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FORMATION OF A DINAPHTHANTHRACENE BY A STILBENE-LIKE PHOTOCYCLIZATION[1]

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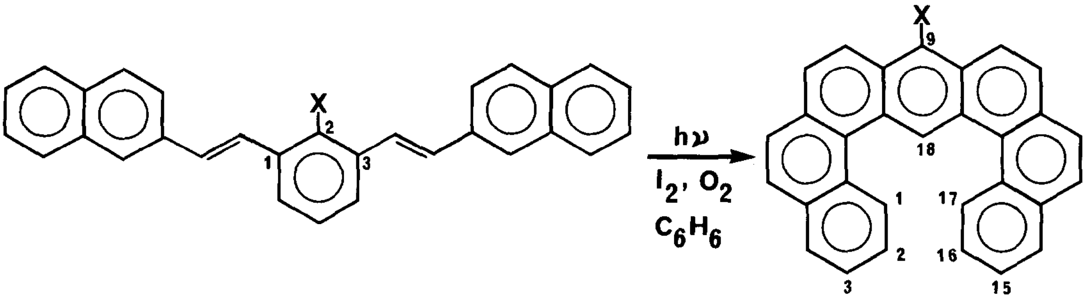
Abstract: Photocyclization of 1,3-bis[2-(2-naphthyl)vinyl]benzene leads regioselectively to dinaphth[1,2-*a*:2',1'-*j*]anthracene without the need for a blocking bromine substituent at C-2 in the starting material as assumed previously by other workers.

Ultraviolet irradiation of bromo compound 1 in the presence of iodine and oxygen in benzene solution has been reported by Wilcox and coworkers to produce, in 62% yield, the 9-bromo derivative 2 of dinaphth[1,2-*a*:2',1'-*j*]anthracene, an interesting and novel polynuclear aromatic system.[3] It was reasoned[3] that the bromine substituent in 1, by blocking any competing ring closure at C-2 of the benzene ring, played a crucial regiochemical role in directing this double stilbene-like photocyclization toward the formation of 2. We were intrigued by this interpretation because previously reported attempts to use bromine as a blocking substituent to control the regiochemistry of stilbene-like photocyclizations in polynuclear aromatic systems with more than one ring-closure pathway have met with little[4] or no[5] success. Therefore we undertook a photochemical study of the compound lacking the bromine substituent, hydrocarbon 3.[6]

