fraction gave a crystalline residue which, after recrystallization from methanol, yielded 26 mg (65%) of green plates, mp 119–120°, identical in all respects with an authentic sample of **1**.

Reduction of 2,7-Diacetoxy-*trans*-15,16-dimethyldihydropyrene with Zinc in Alkaline Solution. Under an atmosphere of nitrogen a solution of 400 mg of potassium hydroxide in 2 ml of water was added to a solution of 25 mg of 2,7-diacetoxy-*trans*-15,16-dimethyldihydropyrene (**16**) in 5 ml of methanol, and then 300 mg of zinc dust was added in portions with swirling. The color of the solution rapidly changed from green to red to colorless. After addition of 2 ml of methyl iodide, the mixture was allowed to stand at room temperature for 2 hr. The mixture was concentrated to half-volume under reduced pressure before adding 25 ml of ether. The ether layer was separated, washed with water, dried, and concentrated. The residual solid was taken up in chloroform and chromatographed over neutral alumina (Woelm, No. 1). The first colorless eluate was concentrated and the residue crystallized from methanol to give 12 mg (57%) of white crystals, mp 210–211°, identical in all respects with a sample of 8,16-dimethyl-5,13-dimethoxy[2.2]metacyclophane prepared previously.[2]

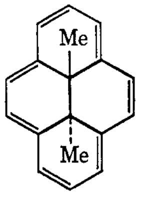
Aromatic Molecules Bearing Substituents within the Cavity of the π-Electron Cloud. Synthesis of *trans*-15,16-Diethyldihydropyrene[1,2]

V. Boekelheide and T. Miyasaka

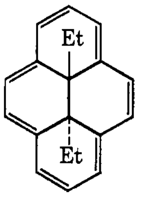
Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon. *Received October 19, 1966*

Abstract: The synthesis of *trans*-15,16-diethyldihydropyrene (**2**) is described. The molecule shows typical aromatic properties.

The successful synthesis of *trans*-15,16-dimethyldihydropyrene[3] (**1**) and our interest in the chemical and physical properties of aromatic molecules having substituents within the cavity of the aromatic π-electron cloud have led us to investigate the synthesis of other examples of this class of compounds. Such questions as the size of the cavity present in an aromatic 14-π-electron cloud, the contour of the magnetic field of the induced ring current (as measured by the chemical shift of internal substituent atoms), and the steric interaction of the π-electron cloud with bulky substituents within the cavity are of particular interest.



1



2

To study the consequences of increasing the bulk of the substituent within the cavity of the 14-π-electron cloud, the next logical substituent to investigate was ethyl, and so our attention turned to the synthesis of *trans*-15,16-diethyldihydropyrene (**2**). At the start we had expected that, by substituting *p*-ethylphenol for *p*-cresol, we could follow the same general scheme used for the synthesis of **1**.[3] Unfortunately such an adaption failed in the very first step.

In the case of *p*-cresol we had been able to devise a bromination–rearrangement procedure whereby *p*-cresol was converted in one step to 3,5-dibromo-4-methylphenol.[3] This was based on earlier work of Baddeley and Plant in which they had shown that 2,6-dibromo-4-methylphenol undergoes an aluminum chloride catalyzed rearrangement at 130° to give 3,5-dibromo-4-methylphenol.[4] Baddeley and Plant also reported that the bromination of *p*-ethylphenol followed by a similar rearrangement gave 3,5-dibromo-4-ethylphenol in an over-all yield of 23%.[4] However, despite many attempts to do so, we have not been able to duplicate their results. In our hands 3,5-dibromo-4-ethylphenol was never produced in more than a few per cent yield and as part of a complex, tarry mixture.[5]

It was necessary, therefore, to find an alternative route, and the possibility was investigated of taking an intermediate at some later stage in the synthesis of **1** and carrying out a series of transformations such that the methyl substituent would be converted to ethyl. The intermediate chosen was **3**, and the reaction sequence by which it was transformed to 8,16-diethyl-5,13-dimethoxy[2.2]metacyclophane (**13**)[6] is outlined in Scheme I.

The reaction of **3** with N-bromosuccinimide proceeded in high yield to give the bromomethyl derivative **4** which, on reaction with cyanide ion, was smoothly converted to the nitrile **5**. Several methods of reducing the nitrile were investigated, but reduction over a palladium-on-charcoal catalyst in the presence of dimethylamine proved most successful, giving the desired tertiary amine **6** in 69% yield. Reduction of **6** to the diol **7** occurred in 92% yield by means of lithium aluminum hydride. Subjecting **7** to the conditions of a Hofmann elimination led to the styrene derivative **9**

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(1) We are very much indebted to the National Science Foundation for support of this investigation.

(2) For the previous communication in this series, see J. B. Phillips, R. J. Molyneux, E. Sturm, and V. Boekelheide, *J. Am. Chem. Soc.*, **89**, 1704 (1967).

