.5, 161.5, 133.6, 130.2, 105.0, 53.5, 45.6, 40.6, 30.5, 29.6, 19.6; MS, m/z (M^+) calcd 173.0840, obsd 173.0834.

Photoisomerization of 4-Chloro-5,8-dihydro-5,8-methanoquinoline (9a). A solution of **9a** (60 mg) and acetophenone (50 μL) in benzene (30 mL) was irradiated as before for 1.5 h. The 33:67 mixture of **15** and **16** was separated by MPLC on silica gel (gradient elution with 25–60% ethyl acetate in petroleum ether with peak shaving) to return a total of 54 mg (90%) of the two components.

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15: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.14 (d, J = 6.0 Hz, 1 H), 7.02 (d, J = 6.0 Hz, 1 H), 3.62 (dt, J = 7.5, 2.9 Hz, 1 H), 3.44 (m, 1 H), 3.04 (ddd, J = 9.4, 7.5, 3.1 Hz, 1 H), 2.84 (t, J = 5.1 Hz, 1 H), 2.23 (m, 1 H), 0.89 (dd, J = 9.4, 2.7 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 165.3, 147.2, 139.2, 135.4, 120.4, 44.7, 39.5, 31.4, 28.6, 19.8; MS, m/z (M$^+$) calcd 177.0345, obsd 177.0329.

16: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.04 (d, J = 5.6 Hz, 1 H), 7.01 (d, J = 5.6 Hz, 1 H), 3.46 (dt, J = 7.8, 2.6 Hz, 1 H), 3.30 (m, 1 H), 3.00 (ddd, J = 9.5, 7.8, 3.2 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 171.1, 145.7, 138.9, 134.1, 121.1, 44.9, 43.5, 28.3, 26.0, 20.5; MS, m/z (M$^+$) calcd 177.0345, obsd 177.0344.

Photoisomerization of 4-Methoxy-5,8-dihydro-5,8-methanoquinoline (9b). A solution of **9b** (70 mg) and acetophenone (50 μL) in dry benzene (30 mL) was irradiated in the usual manner for 1 h. The two photoproducts (ratio 25:75) were obtained in 89% combined yield by MPLC on silica gel (elution with ethyl acetate and peak shaving).

17: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.17 (d, J = 5.9 Hz, 1 H), 6.57 (d, J = 5.9 Hz, 1 H), 3.82 (s, 3 H), 3.54 (dt, J = 6.9, 2.9 Hz, 1 H), 3.30 (m, 1 H), 2.93 (ddd, J = 9.1, 8.0, 3.0 Hz, 1 H), 2.67 (t, J = 5.3 1 H), 2.08 (m, 1 H), 0.79 (dd, J = 9.1, 2.7 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 165.3, 158.5, 148.1, 104.2, 55.2, 44.8, 37.6, 30.9, 28.9, 19.6; MS, m/z (M$^+$) calcd 173.0845, obsd 173.0842.

18: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.08 (d, J = 5.9 Hz, 1 H), 6.60 (d, J = 5.9 Hz, 1 H), 3.90 (s, 3 H), 3.38 (dt, J = 7.8, 2.7 Hz, 1 H), 3.17 (m, 1 H), 2.92 (ddd, J = 9.2, 7.8, 3.2 Hz, 1 H), 2.64 (t, J = 5.2 Hz, 1 H), 2.08 (m, 1 H), 0.82 (dd, J = 9.2, 2.8 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 171.5, 162.2, 147.2, 121.9, 104.7 (2C), 55.2, 44.8, 42.9, 28.6, 23.9, 20.0; MS, m/z (M$^+$) calcd 173.0845, obsd 173.0835.

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Registry No. 7, 108744-29-2; **8a**, 108744-30-5; **8b**, 108744-31-6; **9a**, 108744-32-7; **9b**, 108744-33-8; **10**, 108744-34-9; 11, 108744-35-0; 12, 108744-36-1; **13**, 108744-37-2; **14**, 108744-38-3; **15**, 108744-39-4; 16, 108744-40-7; 17, 108744-41-8; 18, 108744-42-9.

Synthesis of the Parent 1,7-Cyclohexenonorbornadiene and Its Quadricyclane Valence Tautomer

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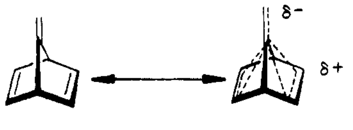
Cyclopentadiene is transformed in five steps into 1,7-cyclohexenonorbornadiene (**10**). Sensitized irradiation of this triene led to quadricyclane formation (**11**). The ^{1}H and ^{13}C NMR spectra of these hydrocarbons are compared to each other and to those of simpler, nonannulated analogues. The level of homoconjugation in **10** is high, indicating at best a modest strain increase relative to the parent triene. This conclusion is supported by photoelectron spectroscopic measurements and MMP2 calculations. Both **10** and **11** undergo polymerization during attempts at oxidation. The precursor disulfone **9** can, however, be oxidized and monodesulfonylated effectively.



1a 1b

That the arrangement of double bonds peculiar to methylenenorbornadiene (**1a**) lends itself to substantial homoconjugative interaction as in **1b** was first recognized 15 years ago.[1] The intense ground-state electronic delocalization is perhaps best revealed by ^{13}C NMR spectroscopy. In 1, C-7 resonates at 177.1 ppm, a record downfield shift for an olefinic carbon atom.[2] More recent spectroscopic studies of 7-alkylidenenorbornadienes show that the extent of homoconjugation is closely linked to the size of the coefficient at C-7, a parameter that can be modified by the number and nature of substituents at C-8.[3,4] The relationship between semicyclic π-bond polarization and $\Delta\delta$ (^{13}C) is not linear, although the difference in total atomic charge does make a major contribution.[4] Photoelectron spectroscopy constitutes an alternative technique for assaying the same electronic effects.

The considerable attention paid in the last few years to carbocyclic frameworks typified by **2**,[5] **3**,[6] and **4**[7] prompted us to develop a protocol for the conversion of the 7-oxanorbornyl ester **5** to the 1,7-cyclohexenonorbornadiene **6** for the purpose of determining the effect of annulation on orbital overlap.[8] Since this approach to **6** necessarily places a substituent R on the cyclohexene subunit, an alternative route was sought to make possible direct access

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