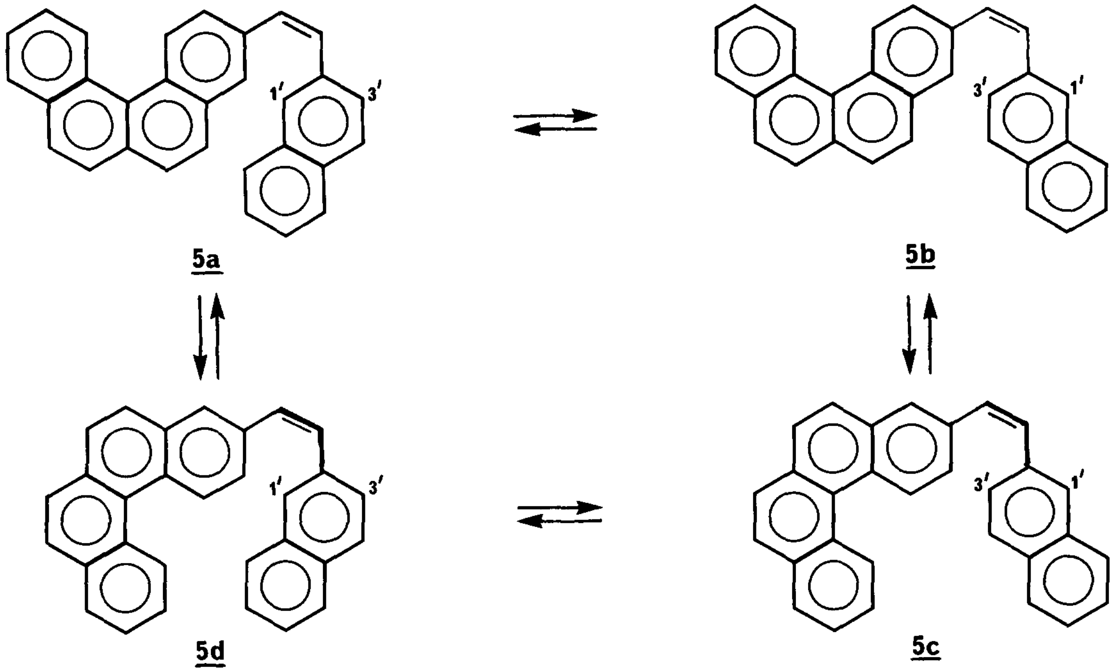


1 X = Br
3 X = H

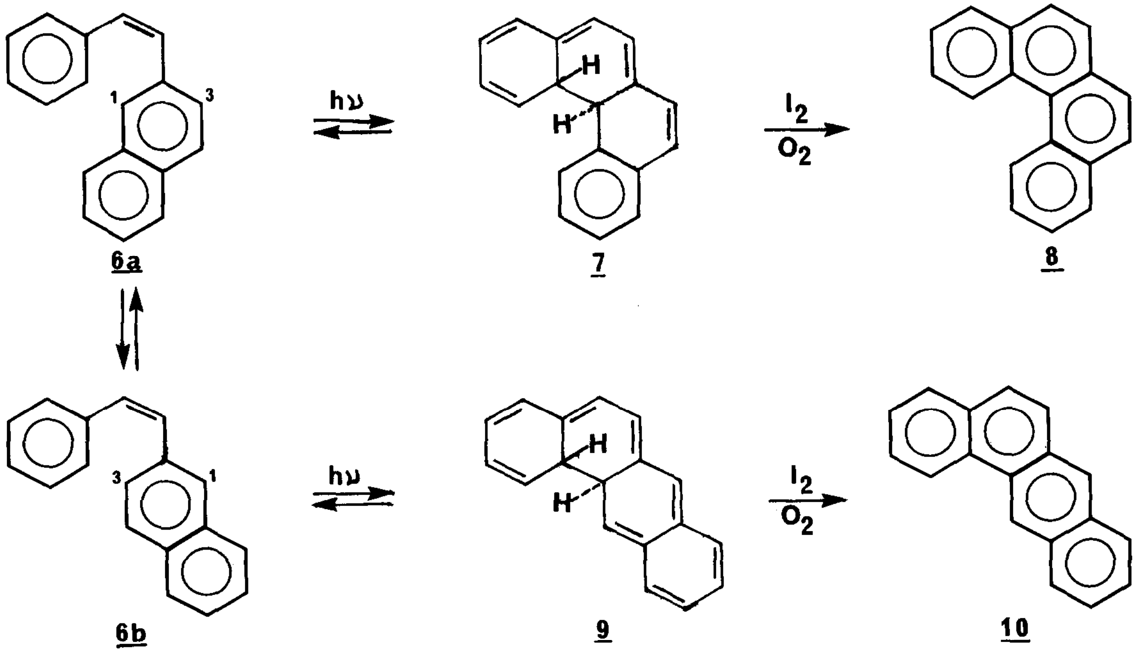
2 X = Br
4 X = H

We report here our experimental finding that ultraviolet irradiation of 3 in xylene solution in the presence of iodine and oxygen gives the parent dinaphthanthracene 4 in 75% yield![7] This result implies that the bromine substituent in 1 does *not* serve as a blocking group in the photochemical transformation of 1 to 2.

