# Regioselectivity of Pyridine Ring Migration during Triplet-Sensitized Di-π-methane Photorearrangements of 5,8-Dihydro-5,8-methanoisoquinoline Derivatives. The Case for Heteroatom Control

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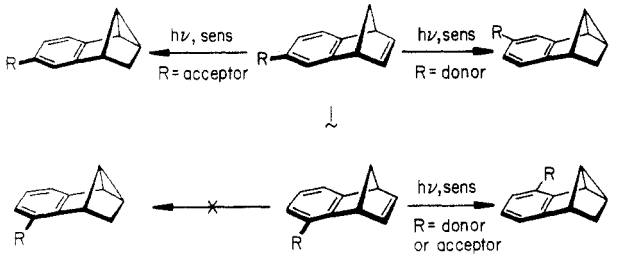
Four 5,8-dihydro-5,8-methanoisoquinolines were synthesized and subjected to sensitized photoisomerization. For the parent heterocyclic system, the ring nitrogen atom was found to exert a directing influence favoring migration of $C_{para}$ to the extent of 75%. The "meta"-Cl and -$OCH_3$ examples represent cases where the substituents should work cooperatively, and an additive effect was noted for the methoxyl case. Electron density values, in tandem with past photoelectron spectroscopy data, suggest that the overall regioselectivity pattern is the result of LUMO control. When the methoxy group is positioned "ortho", however, the substituents are positioned to direct in an antagonist fashion. The formation of a single photoproduct identified as **13** reveals that $OCH_3$ totally controls the course of the di-π-methane rearrangement. This behavior conforms to expectations based upon the HOMO as the discriminating regioselectivity factor. The parallelism between the response of the title compounds and similarly substituted benzonorbornadienes is striking.

Benzonorbornadiene (**1**, R = H) is a conformationally inflexible molecule having nonconjugated π components in close proximity. One consequence of this structural arrangement is the latent ability to function as a dual-channeled di-π-methane system. For the parent hydrocarbon,[2] these triplet state processes are enantiomerically related and consequently isoenergetic. When the symmetry of the benzonorbornadiene is lowered, for example, by monosubstitution of the aromatic ring, nonidentical competitive isomerization pathways can become operative.

Several years ago, we initiated an investigation whose purpose was to assess the controlling effect of substituents having widely different electronic properties on the course of benzonorbornadiene photoisomerizations. Importantly, the same di-π-methane route operated over the full range of R groups examined. When *m*-aryl substituents are involved as in **1** (R = H), dramatic differences in regioselectivity are seen depending upon the acceptor or donor properties of the pendant group.[3] In the *o*-aryl cases, large

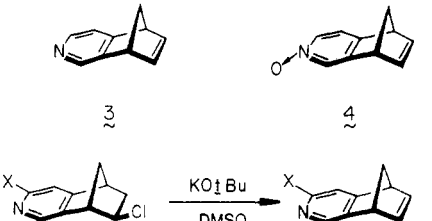



directive effects are also exerted, although these are all now in the same direction.[4] Good regiocontrol has also been noted when either the olefinic double bond[5] or a bridgehead site carries the R group.[6]

Since these processes have proven themselves to be highly revealing of electronic state substituent influences and di-π-methane mechanistic details, we have expanded the scope of our investigations to include 5,8-dihydro-5,8-methanoisoquinoline (**3**) and a number of its derivatives. Since no heteroaromatic duel-channeled substrate had previously been subjected to triplet-state photorearrangement, we anticipated that the present study would be particularly informative of the ability of pyridine nitrogen to vie for control of the different rebonding pathways.

## Results

The parent heterocycle **3** and its *N*-oxide **4** were prepared by the multistep route beginning with cyclopentadiene and glutinic acid as previously reported.[7] Access to the more highly substituted compounds **6a–c** was gained by dehydrohalogenation of the respective known chlorides **5a–c**.[8] The $^1H$ and $^{13}C$ NMR spectra of the three new olefins are detailed in the Experimental Section.