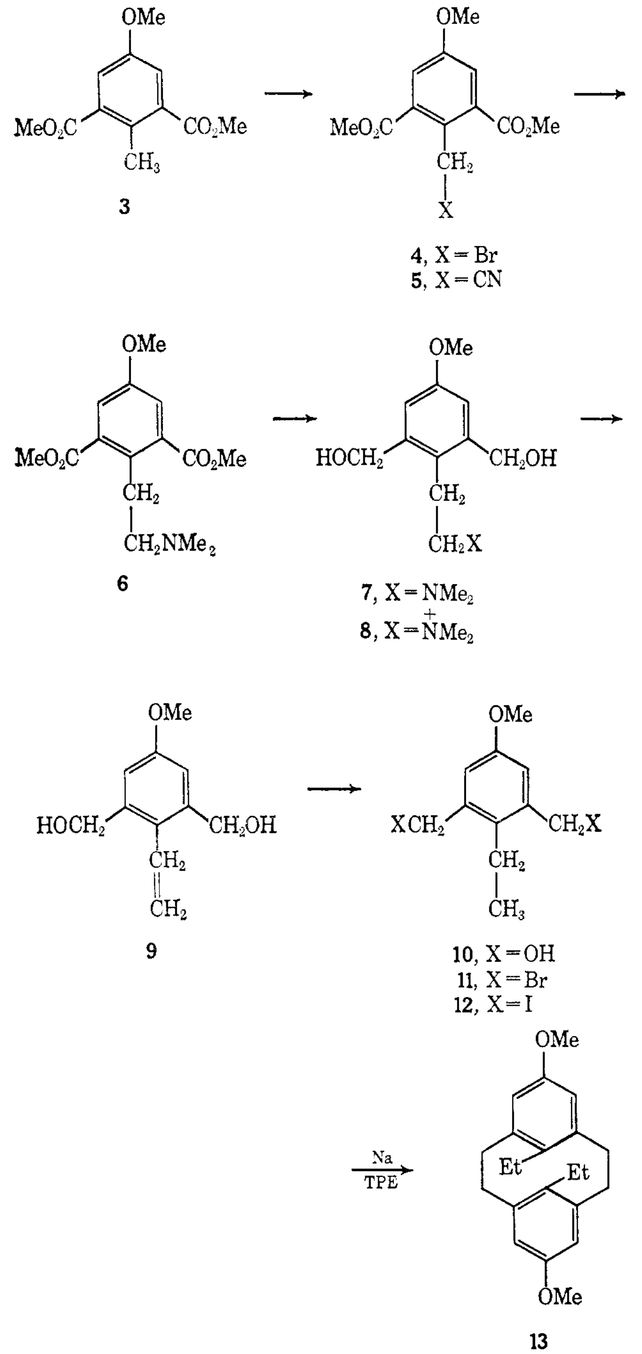
(3) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **89**, 1695 (1967).

(4) G. Baddeley and J. Plant, *J. Chem. Soc.*, 525 (1943).

(5) R. J. Barnhard, M.S. Thesis, University of Oregon, 1965.

(6) The nomenclature used for the [2.2]metacyclophanes is that recommended by B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964, p 8.

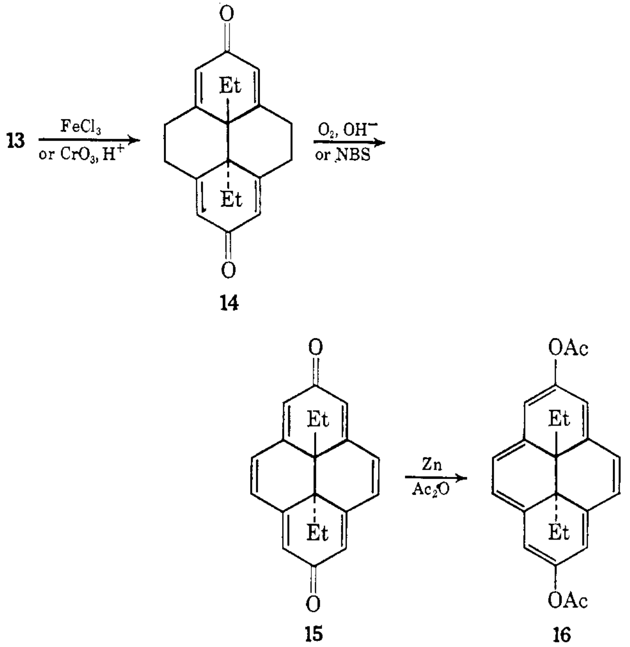
Scheme I



in 93% yield. Catalytic hydrogenation of **9** yielded the ethyl derivative **10** which, with phosphorus tribromide, led to **11**, and this, in turn, with sodium iodide gave the diiodide **12**, all of these steps proceeding in high yield. The dimerization of **12** with sodium in the presence of tetraphenylethylene (TPE) was carried out following the procedure developed in our earlier studies and gave the desired metacyclophane **13** in 18% yield.