It remains to account for the observed regioselectivity in the photochemical conversion of 3 to 4. We presume that the first steps in this overall transformation are unexceptional: trans ⟶ cis photoisomerization of one of the olefinic linkages of 3, stilbene-like photocyclization of the resulting cis-diarylethylene unit to give the usual sort of dihydroaromatic intermediate,[8] oxidative trapping of that intermediate,[8] and then a second trans ⟶ cis photoisomerization[9] to give an interconverting set of four conformers, 5a-d. The challenge is to explain why the final steps, comprising the second oxidative photocyclization, seem to proceed selectively through conformer 5d to give the observed product 4.

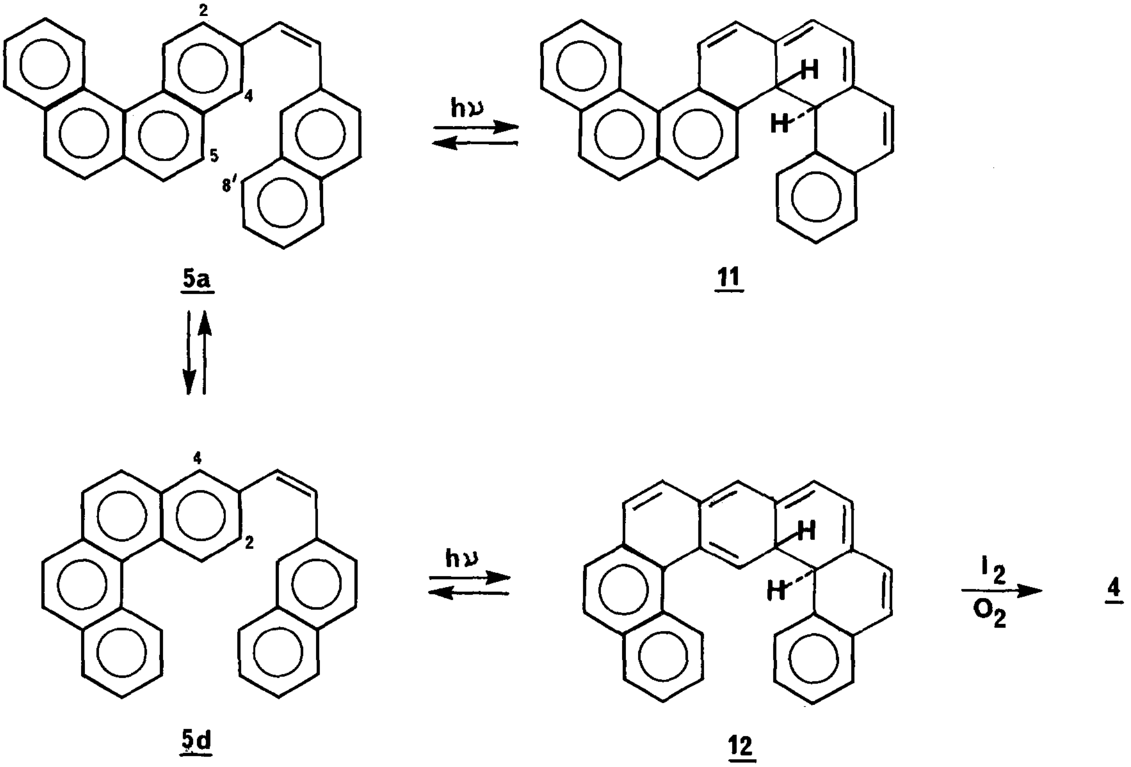


The apparent unimportance of photocyclization involving conformers 5b and 5c can be rationalized as a manifestation of the high regioselectivity normally exhibited by 2-naphthyl groups in photocyclizations of this type.[10] For example, the cis-2-styrylnaphthalene system 6a ⇄ 6b



undergoes oxidative photocyclization almost exclusively by way of the more resonance-stabilized dihydroaromatic intermediate 7 to give benzo[c]phenanthrene 8 rather than by way of the less resonance-stabilized dihydroaromatic intermediate 9 to give benz[a]anthracene 10; the maximum 10/8 product ratio, achieved at high iodine concentrations such that both intermediates 7 and 9 are trapped oxidatively with 100% efficiency in competition with the 7 ⟶ 6a and the faster 9 ⟶ 6b ring openings, is only 1.5/98.5.[10] This strong preference for ring closure at C-1 rather than C-3 of the 2-naphthyl group seems well understood theoretically.[11]

