those isolated above. Recrystallization from methanol gave 22 mg (90%) of white plates: mp 91.0–91.5°; nmr ($CDCl_3$) multiplet at τ 2.8–3.2 (6 H, Ar*H*), a singlet at 6.28 (1 H, Ar*H*), a multiplet at 6.8–8.2 (8 H, ArCH_2–), and a singlet at 9.52 (3 H, ArCH_3).

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.64; H, 8.19.

Reaction of 8-Methyl[2.2]metacyclophan-1-ene with N-Bromosuccinimide. A solution of 110 mg of **4** (R_1 = $-CH_3$; R_2 = –H) and 115 mg of N-bromosuccinimide in 30 ml of carbon tetrachloride containing 5 mg of azobisisobutyronitrile was boiled under reflux for 2 hr. After removal of the succinimide and concentration of the filtrate, the residue was taken up in hexane and chromatographed over neutral alumina (Woelm, activity 1). No green absorption bands were evident. From the eluate two main fractions were isolated. The first contained 45 mg of recovered **4** (R_1 = $-CH_3$; R_2 = –H). The second contained 40 mg of white crystals, mp 154–156°, identical in all respects with an authentic specimen of pyrene.

Reaction of 8-Methyl[2.2]metacyclophan-1-ene with DDQ. A solution of 55 mg of **4** (R_1 = $-CH_3$; R_2 = –H) and 115 mg of 2,3-dichloro-5,6-dicyanoquinone (DDQ) in 20 ml of toluene was boiled under reflux for 2 hr. After concentration the residue was taken up in hexane and chromatographed over neutral alumina (Woelm, activity 1). The first eluate fraction contained 20 mg of recovered **4** (R_1 = $-CH_3$; R_2 = –H). The second eluate fraction contained 20 mg of a mixture of pyrene and 1-methylpyrene. This mixture could be separated by vapor phase chromatography using SE-30 on a Chromosorb W column at 255°. Under these conditions, pyrene had a retention time of 9 min and 1-methylpyrene, 13.5 min. The identity of the two samples was confirmed by spectral comparison with authentic specimens. Furthermore, the sample of 1-methylpyrene was converted to the corresponding picrate, obtained as yellow crystals, mp 209–210° (lit.[23] mp 211–212°).

Other attempts at dehydrogenation of **4** (R_1 = $-CH_3$; R_2 = –H) using tetrachloro-*p*-benzoquinone or tetrachloro-*o*-benzoquinone gave similar mixtures of pyrene and 1-methylpyrene. Furthermore, irradiation of either **4** (R_1 = $-CH_3$; R = –H) or **4** (R_1 = R_2 = –H) in hexane solution in the presence of oxygen gave in good yield 4,5-dihydropyrene (**28**), identical in all respects with the authentic specimen described previously.

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(23) H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Ann.*, 531, 112 (1937).

Photochromism of [2.2]Metacyclophan-1-enes and the Thermal Isomerization of 4,5,15,16-Tetrahydropyrenes[1-3]

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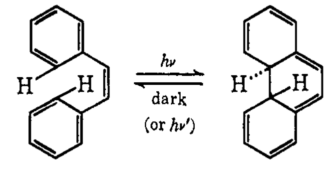
Abstract: Irradiation of [2.2]metacyclophan-1-enes (**3**, **4**, and **5**) with light in the region of 300 mμ gives photostationary equilibria in which the colored photoisomers, the 4,5,15,16-tetrahydropyrenes (**6**, **7**, and **8**), predominate. Such solutions of 4,5,15,16-tetrahydropyrenes are, in turn, bleached by light in the region of 500 mμ to give back the [2.2]metacyclophan-1-enes. The isomerization of 4,5,15,16-tetrahydropyrenes to their corresponding[2.2]-metacyclophan-1-enes also occurs thermally in the dark, and the kinetics of this thermal isomerization are discussed.