**a**, X = $OCH_3$, Y = H; **b**, X = Cl, Y = H; **c**, X = H, Y = $OCH_3$

The photoisomerizations were uniformly performed through Pyrex and under nitrogen with 3500-Å light on dilute benzene solutions containing acetophenone as sensitizer. Direct irradiation under otherwise identical conditions proved ineffective. The response of **3** was to afford

(1) Campus Chemical Instrumentation Center, The Ohio State University.
(2) Edman, J. R. *J. Am. Chem. Soc.* **1966**, *88*, 3454; **1969**, *91*, 7103.
(3) (a) Paquette, L. A.; Cottrell, D. M.; Snow, R. A.; Gifkins, K. B.; Clardy, J. *J. Am. Chem. Soc.* **1975**, *97*, 3275. (b) Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *Ibid.* **1977**, *99*, 3723.
(4) (a) Santiago, C.; Houk, K. N.; Snow, R. A.; Paquette, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 7443. (b) Snow, R. A.; Cottrell, D. M.; Paquette, L. A. *Ibid.* **1977**, *99*, 3734.
(5) (a) Paquette, L. A.; Ku, A. Y.; Santiago, C.; Rozeboom, M. D.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 5972. (b) Ku, A. Y.; Paquette, L. A.; Rozeboom, M. D.; Houk, K. N. *Ibid.* **1979**, *101*, 5981. (c) Paquette, L. A.; Bay, E.; Ku, A. Y.; Rondan, N. G.; Houk, K. N. *J. Org. Chem.* **1982**, *47*, 422.
(6) (a) Paquette, L. A.; Bay, E. *J. Org. Chem.* **1982**, *47*, 4597; *J. Am. Chem. Soc.* **1984**, *106*, 6693. (b) Paquette, L. A.; Varadarajan, A.; Bay, E. *Ibid.* **1984**, *106*, 6702. (c) Varadarajan, A., unpublished observations.
(7) Tanida, H.; Irie, T.; Hayashi, Y. *J. Org. Chem.* **1984**, *49*, 2527.
(8) Tanida, H.; Irie, T.; Hayashi, Y. *J. Org. Chem.* **1985**, *50*, 821.

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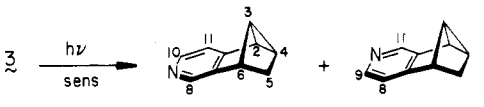
**Table I. Selected Comparative $^1H$ and $^{13}C$ NMR Chemical Shift Data for the 5,8-Dihydro-5,8-methanoisoquinoline Photoproducts ($CDCl_3$ Solutions)**

| | absorption, ppm | | | | | |
|---|---|---|---|---|---|---|
| | 7 | 8 | 9 | 10 | 11 | 12 |
| H-8 | 8.30 | 8.55 | 7.67 | 8.10 | 7.93 | 8.35 |
| H-11 | 7.33 | 6.93 | 6.79 | 6.42 | 7.34 | 6.97 |
| C-8 | 151.9 | 115.5 | 156.1 | 102.9 | 148.8 | 116.0 |
| C-11 | 118.9 | 146.3 | 106.0 | 137.2 | 119.3 | 147.6 |

after 3 h a 3:1 mixture of **7** and **8** in 75% combined yield after medium-pressure liquid chromatography (MPLC) on silica gel. Although repeated attempts to effect separation

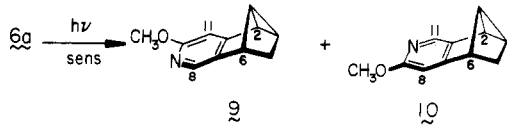


of these relatively labile isomers proved unsuccessful, the large imbalance in their relative proportion allowed individual spectral assignments to be made with confidence.

