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**.

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

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.

(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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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

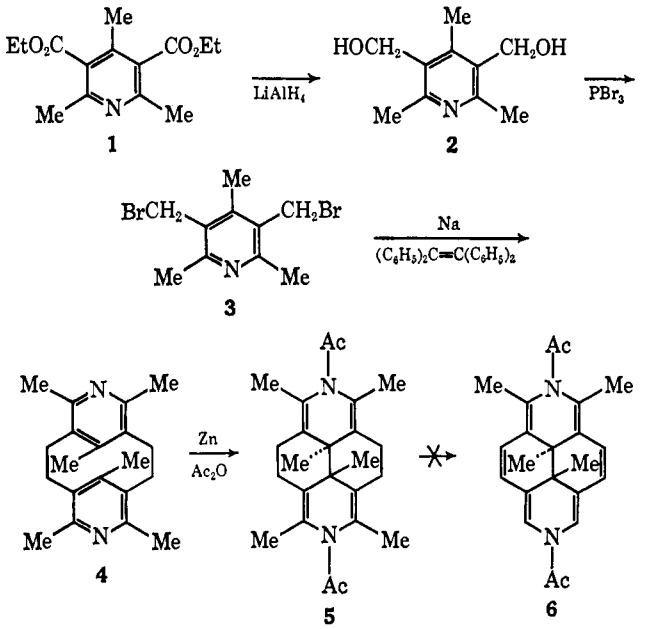
(1) We thank the National Science Foundation and the Office of Naval Research (Contract Nonr-2771 (OR), NR-055-468) for their support of this investigation.

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

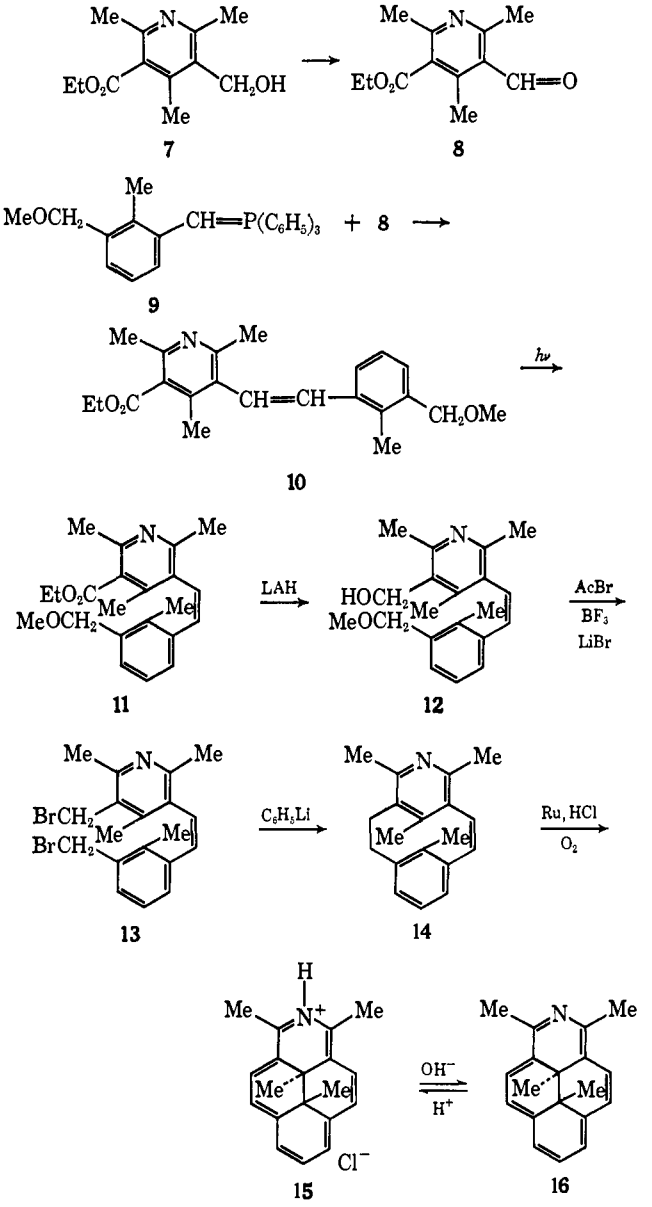
(3) This is paper XXII in our series on Aromatic Molecules Bearing Substituents within the Cavity of the π-Electron Cloud. For the preceding communication, see C. E. Ramey and V. Boekelheide, *J. Amer. Chem. Soc.*, 92, 3681 (1970).