Considerable evidence has accumulated to show that substituents located at the internal 8- and 16-positions of [2.2]metacyclophanes strongly feel the induced ring current in the opposite aromatic ring.[3,7,8] Thus, the signals for the methyl groups at the 8- and 16-positions of [2.2]metacyclophanes show a shift to higher field of about 1.5–1.6 ppm as compared to toluene. In support of structure **13**, the 8- and 16-ethyl groups show a similar effect due to the ring current in the neighboring aromatic ring. The methylene protons appear as a quartet at τ 8.80, a shift to higher field of 1.5 ppm as compared to ethylbenzene, whereas the methyl groups of **13** appear as a triplet at τ 9.66, a shift to higher field of only 0.9 ppm as compared to ethylbenzene. The nmr spectrum provides evidence that the 8- and 16-ethyl groups of **13** are free to rotate and that the preferred conformation has the methyl groups rotated away from the face of the opposite aromatic ring.

The further steps in the synthesis of *trans*-15,16-diethyldihydropyrene (**2**) followed closely the procedures worked out during the synthesis of the dimethyl analog **1**. Oxidation of the metacyclophane derivative **13** to the corresponding bis-dienone **14** was accomplished in high yield using either the ferric chloride or the chromic acid procedures, although the latter is the more convenient. Again, the conversion of the bis-dienone **14** to the quinone **15** proceeded smoothly by air oxidation in the presence of alkali or by treatment with N-bromosuccinimide, with the latter procedure being the more convenient and proceeding in 94% yield. Reduction of the quinone **15** with zinc dust in the presence of acetic anhydride gave the expected hydroquinone diacetate **16** in 63% yield.



The physical properties of the hydroquinone diacetate **16** clearly revealed the presence of the aromatic dihydropyrene system. Thus, the deep green crystals of **16** showed absorption maxima at 348 mμ (ε 76,000), 361 (30,300), 385 (35,900), 494 (8850), 658 (1030), and 669 (2090), a spectrum very similar to that of the corresponding 15,16-dimethyl analog except for a slight shift to longer wavelengths. Likewise, in the nmr spectrum, the signals of the protons of the internal ethyl groups are shifted to very high field. The methylene protons of the ethyl groups appear as a quartet at τ 13.83, whereas the methyl protons appear as a triplet at τ 11.67.

To obtain the parent hydrocarbon **2** the quinone **15** was reduced at −80° with a lithium aluminum hydride–

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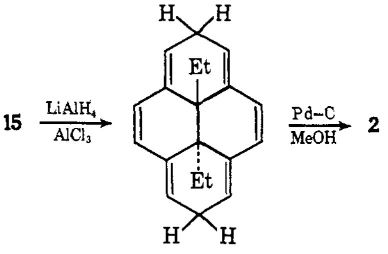
(7) D. J. Wilson, V. Boekelheide, and R. W. Griffin, Jr., *J. Am. Chem. Soc.*, **82**, 6302 (1960).

(8) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *ibid.*, **83**, 943 (1961).

aluminum chloride mixture. This gave the corresponding bis-triene **17**. When the bis-triene was stirred at room temperature in a methanol solution containing a palladium-on-charcoal catalyst, it underwent dehydrogenation to give the desired *trans*-15,16-diethyldihydropyrene (**2**) in 61 % yield.



17

Examination of the physical and chemical properties of the deep green crystals of **2** quickly confirmed the fact that **2** meets all of the usual criteria for aromaticity. Its ultraviolet and visible absorption spectra are very similar to those of *trans*-15,16-dimethyldihydropyrene (**1**), the maxima being shifted slightly to longer wavelengths, and so are in accord with the absorption spectra predicted theoretically for a perimeter 14-π-electron system.[3]

The nmr spectrum of **2** is shown in Figure 1 and is in accord with the presence of a strong induced ring current. The peripheral protons show a shift to lower field with the 2- and 7-protons appearing as a triplet (J = 7 cps) centered at τ 2.05, the 1-, 3-, 6-, and 8-protons as a doublet (J = 7 cps) centered at τ 1.33, and the 4-, 5-, 9-, and 10-protons as a singlet at τ 1.36. On the other hand, the protons of the 15- and 16-ethyl groups appear at very high field with the methyl protons as a triplet (J = 7.5 cps) centered at τ 11.86 and the methylene protons as a quartet (J = 7.5 cps) centered at τ 13.96. It is of interest that the methylene protons appear at higher field than do the methyl protons. Although this result might be expected on the basis that the methyl protons are farther removed from the center than the methylene protons and are, in fact, sticking out through the cavity of the π-electron cloud, examination of molecular models shows that the methyl protons must impinge on the π-electron cloud much more than do the methylene protons. The effects of such an impingement, however, are not manifest in the nmr spectrum. This encourages the idea that introduction of larger alkyl groups at the 15- and 16-positions of dihydropyrene will allow a mapping of the magnetic field resulting from the induced ring current.