As usual for the tetracyclo[5.4.0.0$^{2,4}$.0$^{3,6}$]undeca-1-(7),8,10-triene framework found in **7** and **8**, the six aliphatic protons in each photoproduct display at 300 MHz distinctly different chemical shifts, with multiplicities unequivocally diagnostic of their specific position.[2-6] However, the small differences in the relative location of these upfield signals in **7** and **8** are not conducive to a convincing solution of the structural assignment question. On the other hand, the aryl regions are appropriately distinctive in their $^1H$ and $^{13}C$ NMR spectra. Thus, while H-8 in **7** appears at $\delta$ 8.30, the corresponding proton in **8** (H-11) is shifted downfield to $\delta$ 8.55 as a consequence of deshielding by the neighboring cyclopropane ring.[9] The inductive and mesomeric contributions of an aryl-fused cyclopropane ring are known to shield the ortho and para carbon atoms to a greater extent than the meta.[10] On this basis, the expectation is that C-8 in **7** (151.9 ppm) should appear downfield of C-11 in **8** (146.3 ppm), and this is indeed observed. In view of the excellent correlation of these data with those observed for the other compounds examined in this study (Table I), it is assured that **7** is the major photoproduct of **3**.

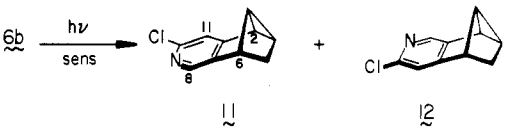
When photoexcited under comparable conditions, the *N*-oxide **4** was gradually converted to an insoluble brown polymer. Spectral analysis of aliquots taken at various time intervals gave a hint that very small amounts of di-$\pi$-methane product(s) might be present. However, all attempts to isolate material corresponding to these weak $^1H$ NMR signals were uniformly to no avail.

The acetophenone-sensitized irradiation of **6a** promoted efficient conversion to an 85:15 mixture of two readily separable and noticeably more stable photoisomers (92.6% isolated). The gross structures of these products were easily deduced to be **9** and **10**. The major constituent was



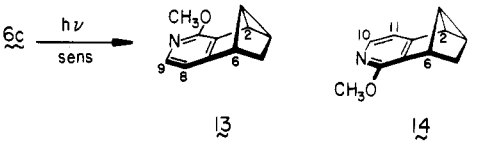
identified as **9** on the strength of chemical shift comparisons with **10** and nuclear Overhauser experiments carried out on both isomers at 500 MHz. The consequences of cyclopropane anisotropy happen again to be well defined in these compounds, as reflected in the appearance of H-8 in **9** ($\delta$ 7.67) upfield of the signal corresponding to H-11 in **10** ($\delta$ 8.10). Reciprocal effects are seen in H-11 of **9** ($\delta$ 6.79) and its counterpart (H-8) in **10** ($\delta$ 6.42, see Table I). Double irradiation experiments proved nicely confirmatory. In the case of **9**, separate irradiation of H-2 and H-6 gave rise to approximately 2% NOE enhancements of the integrals for H-11 and H-8, respectively. Precisely the reverse set of interactions was noted for **10**.

Our attention was next directed to **6b**, comparable triplet-sensitized irradiation of which proceeded to give a 79:21 mixture of **11** and **12** in 55% yield. These tetracycloundecatrienes were sufficiently stable to allow for chromatographic separation. Spectral analysis revealed



a direct parallelism of chemical shift parameters with those for **7**–**10** (Table I). Additional confirmation of **11** as the dominant photoproduct was gained as before by NOE experiments. While irradiation of H-2 caused a 2.5% enhancement in the H-11 signal, analogous perturbation of H-6 induced a somewhat smaller effect on H-8. Consequently, the proximal relationship of these pairs of protons is established.

Photoisomerization of the methoxy positional isomer **6c** proved unique in that a single tetracycloundecatriene was produced in this instance (73% isolated following chromatographic separation from the sensitizer). In the absence of a second regioisomer, comparative analysis of the proton and carbon shifts from the pyridine ring becomes, of course, impossible. The structural assignment to **13**



rests entirely on convincing NOE findings. Strikingly, irradiation of H-2 ($\delta$ 2.64) had absolutely no effect on either pyridine ring proton, indicating that C-11 was substituted with a group other than hydrogen. This is not the case in **14**, which consequently can be dismissed on this basis alone. However, further analysis revealed that irradiation of H-6 does indeed induce a 2% NOE enhancement in the integral of the H-8 absorption ($\delta$ 6.64). That the photoproduct is indeed **13** was independently ascertained by double irradiation of both pyridine proton signals. As expected, the proton immediately adjacent to nitrogen ($\delta$ 7.89) had no effect, while the second at $\delta$ 6.64 perturbed only the non-cyclopropyl bridgehead proton H-6 ($\delta$ 3.31).