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

Scheme I



Scheme II



a photoequilibrium in which the *cis* isomer was now favored by a ratio of 4:1. With the *cis*-stilbazole **11** available as the predominant isomer, ways of effecting cyclization to the desired metacyclophane **14** were explored.

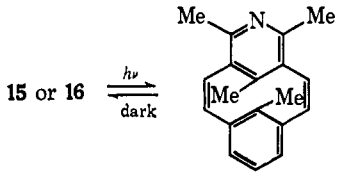
The most satisfactory route proved to be that shown in Scheme II. Treatment of **11** with lithium aluminum hydride gave **12** in 74% yield. Reaction of **12** with acetyl bromide and boron trifluoride etherate in the presence of excess lithium bromide yielded the dibromide **13** directly. It is of interest that in the absence of added lithium bromide the product was the corresponding bromoacetate. Although the pyridylmethyl group is less able to stabilize a carbonium ion than benzyl, the acetoxy group readily undergoes a nucleophilic displacement reaction with bromide ion. Treatment of the dibromide **13** with phenyllithium then gave the metacyclophan-1-ene **14**.

In contrast to the behavior of 8,16-dimethyl[2.2]-metacyclophan-1-ene, which readily underwent dehydrogenation to give 15,16-dimethyldihydropyrene,[4] **14** resisted dehydrogenation under comparable conditions, both catalytic and with 2,3-dichloro-5,6-dicyanoquinone. Eventually, it was found that a ruthenium-on-alumina catalyst in boiling aqueous acid solution slowly effected dehydrogenation of **14**. When, in addition, oxygen was bubbled through the solution, dehydrogenation was much accelerated and conversion to the 2-azadihydropyrene **15** proceeded in high yield.

The physical properties of *trans*-1,3,15,16-tetramethyl-2-azadihydropyrene (**16**) are analogous to those of the other 15,16-dihydropyrenes. It forms almost black needles, mp 105–106°, which give deep green solutions in organic solvents. Its absorption spectrum in cyclohexane shows maxima at 199 mμ (ε 22,000), 233 (7900), 349 (53,000), 393 (16,000), 472 (3800), 540 (280), 593 (280), 602 (330), and 655 (1800). In the nmr, the internal methyls appear as two singlets at τ 13.75 and 13.80, the external methyls as a singlet at τ 6.57, and the ring protons as an aromatic multiplet at τ 1.0–1.9. Protonation of **16** occurs readily with dilute aqueous acid resulting in a sharp change in the color of the solution from green to a deep purple. The nmr spectrum of the hydrochloride **15** in deuteriochloroform shows signals for the internal methyls at τ 13.80 and 13.82, a small shift to higher field as compared to the free base. Since the effect of the positive charge should have been to cause a downfield shift, the observed upfield shift must be attributed to the presence of a stronger diamagnetic ring current in **15** than in the free base **16**. For the peripheral protons, where both effects act in the same direction, marked downfield shifts are observed. Thus, the protons of the external methyls of **15** appear at τ 6.13 and the aromatic multiplet at τ 0.5–1.3.

One of the more interesting features of the dihydropyrenes is their photoisomerization to the corresponding metacyclophane-1,9-diene valence tautomers. Both **15** and **16** readily undergo this isomerization with visible light to give **18** and **17**, respectively. The dark, thermal isomerization of **18** and **17** back to the corresponding dihydropyrenes also occurs at a measurable rate. It is of interest that the dark reaction for the free base **17** is exceedinglys low in cyclohexane ($k_{\text{half-life}}$ = 3500 min). By contrast the rate of the dark reaction for

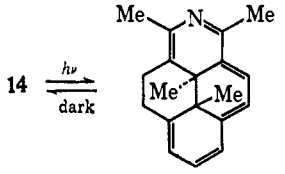
the hydrochloride **18** was too fast to measure at room temperature, but at 17° in methanol, $k_{\text{half-life}}$ = 8 sec. This is the fastest dark reaction yet measured in the dihydropyrene series[5] and is in accord with the concept that development of charge in one aromatic ring promotes interaction and bond formation with the opposite ring.