Another criterion for aromaticity is that of bond lengths. Hanson has made an X-ray crystallographic examination of *trans*-15,16-diethyldihydropyrene (**2**).[9] The bonds in the perimeter of **2** vary between 1.392 and 1.400 A, which is in very good accord with the accepted value for an aromatic bond of 1.397 A as found in benzene.[10] Although the aromatic perimeter is quite planar, showing a maximum deviation from a mean plane of only 0.081 A, it is distorted slightly more than the aromatic perimeter of **1**. Also, the carbon–carbon bond holding the internal ethyl groups in **2** is 1.573 A, being slightly longer than the corresponding bond (1.564 A) holding the internal methyls of **1**.

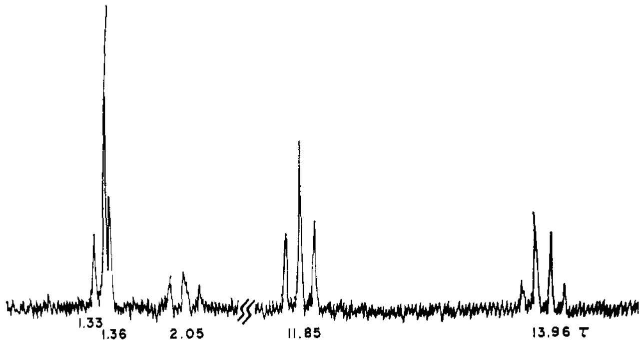
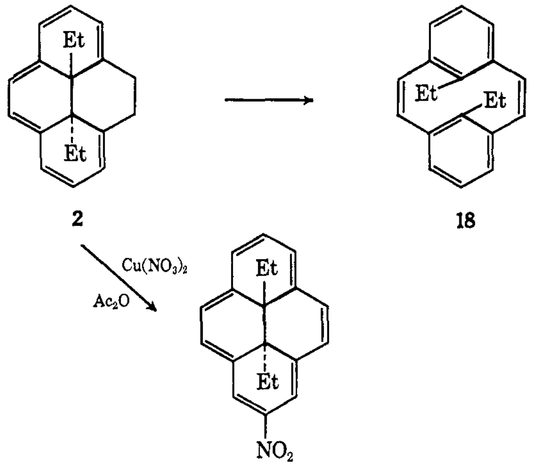


Figure 1. Nmr spectrum of *trans*-15,16-diethyldihydropyrene, measured in deuteriochloroform solution using a Varian A-60 spectrometer.

Finally, nitration of **2** occurred smoothly in good yield using cupric nitrate in acetic anhydride to give the 2-substituted isomer **19**. Thus, *trans*-15,16-diethyldihydropyrene meets the classic criterion of undergoing substitution reactions.

Since **2** may undergo valence tautomerism to yield the corresponding metacyclophane derivative **18**, it was of interest to investigate the possibility of this interconversion and the energy relationships between the two valence tautomers. In the purification and handling of **2** it was found that care must be exercised and solutions of **2** had to be handled at room temperature or below to avoid loss. When a pure sample of **2** was heated in boiling cyclohexane, isomerization occurred to give a colorless isomer. The course of this reaction can easily be followed by either nmr or ultraviolet and visible absorption spectroscopy. The thermal isomerization follows first-order kinetics and its half-life in boiling cyclohexane is about 12 hr.



The thermal isomerization product appears to react very readily with oxygen and is difficult to handle, so that it has not been obtained in an analytically pure state. However, its nuclear magnetic resonance and ultraviolet absorption spectra suggest structure **18**. The methylene protons of the ethyl groups appear as a quartet centered at τ 9.26 (J = 7 cps), whereas the methyl groups give rise to a triplet centered at τ 9.40 (J = 7 cps). In the ultraviolet there is a strong

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(9) We are very much indebted to Dr. A. W. Hanson of the National Research Council of Canada, Ottawa, Canada, for making these results available to us prior to his own publication.

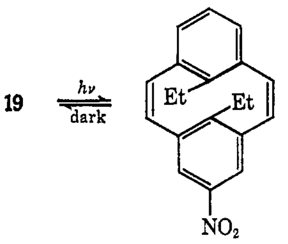
(10) B. P. Stoicheff, *Can. J. Phys.*, **32**, 339 (1954).

absorption maximum at 258 mμ with a small band, appearing more or less as a shoulder at 273 mμ.

As further evidence of the relationship between **2** and its thermal rearrangement product, it was found that nitration of the thermal isomer occurred smoothly to give 2-nitro-*trans*-15,16-diethyldihydropyrene (**19**), the same product obtained by direct nitration of **2**. Again this is a behavior that would be predicted for structure **18**.

Solutions of the thermal isomer held at room temperature showed no tendency to isomerize back to **2**. This is in contrast to the situation in the 15,16-dimethyldihydropyrene series where **1** is the more stable isomer at room temperature. Apparently, the steric interaction of the ethyl groups with the aromatic π-electron cloud is sufficiently greater than that of the methyl groups to change the energy relationships.