## Discussion

The primary photoproducts of the sensitized irradiation of 5,8-dihydro-5,8-methanoisoquinoline (**3**) are **7** (75%) and **8** (25%). Their dual formation indicates that pyridine nitrogen is not capable of directing di-$\pi$-methane rearrangement exclusively along one reaction channel, although involvement of the para carbon is heavily favored. This excited-state regiochemical preference conforms in direction to that anticipated from the differences in electron densities present in the SOMO of the pyridine molecule.[4,5,11] In this connection, the earlier ab initio molecular

(9) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; pp 98–101.
(10) Kalinowski, H.-O.; Berger, S.; Braun, S. "$^{13}C$-NMR-Spektroskopie", Georg Thieme Verlag: Stuttgart, 1984; p 284.

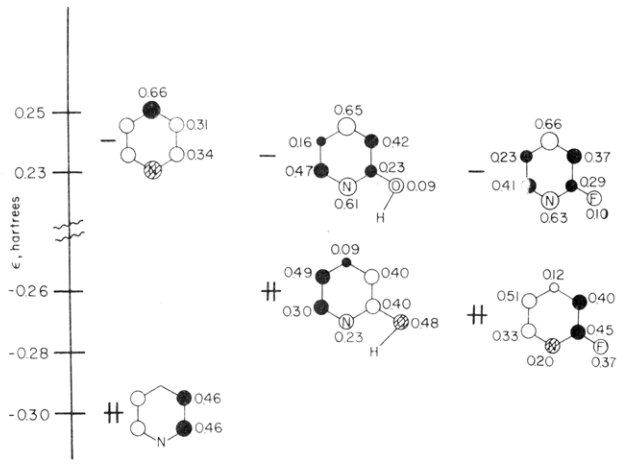



**Figure 1.** HOMO–SOMO orbitals and electron densities of pyridine and its syn-2-hydroxy and -2-fluoro derivatives.[12]

orbital study of Del Bene[12] has proven useful. As seen in Figure 1, the effect of the nitrogen substituent in the first excited state of pyridine is to provide greater electron density to $C_{para}$ than to $C_{meta}$. Although this simple model does not take into account the extent of donor–acceptor interaction present in **3**,[13] it correctly predicts the major isomerization pathway.

The data of Figure 1 reveal further that introduction of a syn-hydroxyl group at C-2 of a pyridine ring does not cause C-4 to lose its position as the site of highest electron density in the SOMO. On the assumption that the much smaller change of OH for $OCH_3$ will have minimal additional effect,[14] **6a** would be expected to photoisomerize predominantly to **9**. Experimentally, regiocontrol in this direction is encountered to the extent of 85%.

The behavior of **6a** can also be considered from a different viewpoint. Specifically, the conversion of **9** is favored by both the pyridine nitrogen and the "meta"-methoxyl group.[15] By use of the ratios of isomers formed from the individual monosubstituted compounds as an index of the preference for photoisomerization, the predicted product ratio (75/25 × 78/22 = 91:9) compares quite favorably with that observed following sensitized excitation of **6a** (85:15). This correspondence, which falls within experimental error of the observed ratios, implies that substituent effects may be additive, at least when the pendant hetaryl substituent is positioned "meta" on the 5,8-methanoisoquinoline framework.

Del Bene did not examine 2-chloropyridine but did give attention to the 2-fluoro derivative (Figure 1).[12] An electronic perturbation of this magnitude still does not override the now-standard pattern of dominant electron density at C-4 in the SOMO. The photochemistry of "meta"-F benzonorbornadiene has been earlier studied and found to parallel "meta"-$OCH_3$ in direction, although with somewhat greater regiocontrol (91:9).[3] Consequently, the chlorine and nitrogen atoms in **6b** can be expected to likewise work cooperatively and bring about favored conversion to **11**. In agreement with this analysis, the relative percentage of **11** was found to be 79%.