17

18 = HCl of **17**

Similarly, it has been shown that the metacyclophan-1-enes undergo photoisomerization to the corresponding dihydrophenanthrene derivatives.[3] When a solution of **14** in cyclohexane was irradiated with ultraviolet light, it became a deep red with a broad absorption maximum at 507 mμ. On removal from the ultraviolet light, the deep color rapidly faded, being gone within 2 min. The absorption spectrum of the deep red solution is in accord with that expected for the dihydrophenanthrene valence tautomer **19** and the loss in color conforms to the expected thermal reversion to **14** in the dark. It is curious that the hydrochloride of **14** when irradiated in methanol solution appeared to be unaffected by ultraviolet light.



19

Experimental Section[6]

3,5-Bis(bromomethyl)-2,4,6-trimethylpyridine (3). A mixture of 250 ml of 48% aqueous hydrobromic acid and 20 g of 3,5-bis(hydroxymethyl)-2,4,6-trimethylpyridine[7] was boiled under reflux for 14 hr and then was poured into 800 ml of a 20% aqueous sodium carbonate solution. The white precipitate was collected by filtration and recrystallized from a hexane–cyclohexane mixture to give 28.0 g (82%) of white crystals: mp 118–119°; nmr (CCl_4) singlets at τ 5.54 (4 H, $-CH_2Br$), 7.47 (6 H, $-CH_3$), and 7.62 (3 H, $-CH_3$).

Anal. Calcd for $C_{10}H_{13}NBr_2$: C, 39.12; H, 4.26. Found: C, 39.25; H, 4.40.

4,6,8,12,14,16-Hexamethyl-5,13-diaza[2.2]metacyclophane (4). To a vigorously stirred mixture of 11.5 g of sodium shot and 2.0 g of tetraphenylethylene in 1 l. of dry tetrahydrofuran under a nitrogen atmosphere there was added dropwise from a Hershberg funnel a solution of 15 g of 3,5-bis(bromomethyl)-2,4,6-trimethylpyridine (**3**) in 800 ml of tetrahydrofuran over a period of 4.5 days. The mixture was then filtered and the solid precipitate so collected was mechanically separated from the remaining sodium shot. After the filtrate was concentrated, this residue was combined with the previous precipitate and taken up in chloroform. The chloroform solution was then extracted with 2 *N* aqueous hydrochloric acid and the aqueous extract was made basic. The resulting precipitate was collected, taken up in a 10% methanol in chloroform solution, and chromatographed over Florisil. The main eluate fraction gave a cream-colored solid which, after recrystallization from carbon tetrachloride, yielded 1.18 g (15%) of white crystals: mp 244–246°; nmr ($CDCl_3$) multiplet at τ 6.6–7.7 (8 H, $-CH_2CH_2-$), and singlets at 7.42 (12 H, $-CH_3$) and 9.48 (6 H, $-CH_3$).

Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.38; H, 9.01; N, 9.41.

***trans*-1,3,6,8,15,16-Hexamethyl-2,7-diacetyl-2,7-diazapyrene (5).** A mixture of 738 mg of **4** and 900 mg of freshly activated zinc dust in 60 ml of acetic anhydride was boiled under reflux for 2 hr. After filtration to remove the excess zinc dust, the filtrate was concentrated and the resulting residual oil was taken up in 150 ml of methylene chloride. The methylene chloride solution was washed successively with 2 *N* aqueous hydrochloric acid, water, 5% aqueous sodium carbonate solution, and water. Concentration of the methylene chloride solution then gave 790 mg of a brown solid which was taken up in chloroform and chromatographed over Florisil. The main eluate fraction gave 722 mg of a yellow solid that was recrystallized from methanol to give 344 mg (36%) of pale yellow crystals: mp 253–257°; ir $\nu_{max}^{CHCl_3}$ 3000, 2945, 1660 (-C(=O)N<), and 1640 cm^{-1}; nmr ($CDCl_3$) broad singlet at τ 7.56 (8 H, $-CH_2CH_2$), and singlets at 7.85 (6 H, $-NC(=O)CH_3$), 7.95 (12 H, $-CH_3$), and 9.02 (6 H, $-CH_3$).

Anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.60; H, 8.37; N, 7.49.