In 1940, Lewis, Magel, and Lipkin observed the formation of an unstable yellow intermediate during the low-temperature, ultraviolet irradiation of *cis*-stilbene (**1**) solutions.[4] Subsequent investigations have shown the unstable intermediate to be 4a,5a-dihydrophenanthrene (**2**),[5] and the easy oxidation of 4a,4b-dihydrophenanthrenes has made this an attractive synthetic route to phenanthrene derivatives.[6] More recently, Muszkat and Fischer have reported a detailed study of the photoisomerization of various *cis*-stilbenes to 4a,-4b-dihydrophenanthrenes as well as the reversal of this reaction either by light or thermally in the dark.[7] In an accompanying paper,[3] we have described the preparation of three [2.2]metacyclophan-1-enes (**3**, **4**, and **5**), which contain rigidly constrained *cis*-stilbene moieties. In view of the extensive and detailed studies by Muszkat and Fischer with the simple *cis*-stilbenes, it seemed appropriate to make a comparative study of the photoisomerization of our more rigid molecules as well as to examine the kinetics of the reverse, thermal, dark reaction.



1 **2**

In each case irradiation of solutions of the [2.2]-metacyclophan-1-enes (**3**, **4**, and **5**) led to a photostationary state in which the [2.2]metacyclophan-1-ene was in equilibrium with the corresponding 4,5,15,16-tetrahydropyrene (**6**, **7**, and **8**). As expected, the photoisomer **6** is extremely sensitive to oxygen, being readily oxidized to 4,5-dihydropyrene (**9**). This sensitivity of 4a,4b-dihydrophenanthrenes to oxygen has been well documented previously.[5-7] However, when the 4a and 4b positions are occupied by methyl rather than hy-

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(1) We thank the National Science Foundation and the Office of Naval Research (Contract Nonr-2771(OR), NR-055-468) for their support of this investigation.

(2) Abstracted from the doctoral dissertation of C. E. Ramey, University of Oregon, 1968.

(3) This is paper XXI in our series on "Aromatic Molecules Bearing Substituents within the Cavity of the π-Electron Cloud." For the preceding article, see H. Blaschke, C. E. Ramey, I. Calder, and V. Boekelheide, *J. Amer. Chem. Soc.*, 92, 3675 (1970).

(4) G. N. Lewis, T. T. Magel, and D. Lipkin, *ibid.*, 62, 2973 (1940).

(5) W. M. Moore, D. D. Morgan, and F. R. Stermitz, *ibid.*, 85, 829 (1963).

(6) F. B. Mallory, J. T. Gordon, and C. S. Wood, *ibid.*, 85, 828 (1963).

(7) K. A. Muszkat and E. Fischer, *J. Chem. Soc.*, *B*, 662 (1967).

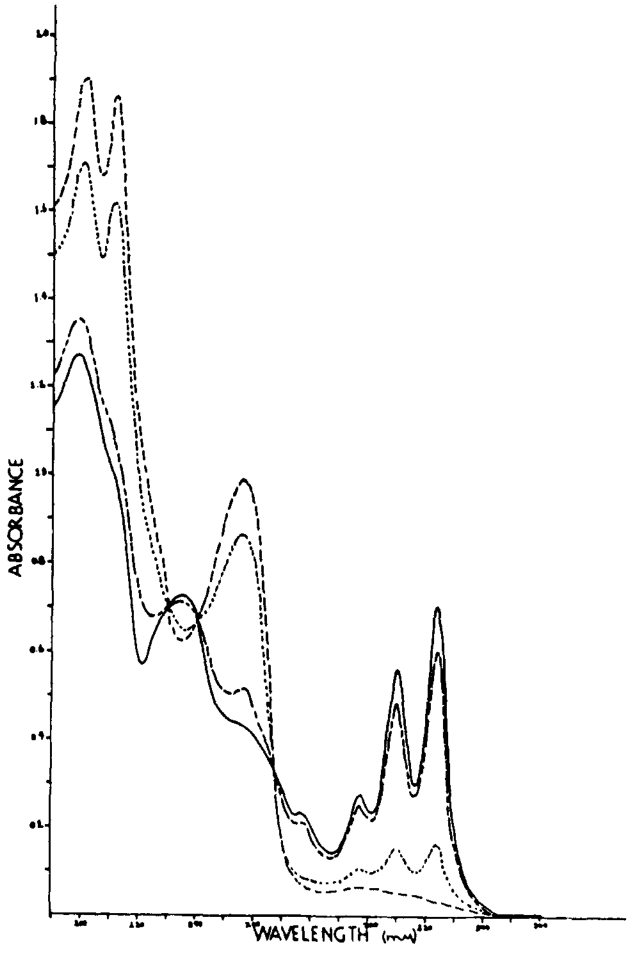
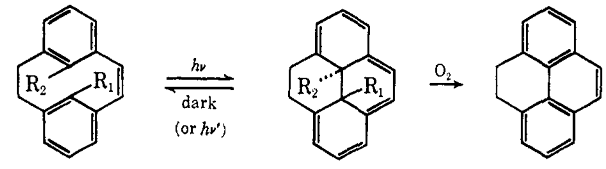