The apparent preference for photochemical ring closure of the 3-benzo[c]phenanthryl group in this system at C-2 in conformer 5d rather than at C-4 in conformer 5a, even though dihydroaromatic intermediate 12 has *less* resonance stabilization than dihydroaromatic intermediate 11, can be rationalized by noting the unfavorable steric interactions that would develop between the 5 and 8' positions during the photocyclization of 5a to 11. Similar steric effects have been invoked in related systems.[12]



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6. For the preparation of 3, the bistriphenylphosphonium salt obtained from the reaction of α, α'-dibromo-*m*-xylene with triphenylphosphine was treated with sodium ethoxide in ethanol and the resulting ylid was subjected to a Wittig reaction with 2-naphthaldehyde. The crude product was treated with iodine in refluxing benzene to effect olefinic cis ⟶ trans isomerization. Purification by recrystallization from xylene gave *trans,trans*-1,3-bis[2-(2-naphthyl)vinyl]benzene 3 as white crystals, mp 267.0-269.5 °C: ^{1}H NMR (200 MHz, CS_2) δ 7.74-7.09 (complex m, 18 H, aromatic protons), 7.21 and 7.14 (AB q, 4 H, trans olefinic protons, J_{AB} = 16 Hz); IR (KBr) 961 cm^{-1} (trans -CH=CH-); UV (cyclohexane) λ_{max} 217, 229, 253, 274, 283, 322 nm; MS, *m/z* 382 (M^+).
7. For the preparation of 4, a solution of 100 mg (0.26 mmol) of 3 in 1.2 L of xylene containing 10 mg (0.04 mmol) of iodine was irradiated open to the air through pyrex with a 450-watt mercury lamp in a Hanovia immersion apparatus for 2 h until the reaction was judged complete by UV spectroscopy. The solution was rotary evaporated and the residue was chromatographed twice on alumina using 1:1 benzene/hexane to give 74 mg (75%) of dinaphth-[1,2-*a*:2',1'-*j*]anthracene 4 as a bright yellow solid: ^{1}H NMR (200 MHz, CS_2) δ 10.81 (s, 1 H, H-18), 9.02 (X part of ABX, 2 H, H-1 and H-17, $J_{1,2} + J_{1,3} = J_{16,17} + J_{15,17}$ = 9.7 Hz), 8.50 (s, 1 H, H-9), 8.01-7.16 (complex m, 14 H, other aromatic protons); MS, *m/z* 378 (M^+). The ^{1}H chemical shift for H-18 in 4 shows a large solvent effect, with δ values of 9.96 ppm in CD_3COCD_3, 10.81 ppm in CS_2, and 10.89 ppm in C_6D_6. A sample of 4 that had been purified further by sublimation at 200 °C and 0.005 torr followed by recrystallization from toluene/hexane gave material with mp 248.0-249.0 °C (evacuated capillary): UV (cyclohexane) λ_{max} (log ε) 247 (4.57), 256 (4.57), 283 (4.44), 296.5 (4.28), 318 (4.59), 332 (4.84), 364.5 (3.80), 382.5 (3.82), 403 nm (3.57). Anal. Calcd for $C_{30}H_{18}$: C, 95.24; H, 4.76. Found: C, 95.43; H, 4.85. The UV and NMR spectra of this final analytical sample differed only in minor ways from the corresponding spectra of the 74-mg sample described above.
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9. Whether the second trans ⟶ cis photoisomerization precedes or follows the first oxidative photocyclization is uncertain.
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