3-Ethoxycarbonyl-5-hydroxymethyl-2,4,6-trimethylpyridine (7). A solution of 177.7 g of **1** in 300 ml of dry tetrahydrofuran was added slowly to a vigorously stirred slurry of 19.0 g of lithium aluminum hydride in 700 ml of tetrahydrofuran cooled in an ice bath. Stirring was continued at ice bath temperatures for 2 hr and then the excess lithium aluminum hydride was decomposed by the careful addition of water. After filtration, the precipitate was extracted with three hot 500-ml portions of ethanol. The ethanol extracts were combined with the filtrate and the whole was concentrated. The residual 193 g of a pale yellow oil was taken up in a 30% chloroform in carbon tetrachloride solution and chromatographed over Florisil. The first eluate fraction contained 36 g of the starting diester **1**. A second eluate fraction contained 21.7 g which by tlc appeared to be a mixture of **1** and **7** in a ratio of 20:3. Then, elution of the column with a 5% methanol in chloroform mixture gave 85 g of a white solid that was recrystallized from a benzene–cyclohexane mixture to give 80.1 g (54%) of white crystals: mp 85–86°; ir $\nu_{max}^{CCl_4}$ 3300 cm^{-1}, 2980, 2935, and 1725 (-C(=O)-); nmr (CCl_4) singlet at τ 5.49 (2 H, $-CH_2OH$), quartet at 5.69 (2 H, $-OCH_2CH_3$, J = 7 Hz), 6.13 (1 H, $-OH$), singlets at 7.65 (3 H, $-CH_3$), 7.68 (3 H, $-CH_3$), and 7.79 (3 H, $-CH_3$), and a triplet at 8.65 (3 H, CH_3-CH_2O-).

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 64.55; H, 7.68; N, 6.27. Found: C, 64.37; H, 7.65; N, 6.18.

5-Ethoxycarbonyl-2,4,6-trimethylpyridine-3-carboxaldehyde (8). To a solution of 54.0 g of chromium trioxide in 1 l. of anhydrous pyridine cooled in an ice bath there was added dropwise with stirring a solution of 40.0 g of **7** in 150 ml of dry pyridine. The resulting mixture was stirred at room temperature for 21 hr before being poured into 1.5 l. of water. The aqueous solution was made strongly basic and extracted with ether. After the combined ether extracts had been dried, they were concentrated to give a light-colored solid. This was recrystallized from hexane to give 26.3 g (66%) of fine white needles: mp 68–69°; ir $\nu_{max}^{CCl_4}$ 2980 cm^{-1}, 2945, 2860, 2760 (-C(=O)*H*), 1725 (-C(=O)OEt), and 1695 (-C(=O)H); nmr (CCl_4) singlet at τ −0.44 (1 H, -C(=O)*H*), quartet at 5.62 (2 H, $-OCH_2CH_3$, J = 7 Hz), singlets at 7.27 (3 H, $-CH_3$) and 7.53 (3 H, $-CH_3$), and a triplet at 8.60 (3 H, CH_3CH_2O-, J = 7 Hz).

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.32; H, 6.70; N, 6.47.

5-Ethoxycarbonyl-3′-methoxymethyl-2,2′,4,6-tetramethyl-3-azastilbenes (10 and 11). To a solution of 49.1 g of (3-methoxymethyl-2-methylbenzyl)triphenylphosphonium bromide[4] in 1 l. of dimethyl sulfoxide there was added dropwise with stirring 62.5 ml of a 1.6 *M* hexane solution of *n*-butyllithium. To the resulting dark orange solution there was then added portionwise 22.1 g of 5-ethoxycarbonyl-2,4,6-trimethylpyridine-3-carboxaldehyde (**8**). After addition was complete, the light yellow solution was stirred at room temperature before adding 10 ml of water. About three-fourths of the dimethyl sulfoxide was removed through distillation under

(5) The details of the photoisomerization studies of the dihydropyrenes and the kinetic studies of the corresponding dark reactions will be published shortly.

(6) Elemental analyses are by A. Bernhardt Microanalytical Laboratories. Ultraviolet and visible spectra were measured with a Cary 14 spectrometer, infrared spectra with a Beckman IR-5 spectrometer, nmr spectra with Varian A-60 or HA-100 MHz spectrometers, and mass spectra with a C.E.C.-110-21B spectrometer. We thank the National Science Foundation for funds used toward the purchase of the Varian A-60 and the C.E.C.-110-21B, and a Joy liquid nitrogen machine.