The remarkable photoisomerization of *trans*-15,16-dimethyldihydropyrene (**1**) to its metacyclophane valence tautomer and the accompanying reversal of this reaction in the dark have been discussed previously.[3,11a,b] A similar photoisomerization occurs with *trans*-15,16-diethyldihydropropyrene derivatives. Irradiation of **19** with visible light causes a quick photoisomerization to the metacyclophane isomer **20**, and this reverts back to **19** very rapidly in the dark. The dark reaction by which **20** reverts to **19** has a half-life of about 1 min at 50°, being about three times as fast as the corresponding dark reaction of the 2-nitro derivative in the dimethyldihydropyrene series.[11b]



20

The effect of the nitro group in stabilizing **19** with respect to its valence tautomer shows the important influence that polar substituents have on this equilibrium. The 2-nitro derivative **19** is isolated as purple plates, mp 135–137°, and shows no evidence of thermal isomerization even at its melting point.

Experimental Section[12]

4-Methoxy-2,6-dicarbomethoxybenzyl Bromide (4). To a solution of 238.0 g (1 mole) of 4-methoxy-2,6-dicarbomethoxytoluene[3,13] (**3**) in 600 ml of dry carbon tetrachloride was added 182 g (1.02 moles) of recrystallized N-bromosuccinimide, and the mixture was boiled under reflux using a 75-w reflector lamp as both a source of heat and for irradiation. Reaction was complete within 1 hr. The succinimide floating on the surface was removed by filtration, and the filtrate was concentrated under reduced pressure. The solid residue was recrystallized from a mixture of methylene chloride and methanol to give 306.0 g (97%) of white prisms, mp 71–74°; infrared, $\nu_{max}^{CCl_4}$ 1730 cm^{-1} (ester carbonyl); nmr, τ 2.63 (singlet, 2 H), 4.70 (singlet, 2 H), 6.11 (singlet, 6 H), and 6.20 (singlet, 3 H).

Anal. Calcd for $C_{12}H_{13}O_5Br$: C, 45.50; H, 4.10; Br, 25.35. Found: C, 45.69; H, 4.33; Br, 25.10.

4-Methoxy-2,6-dicarbomethoxybenzyl Cyanide (5). A solution of 317.0 g (1 mole) of 4-methoxy-2,6-dicarbomethoxybenzyl bromide (**4**) in 2 l. of dimethyl sulfoxide was heated to 50–55°, and a solution of 70.0 g (1.4 moles) of sodium cyanide in 200 ml of water was added dropwise with stirring. Although crystals of **5** began separating during the addition, the mixture was held at 50–55° with stirring for 2 hr after the addition was complete. It was then cooled and diluted by addition of 2 l. of water. The solid, which separated, was collected, washed with cold water, and recrystallized from methanol to give 230 g (88%) of white needles, mp 104–106°; infrared, ν_{max}^{KBr} 2260 (C≡N) and 1730 cm^{-1} (ester carbonyl); nmr, τ 2.32 (singlet, 2 H), 5.55 (singlet, 2 H), 6.02 (singlet, 6 H), and 6.13 (singlet, 3 H).

Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.30; H, 5.14; N, 5.20.

N,N-Dimethyl-2-(4-methoxy-2,6-dicarbomethoxyphenyl)ethylamine (6). To a mixture of 50.0 g of 4-methoxy-2,6-dicarbomethoxybenzyl cyanide and 25 g of a 10% palladium-on-charcoal catalyst in 1.2 l. of methanol was added 175 ml of a 25% solution of dimethylamine in methanol, and the whole was subjected to hydrogenation at 55° under a pressure of 680 psi of hydrogen for 8 hr. After removal of the catalyst and concentration of the solution, the syrupy residue was taken up in 1 l. of ether and extracted with three 200-ml portions of 2 *N* hydrochloric acid. The aqueous extracts were then made basic and extracted with three 200-ml portions of ether. The ether extracts were dried and concentrated. The resulting residual oil was taken up in methylene chloride and passed over a short column of neutral alumina (Woelm, No. 2). Concentration of the main fraction of eluate gave 37.0 g (61%) of a colorless oil whose nmr spectrum (τ 2.59 (singlet, 2 H), 6.07 (singlet, 6 H), 6.17 (singlet, 3 H), 6.50–6.86 and 7.26–7.62 (A_2B_2 multiplet, 4 H), and 7.69 (singlet, 6 H)) is in accord with structure **6**.

The **hydrochloride** of **6** was obtained, after recrystallization from a methanol–ether mixture, as white crystals, mp 130–133°.

Anal. Calcd for $C_{15}H_{22}NO_5Cl$: C, 54.31; H, 6.68; N, 4.22. Found: C, 54.29; H, 7.24; N, 4.46.

The **picrate** of **6** was obtained, after recrystallization from methanol, as yellow crystals, mp 125–1256.5°.

Anal. Calcd for $C_{21}H_{24}N_4O_{12}$: C, 48.09; H, 4.61; N, 10.68. Found: C, 48.02; H, 4.58; N, 11.27.