Figure 1. Ultraviolet spectra of the **5** ⇌ **8** photochromic system in cyclohexane solution. Spectrum of pure **5** is denoted by – – – –, spectrum of the mixture photoequilibrated at 254 mμ by — — —, spectrum of the mixture photoequilibrated at 310 mμ by - - - - -, and the calculated spectrum of pure **8** by ———. Spectra were measured with a Cary 14 spectrometer.

drogen, as in the case of **10** studied by Muszkat, Gegiou, and Fischer,[8] the photoisomer **11** is no longer sensitive to oxygen. Similarly, we found that **8** was not sensitive to oxygen and the photoequilibrium between **5** and **8** could be studied without interference from side reactions.

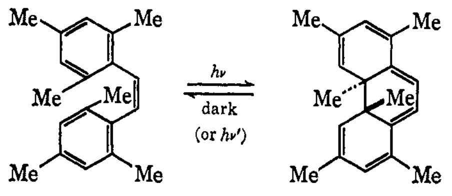


3, $R_1 = R_2 = -H$
4, $R_1 = -CH_3; R_2 = -H$
5, $R_1 = R_2 = -CH_3$

6, $R_1 = R_2 = -H$
7, $R_1 = -CH_3; R_2 = -H$
8, $R_1 = R_2 = -CH_3$

9

Unexpectedly, though, the monomethyl derivative **7** proved to be almost equally as sensitive to oxygen as the unsubstituted compound **6** itself. Again, the major product of the oxidation of **7** is 4,5-dihydropyrene (**9**).[3] The mechanism by which the methyl group is lost remains a mystery. The extreme sensitivity of **6** and **7** to oxygen, though, required that studies of their photochromism be done with carefully degassed solvents using a nitrogen atmosphere and sealed ampoules.



10 **11**

Because of the ease with which the photoisomers (**3**, **4**, and **5**) revert back to the [2.2]metacyclophan-1-enes both thermally and in the presence of light, it has not been possible to isolate any of these photoisomers in a pure state. However, as Fischer has shown,[9] the calculation of photostationary states for systems of the type A ⇌ B can be made even when only A is known in the pure state. This requires irradiation "to completion" using two different wavelengths of light and so providing two different photostationary states. If the assumption is made that the ratio of the quantum yields ϕ_A (A → B) to ϕ_B (B → A) does not differ at the two wavelengths, 1 and 2 can be derived

$$D_B = D_A + \Delta/\alpha \qquad (1)$$

$$\alpha_2 = \left(\frac{\Delta_1}{D_{A_1}} - \frac{\Delta_2}{D_{A_2}}\right) \Big/ \left[1 + \frac{\Delta_1}{D_{A_1}} - n\left(1 + \frac{\Delta_2}{D_{A_2}}\right)\right] \qquad (2)$$

where D_B = optical density of B at a particular wavelength, D_A = optical density of A at a particular wavelength, $\Delta = D_{obsd} - D_A$, α = extent of conversion A → B at this wavelength, $n = \alpha_1/\alpha_2$, where subscripts 1 and 2 indicate photostationary states for wavelengths 1 and 2, respectively. The numerical value of α_2 determined by eq 2 may then be used to calculate the spectrum of pure B by means of eq 1. This method was employed to obtain a calculated spectrum for **8**. Photoequilibration of a 4.26×10^{-5} *M* solution of **5** in cyclohexane was carried out at 254 and 310 mμ, respectively. This gave the following data: $n = \alpha_{254}/\alpha_{310} = 4.20$, $\Delta_{254} = 0.425$, $\Delta_{310} = 0.101$, $D_{254} = 0.840$, and $D_{310} = 0.057$.[10] The spectrum of 8,16-dimethyl[2.2]metacyclophan-1-ene (**5**), the spectra of the mixtures photoequilibrated at 254 and 310 mμ, and the calculated spectrum of the pure 15,16-dimethyl-4,5,15,16-tetrahydropyrene (**8**) are presented in Figure 1.[11]

The principal absorption bands and their extinction coefficients as calculated for **8** are listed in Table I. For comparison the corresponding data for **2** and **11**, which were obtained by Muszkat and Fischer by a similar extrapolation,[7] are also listed. Attempts to extend this method to **6** and **7** were not successful because of the extremely rapid reactions of these photoisomers with even traces of oxygen. The wavelengths of the principal maxima for **6** and **7** were estimated by subtraction though, and are included in Table I. Clearly the

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(8) K. A. Muszkat, D. Gegiou, and E. Fischer, *Chem. Commun.*, 447 (1965).