(7) P. Karrer and S. Malnoni, *Helv. Chim. Acta*, **34**, 2151 (1951).

reduced pressure, before the remaining concentrate was poured into a mixture of 400 ml of water and 800 ml of ether. The aqueous layer was made strongly basic with 5 *N* potassium hydroxide solution and the ether layer separated. The ether extract was then shaken with 1 l. of a 3 *N* aqueous hydrochloric acid solution. After separation, the aqueous layer was extracted repeatedly to remove all of the triphenylphosphine oxide. Basification of the aqueous layer with 40% aqueous potassium hydroxide solution was followed by extraction with chloroform. The combined chloroform extracts were dried and concentrated to give 19.8 g (56%) of a pale yellow oil. This was taken up in a 50% chloroform–benzene mixture and chromatographed over silica gel. The main eluate fraction gave 16.4 g (47%) of a yellow oil whose nmr spectrum indicated it to be a mixture for the *cis* and *trans* isomers of **10** in approximately a 1:5 ratio. The nmr signals of a carbon tetrachloride solution attributed to the *trans* isomer of **10** included a multiplet at τ 2.5–3.2 (5 H, Ar*H* and -C=C*H*-), singlet at 5.56 (2 H, ArCH_2O-), quartet at 5.63 (2 H, CH_3CH_2O-, J = 7 Hz), singlets at 6.65 (3 H, CH_3O-), 7.46 (3 H, ArCH_3), 7.54 (3 H, ArCH_3), and 7.70 (6 H, ArCH_3), and a triplet at 8.63 (3 H, CH_3CH_2O-, J = 7 Hz).

A solution of 1.0 g of this *cis–trans* mixture of **10** in 100 ml of benzene was irradiated with a 200-W, low-pressure Hanovia lamp using a Corex filter. After 1.5 hr an aliquot of the solution was withdrawn whose nmr spectrum indicated that it contained the *cis–trans* mixture of **10** in the ratio of approximately 4:1. When irradiation was continued for another hour, analysis of a similar aliquot indicated no further change in the isomer ratios. Concentration of the solution followed by chromatography over silica gel using a 20% chloroform–benzene mixture for elution gave 790 mg of a pale yellow oil. The nmr signals (CCl_4) assigned to the *cis* isomer **11** included a multiplet at τ 1.8–3.7 (5 H, Ar*H* and -C=C*H*-), singlet at 5.65 (2 H, ArCH_2O-), quartet at 5.73 (2 H, CH_3CH_2O-, J = 7 Hz), singlet at 6.74 (3 H, CH_3O-), singlets at 7.59, 7.75, 7.78, and 8.02 (3 H each, ArCH_3), and a triplet at 8.72 (3 H, CH_3CH_2O-, J = 7 Hz).

Anal. Calcd for $C_{22}H_{27}NO_3$: C, 74.75; H, 7.70; N, 3.96. Found: C, 74.80; H, 7.49; N, 4.05.

5-Hydroxymethyl-3′-methoxymethyl-2,2′,4,6-tetramethyl-3-azastilbene (12). A solution of 13.0 g of the mixture of *cis* and *trans* isomers of **10** in 1300 ml of benzene was irradiated with a 200-W, low-pressure Hanovia lamp using a Corex filter for 1.5 hr. The solution was concentrated under reduced pressure leaving 13.0 g of an oil whose nmr spectrum indicated it to be a mixture of the *cis* and *trans* isomers of **10** in a ratio of 4:1. This was taken up in 100 ml of tetrahydrofuran and added dropwise with vigorous stirring to a slurry of 2.0 g of lithium aluminum hydride in 100 ml of tetrahydrofuran cooled in an ice bath. After addition was complete, the mixture was stirred at room temperature for 4 hr. Then 3.8 ml of water was added carefully and the resulting precipitate was removed by filtration. The precipitate was extracted twice with 100-ml portions of hot chloroform and the chloroform extracts were combined with the original filtrate. This on concentration gave 12.3 g of an orange oil. Chromatography of this oil over silica gel using ether for elution gave as the main fraction 8.51 g (74%) of a clear oil: ir $\nu_{max}^{CCl_4}$ 3220 cm^{-1} (-OH), 3000, 2930, 2820, 1565, 1445, 1375, 1190, 1100, 1025, and 720; nmr (CCl_4) multiplet at τ 1.8–3.7 (5 H, ArH and >C=C*H*-), broad singlet at 5.12 (1 H, -O*H*), singlets at 5.62 and 5.66 (4 H, ArCH_2O-), singlet at 6.76 (3 H, CH_3O-), and singlets at 7.75, 7.88, 7.94 (3 H each, ArCH_3). From the nmr spectrum one can deduce that this oil is essentially pure *cis* isomer **12**.

Anal. Calcd for $C_{20}H_{25}NO_2$: C, 77.13; H, 8.09; N, 4.50. Found: C, 76.97; H, 8.00; N, 4.62.