N,N-Dimethyl-2-(4-methoxy-2,6-bis(hydroxymethyl)phenyl)ethylamine (7). To a slurry of 10.0 g of lithium aluminum hydride in 1.5 l. of dry ether there was added dropwise with stirring over a period of 1 hr a solution of 35.0 g of **6** in 700 ml of dry ether. The mixture was then boiled under reflux for 1 hr before destroying the excess reagent by dropwise addition of a saturated aqueous solution of sodium sulfate. The precipitate was collected in the thimble of a Soxhlet extractor and was continuously extracted with ether for 24 hr. The combined ether solutions from filtration and extraction were concentrated to dryness. The solid residue was recrystallized from a methanol–ether mixture to give 26.0 g (92%) of white prisms, mp 109–110°; nmr, τ 3.09 (singlet, 2 H), 5.13 (broad, 2 (OH) H), 6.20 (singlet, 3 H), 7.05–7.25 and 7.41–7.61 (A_2B_2 multiplet, 4 H), and 7.83 (singlet, 6 H).

Anal. Calcd for $C_{13}H_{21}NO_3$: C, 65.24; H, 8.85; N, 5.85. Found: C, 65.90; H, 8.74; N, 5.87.

N,N,N-Trimethyl-2-(4-methoxy-2,6-bis(hydroxymethyl)phenyl)ethylammonium Iodide (8). A solution of 25.0 g of **7** and 10 ml of methyl iodide in 200 ml of methanol was boiled under reflux for 3 hr. The crystals, which separated, were collected, and the filtrate was concentrated to give a second crop of crystals. The combined crops of crystals were then recrystallized from methanol to give 38.8 g (98%) of white crystals, mp 270–273° dec.

Anal. Calcd for $C_{16}H_{24}NO_3I$: C, 44.20; H, 6.34; N, 3.68. Found: C, 43.72; H, 6.52; N, 3.90.

4-Methoxy-2,6-bis(hydroxymethyl)styrene (9). A mixture of 35.0 g of **8** and 20.0 g of Dowex-2 (OH$^-$) resin in 200 ml of methanol was stirred vigorously at room temperature for 20 min. The mixture was then transferred to a column packed with 30 g of Dowex-2 (OH$^-$) resin and eluted with methanol. The strongly alkaline eluate fraction was concentrated, and the residual oil was placed in a sublimation apparatus. Heating at 130–140° (3 mm) effected the Hofmann elimination reaction and caused the resulting

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[11] (a) H.-R. Blattman, D. Meuche, E. Heilbronner, R. J. Molyneux, and V. Boekelheide, *J. Am. Chem. Soc.*, **87**, 130 (1965). (b) A more detailed study of these photoisomerization reactions will be published elsewhere.

[12] Microanalyses are by Micro-Tech Laboratories and by Pascher and Pascher Laboratories. Ultraviolet and visible spectra were determined with a Cary Model 15 spectrometer, infrared spectra with a Beckman IR-5A spectrometer, and nmr spectra with a Varian A-60 spectrometer. We express our thanks to the National Science Foundation for the funds allowing purchase of the Varian A-60.

[13] We express our deep appreciation to J. R. Geigy, A.G., Basel, Switzerland, for their kindness in making a generous supply of **3** available to us.

styrene to sublime onto the cold finger. The sublimate amounted to 16.5 g (93%) of white crystals, which, after recrystallization from benzene, gave 15.7 g (88%) of white crystals, mp 113.0–113.5°.

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.95; H, 7.28.

4-Ethyl-3,5-bis(hydroxymethyl)anisole (10). A mixture of 10.0 g of **9** and 500 mg of prereduced platinum oxide catalyst in 150 ml of methanol was subjected to hydrogenation at room temperature and 2-atm pressure of hydrogen. After removal of catalyst and solvent, the solid residue was recrystallized from benzene to give 9.7 g (96%) of white needles, mp 80–81°.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.29; H, 8.18.

4-Ethyl-3,5-bis(bromomethyl)anisole (11). To a stirred suspension of 20.0 g of 4-ethyl-3,5-bis(hydroxymethyl)anisole (**10**) in 200 ml of dry benzene, 22.5 g of phosphorus tribromide was added dropwise over a period of 30 min. The mixture was then warmed on a steam bath for 1 hr to complete the reaction. The cooled solution was then poured into 100 ml of ice water, and the organic layer was extracted with benzene. The benzene extract was washed successively with water, aqueous 5% sodium bicarbonate, and water. After concentration of the benzene extract, the solid residue was recrystallized from a methylene chloride–methanol mixture to give 31.0 g (91%) of white columns, mp 90–91°.

Anal. Calcd for $C_{11}H_{14}OBr_2$: C, 41.10; H, 4.38. Found: C, 41.30; H, 4.52.