(9) E. Fischer, *J. Phys. Chem.*, 71, 3704 (1967).

(10) We thank Professor W. T. Simpson for the use of his Bausch and Lomb 250-mm grating monochromator to establish these photoequilibria.

(11) One practical benefit of this extrapolation is the following: If the assumption is made that the ratio of Φ_A/Φ_B does not change appreciably with a change in wavelength, then the greatest conversion of A to B will occur at a wavelength where the ratio of ϵ_A/ϵ_B is the greatest. Thus, for the photostationary states of **5** ⇌ **8**, the conversion of **5** to **8** at 254 mμ is 85% whereas, at 310 mμ, the conversion of **5** to **8** is only 20%. Thus, the choice of wavelength is very important in determining the extent of photoisomerization.

Table I. Ultraviolet and Visible Spectral Data of the Photoisomers[a]

λ_{max}, mμ (ε)				
6	7	8	2	11
237		235 (17,300)	237 (15,200)	245 (15,800)
	298	296 (6,430)	297 (20,700)	
305	308	309 (13,300)	310 (22,200)	310 (7,000)
318.5	322	323 (16,600)		320 (7,100)
487	500	532 (1,790)	450 (6,750)	475 (3,100)

[a] Solutions of **6**, **7**, and **8** in hexane and solutions of **2** and **11** in a 2:1 mixture of methylcyclohexane and isohexane.

bridging ethano group causes a bathochromic shift of the long wavelength absorption band just as does the presence of alkyl groups at the angular positions.

Photochemical evidence has been presented by Hammond and his colleagues[12] and by Muszkat and Fischer[7] that the ring closure of *cis*-stilbenes to 4a,4b-dihydrophenanthrenes takes place through the first excited singlet of the *cis*-stilbene molecule. An analysis of the changes of the symmetry of the molecular orbitals of *cis*-stilbene in its photoisomerization to 4a,4b-dihydrophenanthrene following the Woodward and Hoffmann rules[13,14] leads to the prediction of a conrotatory ring closure to form the *trans*-4a,4b-dihydrophenanthrene. Such an assignment has been made, though without proof.[7] Obviously, the same symmetry considerations apply to the photoisomerization of the [2.2]metacyclophan-1-enes to the 4,5,15,16-tetrahydropyrenes. However, because of the constrained nature of the [2.2]metacyclophan-1-enes only the conrotatory ring closure is possible and the photoisomers can only have the *trans* geometry. Thus, the stereochemical outcome of these photoisomerizations is in full accord with the orbital symmetry rules. Likewise, the orbital symmetry rules are in accord with the photoisomerization being reversible, as it clearly is. In fact irradiation of **6**, **7**, or **8** with light of a wavelength corresponding to their long wavelength absorption bands leads to a quick and complete conversion to the corresponding [2.2]metacyclophan-1-enes, which remain unaffected by light of this wavelength.

However, the relatively rapid thermal conversion of the 4,5,15,16-tetrahydropyrenes (**6**, **7**, and **8**) to their corresponding [2.2]metacyclophanes would not be predicted from orbital symmetry considerations, at least not as a concerted process. It seemed desirable, therefore, to examine the kinetics of these thermal reactions. In each case the reaction was followed by observing the decrease in absorption of the long wavelength absorption band of the tetrahydropyrene (**6**, **7**, and **8**). The reaction rates were first order throughout and measurements were made at several temperatures in order to obtain the activation parameters. The kinetic data are summarized in Table II.