3,5-Bis(bromomethyl)-2,2′,4,6-tetramethyl-3-azastilbene (13). To a solution of 2.0 g of **12** in 30 ml of chloroform there was added with stirring a mixture of 5.0 ml of acetyl bromide, 2.0 g of lithium bromide, and 10.0 ml of boron trifluoride ethereate. After the resulting mixture had been boiled under reflux for 2 hr, it was cooled and poured into 250 ml of a 10% aqueous solution of sodium bicarbonate. This was then extracted with three 100-ml portions of chloroform. The combined chloroform extracts were dried and concentrated under reduced pressure to give 2.67 g (98%) of a pale yellow oil: nmr ($CDCl_3$) multiplet at τ 1.8–3.7 (5 H, ArH and >C=C*H*-), singlets at 5.52 and 5.57 (4 H, ArCH_2Br), and singlets at 7.45, 7.65, 7.69, and 7.93 (3 H each, ArCH_3). Thus, the nmr spectrum indicates the compound to be cleanly the *cis* isomer **13**. Unfortunately, the compound readily undergoes self-quaternization and so is unstable to store or to handle neat. For this reason it was used directly in the next reaction without attempting further purification.

4,6,8,16-Tetramethyl-5-aza[2.2]metacyclophan-1-ene (14). To a vigorously stirred solution of 2.6 g of **13** in 1200 ml of tetrahydrofuran there was added through a syringe 12.0 ml of a 2.1 *M* solution of phenyllithium in a 70:30 benzene–ether mixture. After addition was complete, the mixture was stirred an additional 5 min at room temperature before adding 1 ml of water. Concentration of the solution under reduced pressure left an oily residue. This was taken up in chloroform and chromatographed over neutral alumina (Woelm, activity 1). The main fraction gave an oil which was taken up in benzene and extracted with 2 *N* aqueous hydrochloric acid solution. The aqueous layer was separated, made basic, and extracted with chloroform. Concentration of the chloroform extract gave 269 mg of a yellow oil whose nmr spectrum indicated it to be slightly impure **14**. This was taken up in a 10% ether in carbon tetrachloride solution and chromatographed again over neutral alumina (Woelm, activity 1). The main eluate fraction gave 122 mg (7.5%) of white crystals: mp 89.1–89.6°; uv $\lambda_{max}^{cyclohexane}$ 199 mμ (ϵ 36,000), 209 (31,00), 250 (18,000), and 304 (2500); ir ν_{max}^{KBr} 2950 cm^{-1}, 2850, 1530, 1442, 1433; nmr ($CDCl_3$) multiplet at τ 2.85–3.25 (3 H, Ar-*H*), singlet at 3.34 (2 H, -CH=CH-), multiplet at 6.7–7.9 (4 H, ArCH_2-), singlets at 7.46, 7.54, 9.25, and 9.33 (3 H, each, ArCH_3).

Anal. Calcd for $C_{19}H_{21}N$: C, 86.64; H, 8.04; N, 5.32. Found: C, 86.45; H, 7.98; N, 5.17.

Exposure of a cyclohexane solution of **14** to ultraviolet light caused it to turn a deep red. When removed from the ultraviolet light, the color of the solution faded in several minutes. An absorption spectrum of the solution, taken quickly after exposure to ultraviolet light, showed a broad maxima at 507 mμ with bands of lesser intensity at 305 and 316 mμ. This spectrum is closely analogous to those of the other dihydrophenanthrenes[3] and provides good evidence for the photoisomerization of **14** to **19**. The photoisomerization is reversed in the dark and the whole process can be repeated indefinitely without evidence of any complicating side reactions.

A solution of **14** in 1 *N* aqueous hydrochloric acid showed absorption at 240 mμ (ϵ 12,000), 272 (11,000), and 299 (5800). Irradiation of this solution with ultraviolet light had no observable effect. The nmr spectrum of the hydrochloride of **14** in deuteriochloroform showed a broad multiplet at τ 2.6–3.6 (Ar*H* and -C*H*=C*H*-), a multiplet at 6.5–7.8 (ArCH_2-), and singlets at 7.02, 7.10, 9.07, and 9.12 (3 H each, ArCH_3).