In contrast, the two heteroatomic centers in **6c** are positioned to direct in an antagonist fashion: the ring nitrogen should promote migration of $C_{para}$ and formation of **14**, while the "ortho"-methoxyl should promote involvement of the immediately adjacent pyridine carbon and give **13**. The first photoisomerization pathway does not operate. Rather, the "ortho"-$OCH_3$ substituent heavily dominates in control of the excited-state regioselectivity. The anomalously high methoxyl-directing influence might be ascribed to the $\pi$-electron densities peculiar to a substituted pyridine ring. In this connection, Figure 1 suggests that **6a** should be *more* selective than **6c** if SOMO interactions are the more important. Thus, the SOMO coefficients reveal $C_{para}$ to be much more favored ($C_{para}$–$C_{meta}$ = 0.49) in **6a** than in **6c** ($C_{para}$–$C_{meta}$ = 0.23). This conclusion goes contrary to experimental fact and may signal that the use of AO coefficients as indicators of $\pi$-electron density need not necessarily be a sound practice. However, comparable consideration of the respective HOMO coefficients indicates that destabilization of a radical center by $C_{meta}$ should be greater in **6a** (0.09) than in **6c** (0.40), thus forecasting the latter to be *more* selective. This conclusion holds fascination because MO calculations and photoelectron studies carried out on both aryl–$OCH_3$-substituted benzonorbornadienes have previously suggested that while the SOMO is the discriminating regioselectivity factor where "meta" $OCH_3$ is concerned, the HOMO plays that role in the "ortho" $OCH_3$ example.[13] This end result probably arises from a substantial enhancement of vinyl orbital contribution to the dominant excited-state configuration in the ortho-substituted cases. Thus, to the extent that **6c** undergoes photorearrangement under HOMO control, **13** should be preferred. Although this analysis is entirely consistent with earlier observations,[4,5c,13] it must be kept in mind that the multiconfigurational nature of excited triplets makes it impossible to verify this hypothesis from inspection of ground-state orbitals. Subtle points of this type likely await future calculations carried out directly on triplet-state species.

The data of Figure 1 clearly are not sufficient to predict rationally which orbital, the HOMO or SOMO, might play the discriminating role in regioselectivity control. This point is intertwined to some extent with the mechanism of these reactions. As discussed earlier,[6a,b] two options are available. The first is an "aryl–vinyl bridging" scheme[16] that entails transient disruption of aromatic character of the benzene or pyridine ring. The second, the "1,2-aryl shift" process, bypasses loss of resonance stabilization and proceeds directly to the 1,3-biradical eventually produced in the first mechanism. Both pathways are dependent upon the initial involvement of a $p_\pi$ aryl orbital whether for bridging or for migration to an olefinic carbon. Polarization effects by ethylene perturbation is consequently of potential import. As a consequence, the results described herein do not allow for a resolution of this long-standing mechanistic dichotomy.

## Experimental Section

**5,8-Dihydro-5,8-methanoisoquinoline (3)**:[7] $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.35 (s, 1 H), 8.15 (d, $J$ = 5.0 Hz, 1 H), 7.10 (d,

(11) Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 3380.
(12) 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.
(13) Santiago, C.; McAlduff, E. J.; Houk, K. N.; Snow, R. A.; Paquette, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 6149.
(14) For pertinent photoelectron spectroscopy studies, consult: (a) Pfister-Guillouzo, G.; Guimon, C.; Frank, J.; Ellison, J.; Katritzky, A. *Liebigs Ann. Chem.* **1981**, 366. (b) Cook, M. J.; El-Abbady, S.; Katritzky, A.; Guimon, C.; Pfister-Guillouzo, G. *J. Chem. Soc., Perkin Trans 2* **1977**, 1652. (c) Bursten, B. E.; Cotton, F. A.; Cowley, A. H.; Hanson, B. E.; Lattman, M.; Stanley, G. G. *J. Am. Chem. Soc.* **1979**, *101*, 6244.
(15) The terms "meta" and "ortho" are intended to deal with the locus of substitution on the 5,8-dihydro-5,8-methanoisoquinoline framework as a whole rather than the pyridine ring specifically.
(16) (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531. (b) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Essay 16, pp 131–164.