In Table III the rate constants for these reactions extrapolated to 25° together with the related activation parameters are summarized. For comparison the comparable data reported by Muszkat and Fischer[7] on the reactions, **2** → **1** and **11** → **10**, are included. As shown in Figure 2, the activation entropies are related linearly to the heats of activation. Such an isokinetic relationship occurs frequently in a series of similar reactions and is usually explained as indicating that a lower activation

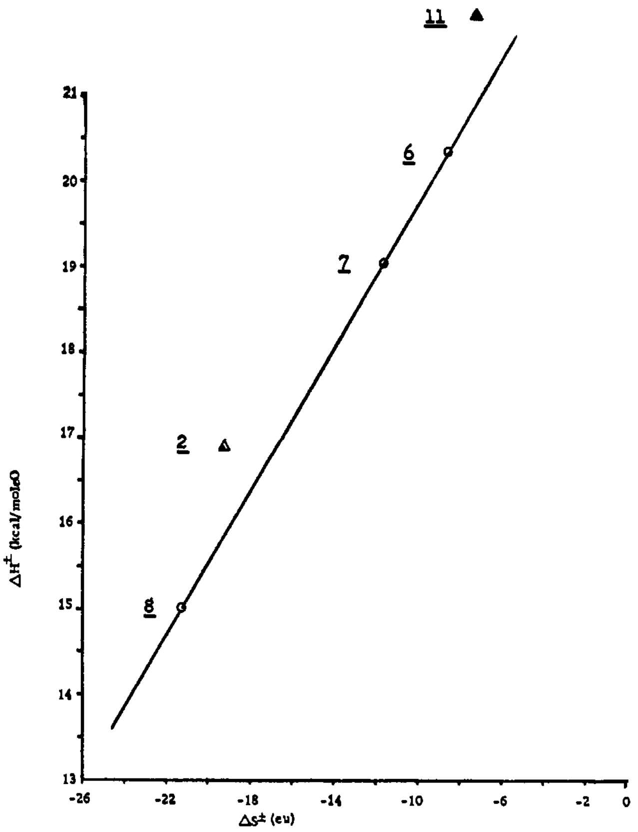

Figure 2. Plot of the heats of activation against the entropies of activation for the thermal isomerizations of **2**, **11**, **6**, **7**, and **8** to show the linear relationship between them.

Table II. Rates of Thermal Isomerization of Tetrahydropyrenes to [2.2]Metacyclophan-1-enes

Reaction	Temp, °C	Rate 10^3k, min^{-1}
6 → **3**	30	0.187 ± 0.001
	40	0.581 ± 0.001
	50	1.54 ± 0.03
	60	4.32 ± 0.08
7 → **4**	30	0.355 ± 0.005
	40	1.02 ± 0.01
	50	2.70 ± 0.05
	60	6.62 ± 0.07
8 → **5**	30	1.85 ± 0.05
	40	4.8 ± 0.10
	50	9.1 ± 0.15

Table III. Activation Parameters for the Thermal Isomerization of Tetrahydropyrenes to [2.2]Metacyclophan-1-enes

Reaction	Rate at 25°, 10^3k, min^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
6 → **3**	0.104	20.3 ± 0.3	−8.5 ± 1.2
7 → **4**	0.203	19.0 ± 0.4	−11.8 ± 2.4
8 → **5**	1.26	15.0 ± 1.2	−21.3 ± 4.0
2 → **1**	7.2	16.9	−19.5
11 → **10**	0.35	21.9	−5.5

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(12) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsel, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(13) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(14) H. C. Longuett-Higgins and E. N. Abrahamson, *ibid.*, **87**, 2045 (1965).

energy is associated with a more ordered transition state.[15]

The rate of thermal isomerization of **2** is about 20 times as fast as **11** and Muszkat and Fischer have interpreted this as a mass effect of the two methyl groups at the 4a and 4b positions requiring more energy for the stretching or twisting in bond fission of the 4a–4b bond in **11** than in the corresponding bond in **2**.

It might be expected that the reaction rates for thermal isomerization of the tetrahydropyrenes would show a similar retardation as methyl groups are substituted at the 15 and 16 positions. However, in fact, introduction of methyl groups at the 15 and 16 positions increases the rate so that the thermal isomerization of **8** is about ten times as fast as that of **6**. Obviously, the ethano bridge is responsible for considerable strain energy in the ground states of both the [2.2]metacyclophan-1-enes and the tetrahydropyrenes, but presumably the effect is larger in the case of the latter. Thus, on this interpretation, it would be the relief of this strain energy that is the factor responsible for the increased rates of **7** and **8** as compared to **6**. This effect is presumably more important than the type of mass effect invoked by Muszkat and Fischer to explain the difference in rates between **2** and **11**.