***trans*-1,3,15,16-Tetramethyl-2-azadihydropyrene (16).** A mixture of 100 mg of a 5% ruthenium-on-alumina catalyst and 50 mg of **14** in 20 ml of a 2 *N* aqueous hydrochloric acid solution was boiled under reflux for 3 days while oxygen was bubbled through the solution using a sintered glass inlet tube. During this period the solution acquired an intense bluish purple color. It was then filtered to remove the catalyst and the filtrate was made basic with 5 *N* aqueous potassium hydroxide. Extraction of the aqueous solution with chloroform followed by concentration of the chloroform extract gave 41 mg (83%) of a dark green solid whose nmr spectrum was in accord with that expected for **16**. This was then taken up in ether and chromatographed over neutral alumina (Woelm, activity 1). The main eluate fraction gave 26 mg (52%) of dark green crystals. These were recrystallized from a 70:30 methanol–water mixture to almost black needles: mp 105–106°; uv $\lambda_{max}^{cyclohexane}$ 199 mμ (ϵ 22,000), 233 (7900), 349 (53,000), 393 (16,000), 472 (3800), 540 (280), 581 (200), 593 (280), 602 (330), 643 (1020), and 655 (1800); ir $\nu_{max}^{CHCl_3}$ 3040 cm^{-1}, 2980, 2940, 2870, 1525, 1445, 1420, 1360, 1335, 1138, 1110, 942, 915, 835, 682, and 652; nmr ($CDCl_3$) multiplet at τ 1.0–1.9 (7 H, Ar*H*), singlet at 6.57 (6 H, ArCH_3), and singlets at 13.75 and 13.80 (3 H each, -CH_3); mass spectrum, a small parent molecular ion, *m/e* 261 with the major peaks being at 246 ($M^+ - CH_3$) and 231 ($M^+ - 2(CH_3)$).

Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.24; H, 7.45; N, 5.33.

When **16** was dissolved in 2 *N* aqueous hydrochloric acid, it gave a deep purple solution. Extraction of this solution with chloroform concentrated all of the purple color in the chloroform layer. After the chloroform layer was dried and concentrated, the hydrochloride **15** was obtained as deep purple crystals which sublimed over a broad range starting at 150° and appeared to be quite hygroscopic. The nmr spectrum of **15** in deuteriochloroform showed a broad multiplet at τ 0.5–1.3 (7 H, Ar*H*), a singlet at 6.13 (6 H, ArCH_3), and singlets at 13.80 and 13.82 (3 H each, -CH_3). The ultraviolet absorption spectrum in 1 *N* aqueous hydrochloric acid showed maxima at 227 mμ (ϵ 6100), 285 (8700), 315 (15,000), 360 (45,000), 379 (16,000), 404 (20,000), 538 (5100), 590 (5500), and 640 (6500).

Table I. Kinetic and Thermodynamic Data for the Thermal Isomerization of Metacyclophane-1,9-dienes (17 and 18) to Dihydropyrenes (16 and 15)[a]

Compound	$k(4°)$	$k(17°)$	$k(30°)$	$k(50°)$	$E_a(30°)$	$\Delta G^{\ddagger}(30°)$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
17[b]			0.00020	0.0016	20.1	25.3	19.5	−19.2
18[c]	0.91	4.8	>6		20.4	18.3	19.8	+4.8

[a] Rates are in min^{-1}, E_a, $\Delta G^{\ddagger}$, and $\Delta H^{\ddagger}$ in kcal/mole, $\Delta S^{\ddagger}$ in $caldeg^{-1}\ mol^{-1}$. [b] Solvent, cyclohexane. [c] Solvent, methanol.

Photoisomerization Studies of *trans*-1,3,15,16-Tetramethyl-2-azadihydropyrene (16). A. Nmr Spectrum of the Photoisomer 17. A solution of **16** in deuteriochloroform contained in an nmr tube was irradiated using a 100-W Mazda lamp until most of the dark green color had disappeared. The loss in intensity of the normal nmr signals for **16** indicated about a 65% conversion to the photoisomer **17**. The new signals introduced by irradiation and assigned to **17** included a multiplet at τ 2.5–3.5 (7 H, Ar*H* and -C*H*=C*H*-), singlet at 7.53 (6 H, $ArCH_3$), and singlets at 8.50 and 8.58 (3 H each, $ArCH_3$). When this sample was allowed to stand in the dark for 3 days, the signals corresponding to **16** increased and those for **17** decreased, indicating a ratio of **16** to **17** of 9:1 after this period of time in the dark.

When a solution of **15** in methanol was irradiated, it quickly became colorless. However, on removal of the solution from the light, the color returned within seconds and it was not possible under these conditions to obtain an nmr spectrum of **18**.