$J$ = 5.0 Hz, 1 H), 6.70 (dq, $J$ = 5.4, 3.0 Hz, 2 H), 3.81 (m, 1 H), 3.79 (br s, 1 H), 2.36 (dt, $J$ = 7.3, 2.6 Hz, 1 H), 1.83 (dt, $J$ = 7.3, 1.6 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 161.6, 147.0, 146.5, 143.3, 141.8, 141.3, 117.5, 70.2, 50.2, 47.9 ppm.

**General Dehydrohalogenation Procedure. 3-Methoxy-5,8-dihydro-5,8-methanoisoquinoline (6a).** A solution of freshly sublimed potassium *tert*-butoxide (127 mg, 1.13 mmol) in dry dimethyl sulfoxide (4 mL) was stirred at 0 °C under a nitrogen atmosphere as a solution of **5a**[7] (75.2 mg, 0.36 mmol) was introduced dropwise via syringe during 5 min. The reaction mixture was stirred at room temperature for 4 h prior to being poured into water (25 mL). The product was extracted into petroleum ether (4 × 30 mL), and the combined organic phases were washed with water (2 × 40 mL) and brine (40 mL) prior to drying. Solvent evaporation furnished 47 mg (75%) of **6a** as a colorless solid, mp 55 °C.

**5a**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.92 (s, 1 H), 6.56 (s, 1 H), 3.89 (s, 3 H), 3.50 (s, 1 H), 2.90 (d, $J$ = 2.1 Hz, 1 H), 2.24 (dt, $J$ = 1.3, 9.5 Hz, 1 H), 2.13 (dq, $J$ = 3.0, 13.4 Hz, 1 H), 2.05–1.85 (m, 3 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 163.4, 160.5, 138.7, 132.9, 103.9, 58.9, 53.4, 49.9, 45.7, 43.4, 40.3 ppm.

**6a**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.82 (s, 1 H), 6.73 (dd, $J$ = 3.0, 5.2 Hz, 1 H), 6.65 (s, 1 H), 6.63 (dd, $J$ = 3.0, 5.3 Hz, 1 H), 3.87 (s, 4 H, methoxyl and one bridgehead proton), 3.82 (br s, 1 H), 2.28 (dt, $J$ = 1.5, 7.4 Hz, 1 H), 2.14 (dt, $J$ = 1.5, 7.2 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 164.3, 161.2, 143.2, 140.7, 139.1, 136.2, 105.7, 67.8, 53.4, 49.9, 46.8 ppm.

**3-Chloro-5,8-dihydro-5,8-methanoisoquinoline (6b).** Reaction of **5b** (97 mg, 0.45 mmol) with potassium *tert*-butoxide (129 mg, 1.13 mmol) in dry dimethyl sulfoxide (4 mL) at 25 °C for 75 min in the predescribed manner provided 59 mg (74%) of **6b** as a colorless oil.

**5b**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.19 (s, 1 H), 7.15 (s, 1 H), 3.88 (dt, $J$ = 2.7, 6.2 Hz, 1 H), 3.57 (br s, 1 H), 3.44 (d, $J$ = 3.2 Hz, 1 H), 2.88 (dt, $J$ = 1.4, 9.8 Hz, 1 H), 2.17 (dt, $J$ = 4.1, 13.7 Hz, 1 H), 2.03–1.96 (m, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 161.7, 149.7, 141.9, 139.0, 117.4, 57.7, 50.2, 46.6, 43.7, 39.7 ppm.

**6b**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.07 (s, 1 H), 6.80 (s, 1 H), 6.77 (dd, $J$ = 3.1, 5.4 Hz, 1 H), 6.69 (dd, $J$ = 3.1, 5.2 Hz, 1 H), 3.92 (br s, 1 H), 3.88 (br s, 1 H), 2.34 (dt, $J$ = 1.5, 7.6 Hz, 1 H), 2.21 (d, $J$ = 7.6 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 165.7, 147.5, 146.4, 143.4, 141.4, 140.2, 118.4, 69.7, 50.2, 47.4 ppm.

**1-Methoxy-5,8-dihydro-5,8-methanoisoquinoline (6c).** Exposure of **5c** (110 mg, 0.526 mmol) to potassium *tert*-butoxide (210 mg, 1.87 mmol) in dry dimethyl sulfoxide (5 mL) with stirring at 25 °C for 3 h according to the usual procedure gave 67 mg (74%) of **6c** as a colorless oil.