Experimental Section

Kinetic Measurements. Two solutions each were prepared by dissolving **6** (5.8 and 5.9 mg, respectively), **7** (5.8 and 4.6 mg, respectively), and **8** (5.0 and 5.4 mg, respectively) in 5.5 ml of cyclohexane in each case. Each solution was placed in a Pyrex ampoule and degassed thoroughly by carrying out ten freeze–thaw cycles on a high-vacuum system at 10^{-5} mm pressure. Each sample was then frozen and sealed under vacuum. After this each sample was equilibrated at the desired temperature for 15 min. While being held in the constant-temperature bath the solution was irradiated using an ultraviolet lamp for about 10 min. The sample was then transferred to a thermostated cell holder in a Cary 15 spectrometer and the rate of disappearance of the tetrahydropyrene was measured by continuously monitoring the absorption at the long wavelength band of the tetrahydropyrene. In the case of **6**, this was at 487 mμ; with **7**, it was at 500 mμ; and with **8**, measurements were made at 532 mμ. The data were collected and processed using a rate constant calculator with an IBM 360-50 computer.[16] Two rate runs were made with each sample at each temperature and the resulting data are summarized in Table II.

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(15) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, Chapter 9.

(16) C. E. Klopfenstein and C. Wilkins, "Chemistry 40 Rate Constant Calculator," University of Oregon, 1964.

A Synthesis of *trans*-1,3,15,16-Tetramethyl-15,16-dihydro-2-azapyrene[1-3]

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Contribution from the Department of Chemistry,
University of Oregon, Eugene, Oregon 97403. *Received October 7, 1969*

Abstract: Cyclization of the appropriate *cis*-stilbazole yields the [2.2]metacyclophan-1-ene **14**. Dehydrogenation of **14** by means of a ruthenium-on-alumina catalyst yields *trans*-1,3,15,16-tetramethyl-15,16-dihydro-2-azapyrene (**16**). Both **16** and its corresponding hydrochloride **15** are photochromic, undergoing isomerization to their valence tautomers **17** and **18**. The reverse thermal reaction of the hydrochloride (**18** → **15**) is extremely fast, whereas the rate of the thermal isomerization of the corresponding free base (**17** → **16**) is comparable to that of the corresponding hydrocarbons.

In an accompanying paper,[4] we have described a new route for the synthesis of *trans*-15,16-dihydropyrene derivatives. We now report the application of this method to the synthesis of a heterocyclic analog, *trans*-1,3,15,16-tetramethyl-15,16-dihydro-2-azapyrene (**16**).

The Hantzsch pyridine synthesis makes 3,5-dicarbethoxy-2,4,6-trimethylpyridine (**1**), a readily available starting material. Dependent upon the conditions used, reduction of **1** with lithium aluminum hydride may be controlled to give mainly either the diol **2** or the hydroxy ester **7**. Initially, our efforts were directed toward the synthesis of a diazadihydropyrene following the route shown in Scheme I. Formation of the metapyridinophane **4** *via* the Wurtz reaction occurred smoothly. Also, reduction of **4** with zinc in acetic anhydride established the central bond, giving **5** in good yield. However, various attempts to effect dehydrogenation of **5** using N-bromosuccinimide or oxidizing agents were unsuccessful and this approach was abandoned.

Alternatively, the hydroxy ester **7**, also available from lithium aluminum hydride reduction of **1**, was converted by oxidation with chromium oxide to the corresponding aldehyde **8** in 66% yield. Treatment of **8** with the ylide **9** in a Wittig reaction then led to the stilbazole **10** in 56% yield. The stilbazole **10**, as obtained from the Wittig reaction, was a mixture of the *cis* and *trans* isomers in a ratio of 1:15 as determined by nmr analysis. However, irradiation of this mixture resulted in

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(1) We thank the National Science Foundation and the Office of Naval Research (Contract Nonr-2771 (OR), NR-055-468) for their support of this investigation.

(2) Abstracted from the doctoral dissertation of Wendell Pepperdine, University of Oregon, 1969.

(3) This is paper XXII in our series on Aromatic Molecules Bearing Substituents within the Cavity of the π-Electron Cloud. For the preceding communication, see C. E. Ramey and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3681 (1970).

(4) H. Blaschke, C. E. Ramey, I. Calder, and V. Boekelheide, *ibid.*, **92**, 3675 (1970).