4-Ethyl-3,5-bis(iodomethyl)anisole (12). A mixture of 30.0 g of 4-ethyl-3,5-bis(bromomethyl)anisole (**11**) and 50.0 g of sodium iodide in 300 ml of acetone was boiled under reflux for 5 hr. After concentration of the mixture, 300 ml of methylene chloride and 100 ml of water were added to the yellow residue. The organic layer was separated, washed with water, dried, and concentrated. The crystalline residue was recrystallized from ether to give 33.0 g of white pillars, mp 126–127°; nmr, τ 3.16 (singlet, 2 H), 5.56 (singlet, 4 H), 6.22 (singlet, 3 H), 7.22 (quartet (J = 7.5 cps), 2 H), and 8.67 (triplet (J = 7.5 cps), 3 H). An additional 2.9 g of crystals was obtained as a second crop from the mother liquor, giving a total yield of 35.9 g (93%).

Anal. Calcd for $C_{11}H_{14}OI_2$: C, 31.80; H, 3.39. Found: C, 31.85; H, 3.61.

8,16-Diethyl-5,13-dimethoxy[2.2]metacyclophane (13). To a stirred suspension of 20.0 g of sodium particles and 2.0 g of tetraphenylethylene (TPE) in 2 l. of dry tetrahydrofuran under a nitrogen atmosphere, there was added a solution of 30.0 g of 4-ethyl-3,5-bis(iodomethyl)anisole (**12**) in 1 l. of tetrahydrofuran using a Hershberg dropping funnel to regulate the speed so that over-all 70 hr was required to complete the addition. The deep red color of the sodium adduct was maintained throughout the period of addition. The unreacted sodium was then removed by filtering the mixture through glass wool, and the filtrate was concentrated under reduced pressure. The fluorescent syrupy residue was then stirred with a mixture of 500 ml of methylene chloride and 500 ml of water. After about 10 ml of 2 *N* hydrochloric acid was added to assist the separation of the two phases, the organic layer was removed and passed over a column of Florisil. About 10.0 g of Celite 545 was added to the filtrate before it was evaporated to give a fine powder. This powder was dried *in vacuo* and then placed at the top of a column of 150 g of neutral alumina (Woelm, No. 1). Elution with benzene gave three main fractions. The first contained 1.2 g of tetraphenylethane. The middle fraction weighed 1.35 g and by nmr was a 7:3 mixture of **13** and tetraphenylethane. The third fraction (2.0 g) was mainly **13**, contaminated by a small amount of tetramer. Sublimation of the third fraction followed by recrystallization of the sublimate from methylene chloride or hexane gave 131 g of white plates, mp 205.0–205.5°; nmr, τ 3.31 (singlet, 4 H), 6.23 (singlet, 6 H), 7.16 (singlet, 8 H), 8.80 (quartet (J = 7 cps), 4 H), and 9.66 (triplet (J = 7 cps), 6 H). Since the presence of tetraphenylethane does not interfere, the middle fraction was employed in the next step without further purification.

Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70; mol wt, 324. Found: C, 81.62; H, 8.66; mol wt (vapor-phase osmometry), 338.

2,7-Diketo-4,5,9,10,15,16-hexahydro-*trans*-15,16-diethylpyrene (14). A. Ferric Chloride Procedure. To a stirred suspension of 5.0 g of anhydrous ferric chloride in 150 ml of dry chloroform, a solution of 670 mg of **13** in 50 ml of dry chloroform was added dropwise. A dark red precipitate formed in about 10 min, and stirring of the mixture was continued for another 10 min. The precipitate was collected using a sintered-glass filter, and then it was digested with a mixture of 20 ml of methylene chloride and 20 ml of 2 *N* hydrochloric acid. After the organic layer had been washed successively with water, 5% aqueous sodium bicarbonate, and water, it was dried and concentrated. The crystalline residue was recrystallized from methanol to give 540 mg (89%) of white pillars, mp 304–306° dec; $\lambda_{max}^{CH_3OH}$ 257 mμ (ϵ 6850) and 250 (6270, inflection); infrared, γ_{max}^{KBr} 1640 and 1615 cm^{-1}; nmr, τ 3.60 (singlet, 4 H), 7.32 (broad multiplet, 8 H), 8.21 (quartet (J = 7 cps), 4 H), and 9.55 (triplet, (J = 7 cps), 6 H).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.73; H, 7.63.

B. Chromic Acid Procedure. The chromic acid reagent was prepared by dissolving 2.67 g of chromium trioxide in 5 ml of water, adding 2.13 g of concentrated sulfuric acid, and diluting the solution with water to a total volume of 10 ml. Then, to an ice-cold suspension of 400 mg of **13** in 20 ml of acetone, 0.470 ml of the chromic acid reagent was added dropwise with stirring. A pale yellow precipitate began forming immediately, its formation being complete in about 5 min. The mixture was stirred for another 10 min, and then 100 ml of water was added all at once. The aqueous mixture was extracted with three 50-ml portions of methylene chloride, and the combined extracts were washed successively with water, a 5% aqueous sodium bicarbonate solution, and water. Concentration gave a solid residue which, after recrystallization from a methanol–methylene chloride mixture, gave 340 mg (94%) of white pillars, mp 304–306° dec, identical with the specimen obtained from procedure A.