B. Kinetic Studies of the Thermal Reversion (17 → 16, and 18 → 15). The kinetics of the thermal reversion were studied by irradiating solutions of **15** or **16** with a 100-W Mazda lamp until essentially all of the color had disappeared and then the solutions were placed in a Cary 15 spectrometer equipped with a temperature-controlled holder and the increase in concentration of **15** or **16** was followed using the change in optical density at 538 mμ for **15** and that 478 mμ for **16**. These data were utilized in a computer program to obtain the activation parameters.[8] The results are summarized in Table I.

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

Alkyl Shifts in Thermolyses. II.[1] Rearrangement of Isopropenylspiropentane and Its Axially Dissymmetric 4-Methyl Derivatives[2]

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Abstract: Upon thermolysis, isopropenylspiropentane is found to undergo unimolecular rearrangement to 5-methylspiro[2.4]hept-4-ene and 1-isopropenyl-2-methylenecyclobutane. Both products are most easily derived by initial 1,2 (peripheral) bond fission, and the latter material is formed by a vicinal alkyl shift pathway that may be related to the cyclopropylcarbinyl radical rearrangement. Evidence for reversible peripheral bond fission was obtained from partial pyrolysis of the four axially dissymmetric 1-isopropenyl-4-methylspiropentanes in which epimerization only at C-1 occurred at the same rate as rearrangement. Discussion focuses on the relative ease of the vicinal alkyl shift in spiropentane thermolysis and on the relative rates of various steps on the energy surface characteristic of the compounds described.

Migrations of groups to adjacent atoms deficient in electrons[3a,b] are well known in organic chemistry, while vicinal shifts to radical[3c,d] and anionic[3e] sites are rare, particularly when the migrating group is a hydrogen or a saturated carbon. Well-known theoretical considerations have justified these observations.[4] On the other hand, vicinal hydrogen atom rearrangements are commonplace in cyclopropane thermolyses,[5] suggesting that there might be favorable electron interaction in the transition state for this process. Unfortunately, there is a dearth of bonafide examples of pyrolytic vicinal alkyl shifts in the cyclopropane series or, for that matter, in any organic system.[6]

A rearrangement which could proceed by a vicinal alkyl shift pathway is the spiropentane (**1**) to methylenecyclobutane (**5**) thermal rearrangement studied by Burkhardt[7] and by Frey[8] who also determined that log k (unimol) at medium to high pressures is $15.86–57{,}570/2.3RT$. There is, however, another likely pathway for this isomerization. The two pathways involve sequential cleavages of the two different kinds of carbon–carbon bonds in the starting material and differ only in

(1) For part I, a preliminary communication of some of these results, see J. J. Gajewski, *Chem. Commun.*, 920 (1967).

(2) Presented in part at the 155th American Chemical Society National Meeting, San Francisco, Calif., 1968, P-28, and at the IUPAC Symposium on "Valence Isomerism," Karlsruhe, Germany, Sept 1968.

(3) (a) "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963; (b) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967; (c) C. Walling in ref 3a, Chapter 7; (d) R. Kh. Freidlinn in "Advances in Free-Radical Chemistry," Vol. I, G. H. Williams, Ed., Academic Press, New York, N. Y., 1965; (e) H. E. Zimmerman in ref 3a, Chapter 6.

(4) See, for example, H. E. Zimmerman in ref 3a, pp 394–379.

(5) H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 148 (1966).

(6) For examples of alkyl shifts in rearrangements, see (a) E. T. McBee, J. A. Bosome, and C. J. Morton, *J. Org. Chem.*, 31, 768 (1966); (b) J. W. Perlaan and H. Kloosterziel, *Rec. Trav. Chim.*, 84, 1594 (1965); (c) M. Jones, Jr., *J. Org. Chem.*, 33, 2538 (1968); (d) C. McKnight and F. S. Rowland, *J. Amer. Chem. Soc.*, 88, 3179 (1966); (e) D. E. McGreer, R. S. McDaniel, and M. G. Vinje, *Can. J. Chem.*, 43, 1389 (1965); (f) W. Adam and Y. M. Cheng, *J. Amer. Chem. Soc.*, 91, 2109 (1969); W. Adam, *et al.*, *ibid.*, 91, 2111 (1969).

(7) P. J. Burkhardt, *Dissertation Abstr.*, 23, 1524 (1962).

(8) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 5550 (1961).