**5c**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.95 (d, $J$ = 5.0 Hz, 1 H), 6.76 (d, $J$ = 5.0 Hz, 1 H), 3.93 (s, 3 H), 3.87 (dt, $J$ = 1.7, 4.0 Hz, 1 H), 3.64 (br s, 1 H), 3.37 (dd, $J$ = 1.1, 3.4 Hz, 1 H), 2.19 (dt, $J$ = 1.3, 9.1 Hz, 1 H), 2.13–2.07 (m, 1 H), 1.97–1.90 (m, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 160.9, 158.8, 146.1, 124.7, 110.9, 57.9, 53.2, 48.6, 46.5, 43.9, 40.1 ppm.

**6c**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.84 (d, $J$ = 4.8 Hz, 1 H), 6.93 (d, $J$ = 4.8 Hz, 1 H), 6.86 (dd, $J$ = 3.1, 5.3 Hz, 1 H), 6.75 (dd, $J$ = 3.1, 5.2 Hz, 1 H), 4.04 (br s, 1 H), 3.96 (s, 3 H), 3.92 (br d, $J$ = 1.2 Hz, 1 H), 2.31 (dt, $J$ = 1.6, 7.2 Hz, 1 H), 2.23 (br d, $J$ = 7.2 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 165.5, 158.2, 143.7, 143.4, 142.2, 132.2, 112.6, 71.1, 53.1, 51.0, 46.1 ppm.

**General Photoisomerization Procedure. 5,8-Dihydro-5,8-methanoisoquinoline (3).** A solution of **3** (67 mg, 0.468 mmol) and acetophenone (3 drops) in dry benzene (45 mL) was placed in a Pyrex tube and deoxygenated 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 30% ethyl acetate in petroleum ether). There was isolated 50 mg (75%) of a 3:1 mixture ($^1$H NMR and HPLC analysis) of **7** and **8**. These rather unstable substances proved not to be separable under various conditions. Although some of the $^1$H absorptions of the minor component were obscured by larger peaks due to **7**, the following assignments could be reliably culled from the spectra.

**7**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.30 (s, 1 H), 8.1 (br s, 1 H), 7.33 (d, $J$ = 2.8 Hz, 1 H), 3.41 (dt, $J$ = 2.7, 7.4 Hz, 1 H), 3.35 (br m, 1 H), 2.95–2.88 (br m, 1 H), 2.52 (t, $J$ = 5.1 Hz, 1 H), 2.10 (m, 1 H), 0.74 (dd, $J$ = 2.6, 9.0 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 158.1, 151.9, 147.7, 139.9, 118.9, 47.1, 41.2, 29.5, 29.2, 20.0 ppm; mass spectrum, $m/z$ ($M^+$) calcd for $C_{10}H_9N$ 143.0735, obsd 143.0725.

**8**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.55 (s, 1 H), 8.1 (br s, 1 H), 6.93 (d, $J$ = 2.8 Hz, 1 H), [signal for bridgehead proton obscured], 3.25 (m, 1 H) [signal for $H5_{exo}$ obscured], 2.54 (t, $J$ = 5.2 Hz, 1 H), 1.95 (m, 1 H), 0.67 (dd, $J$ = 1.7, 6.0 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 157.0, 146.1, 143.4, 140.7, 115.5, 45.3, 43.1, 29.1, 27.2, 19.2 ppm; mass spectrum, $m/z$ ($M^+$) calcd for $C_{10}H_9N$ 143.0735, obsd 143.0732.

**Photoisomerization of 3-Methoxy-5,8-dihydro-5,8-methanoisoquinoline (6a).** A solution of **6a** (42 mg, 0.242 mmol) and acetophenone (2 drops) in benzene (40 mL) was irradiated in the predescribed manner for 10 h. Solvent removal and purification of the residue by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether) resulted in the isolation of 33.1 mg (78.8%) of **9** and 5.8 mg (13.8%) of **10**.

**9**: colorless oil; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.67 (s, 1 H), 6.79 (s, 1 H), 3.90 (s, 3 H), 3.36–3.30 (m, 2 H), 2.86 (m, 1 H), 2.44 (t, $J$ = 5.0 Hz, 1 H), 2.04 (m, 1 H), 0.81 (dd, $J$ = 2.7, 8.8 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 163.2, 156.1, 138.4, 135.3, 106.0, 53.6, 46.1, 40.2, 29.9, 29.3, 20.5 ppm; mass spectrum, $m/z$ ($M^+$) calcd for $C_{11}H_{11}NO$ 173.0841, obsd 173.0847.

**10**: colorless oil; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.10 (s, 1 H), 6.42 (s, 1 H), 3.92 (s, 3 H), 3.31 (dt, $J$ = 2.4, 7.7 Hz, 1 H), 3.2 (m, 1 H), 2.90 (m, 1 H), 2.51 (t, $J$ = 5.1 Hz, 1 H), 2.00 (m, 1 H), 0.80 (dd, $J$ = 2.6, 9.2 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 161.4, 137.2, 132.4, 102.9 (2 C), 54.8, 43.6, 43.0, 29.4, 26.1, 19.2 ppm; mass spectrum, $m/z$ ($M^+$) calcd for $C_{11}H_{11}NO$ 173.0841, obsd 173.0849.

**Photoisomerization of 3-Chloro-5,8-dihydro-5,8-methanoisoquinoline (6b).** A solution of **6b** (59 mg, 0.333 mmol) and acetophenone (3 drops) in benzene (50 mL) was irradiated as before for 9 h. Solvent removal and purification of the residue by MPLC on silica gel (elution with 8% ethyl acetate in petroleum ether) afforded 25.7 mg (43.6%) of **11** and 6.7 mg (11.4%) of **12**.

**11**: colorless oil; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.93 (s, 1 H), 7.34 (s, 1 H), 3.44–3.39 (m, 2 H), 2.97–2.91 (m, 1 H), 2.52 (t, $J$ = 5.1 Hz, 1 H), 2.13 (m, 1 H), 0.77 (dd, $J$ = 2.6, 9.6 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 155.9, 148.8, 143.7, 139.3, 119.3, 47.7, 40.5, 29.4, 29.2, 20.5 ppm; mass spectrum, $m/z$ ($M^+$) calcd for $C_{10}H_8ClN$ 177.0345, obsd 177.0326.

**15**: colorless solid, mp 41–42.5 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.35 (s, 1 H), 6.97 (s, 1 H), 3.40–3.25 (m, 2 H), 3.00–2.85 (m, 1 H), 2.57 (t, $J$ = 5.0 Hz, 1 H), 2.15–2.05 (m, 1 H), 0.77 (dd, $J$ = 2.6, 9.1 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 161.8, 147.6, 143.0, 137.7, 116.0, 45.4, 42.8, 29.0, 26.5, 19.3 ppm; mass spectrum, $m/z$ ($M^+$) calcd for $C_{10}H_8ClN$ 177.0345, obsd 177.0341.

**Photoisomerization of 1-Methoxy-5,8-dihydro-5,8-methanoisoquinoline (6c).** A solution of **6c** (52 mg, 0.30 mmol) and acetophenone (2 drops) in dry benzene (45 mL) was irradiated in the usual manner for 5 h. Solvent evaporation and MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether) delivered 38 mg (73%) of **13** as the only product observed: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.89 (d, $J$ = 5.0 Hz, 1 H), 6.64 (d, $J$ = 5 Hz, 1 H), 4.02 (s, 3 H), 3.31 (dt, $J$ = 2.6, 7.7 Hz, 1 H), 3.18 (m, 1 H), 2.87 (m, 1 H), 2.64 (t, $J$ = 5.2 Hz, 1 H), 2.07 (m, 1 H), 0.68 (dd, $J$ = 2.6, 9.0 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 160.8, 160.5, 143.6, 123.0, 110.3, 53.1, 44.6, 43.5, 29.2, 25.3, 19.0 ppm; mass spectrum, $m/z$ ($M^+$) calcd for $C_{11}H_{11}NO$ 173.0841, obsd 173.0835.

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