***trans*-15,16-Diethyldihydropyrene-2,7-quinone (15). A. Oxidation in Alkaline Solution.** To a solution of 500 mg of **14** in 150 ml of hot ethanol through which oxygen was rapidly being bubbled, there was added a solution of 3.0 g of potassium hydroxide in 50 ml of ethanol. The oxygen stream was continued at room temperature for 4 hr. Then the solution was neutralized with 2 *N* hydrochloric acid and concentrated under reduced pressure. The residue was stirred with a mixture of 100 ml of chloroform and 100 ml of water. The organic layer was separated, dried, and concentrated. The residual orange crystals were recrystallized from methanol to give 400 mg (82%) of yellow pillars, mp 276–278°; $\lambda_{max}^{CH_3OH}$ 227 mμ (ϵ 27,000), 275 (42,500), 281 (41,900, inflection), 317 (14,700), 330 (16,800), and 344 (12,700); infrared, ν_{max}^{KBr} 1645, 1620, and 1595 cm^{-1}; nmr, τ 3.72 (singlet, 4 H), 3.77 (singlet, 4 H), 7.67 (quartet (J = 7.5 cps), 4 H), and 9.20 (triplet (J = 7.5 cps), 6 H).

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.69; H, 6.59.

B. Oxidation with N-Bromosuccinimide. A mixture of 400 mg of **14**, 508 mg of recrystallized N-bromosuccinimide, and 10 mg of azobisisobutyronitrile in 50 ml of carbon tetrachloride was boiled under reflux for 30 min. In about 5 min a yellow color developed and hydrogen bromide evolution, which was rapid at first, ceased after about 20 min. The mixture was concentrated under reduced pressure; the residue was taken up in methylene chloride and chromatographed over neutral alumina (Woelm, No. 2). The eluate fraction containing the bright yellow component was concentrated leaving a crystalline residue. This, after recrystallization from a methylene chloride–ether mixture, gave 368 mg (94%) of yellow pillars, mp 276–278°, identical in all respects with the specimen obtained by procedure A.

2,7-Diacetoxy-*trans*-15,16-diethyldihydropyrene (16). To an ice-cold solution containing 100 mg of **15** and 70 mg of triethylamine in 1.5 ml of acetic anhydride, 130 mg of powdered zinc was added with stirring. The yellow color of the quinone swiftly changed to a deep green. After 5 min the supernatant solution was decanted into 10 ml of ice water. When the acetic anhydride was decomposed, the mixture was extracted with three 20-ml portions of methylene chloride. The methylene chloride extracts were concentrated to a small volume under reduced pressure and were then passed onto a column of silica gel. The green band was eluted with chloroform and the eluate concentrated under reduced pressure. The resulting dark green needles were dissolved in methylene chloride and cooled in a Dry Ice–acetone bath, and a few drops of methanol was added. There separated 82 mg (63%) of dark green prisms, mp 164–166°; $\lambda_{max}^{CH_3OH}$ 348 mμ (ϵ 76,000), 361 (30,300), 385 (35,900), 478 (8130, inflection), 494 (8850), 658 (1030), and 669 (2090); infrared, ν_{max}^{KBr} 1760, 1205, and 1130 cm^{-1}; nmr, τ 1.42 (singlet, 4 H), 1.58 (singlet, 4 H), 7.50 (singlet, 6 H), 11.67 (triplet (J = 7.5 cps), 6 H), and 13.83 (quartet (J = 7.5 cps), 4 H).

Anal. Calcd for $C_{24}H_{24}O_2$: C, 76.57; H, 6.43. Found: C, 76.22; H, 6.45.

***trans*-15,16-Diethyl-2,7,15,16-tetrahydropyrene (17).** A solution was prepared by heating a mixture of 4.0 g of lithium aluminum hydride in 240 ml of ether for 2 hr, adding 14.0 g of aluminum chloride and boiling under reflux again for 2 hr, and transferring 130 ml of the clear supernatant solution to a flask held at −80°. To this was added dropwise with stirring a solution of 300 mg of **15** in a mixture of 70 ml of benzene and 150 ml of dry ether. After the addition was complete, the orange-tinted solution was stirred at −80° for 2 hr. Then, the mixture was warmed to room temperature, the excess lithium aluminum hydride was destroyed by addition of ethyl acetate, and 50 ml of water was added. The organic layer was separated, washed with water, dried, and concentrated to a small volume. It was then chromatographed over silica gel using petroleum ether (bp 30–60°) for elution. The yellow eluate fraction was concentrated, and the solid residue was recrystallized from petroleum ether by cooling to −80° to give 154 mg (57%) of yellow plates, mp 162–165°; $\lambda_{\max}^{\text{cyclohexane}}$ 258 mμ (ϵ 61,700) and 250 (49,100, inflection); infrared, $\nu_{\max}^{\text{KBr}}$ 1620, 958, 885, and 829 cm^{-1}; nmr, τ 4.08 (singlet, 4 H), 4.18 (triplet, 4 H), 7.08 (2 triplets, 4 H), 8.55 (quartet (J = 7.5 cps), 4 H), and 9.37 (triplet, (J = 7.5 cps), 6 H).

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.33; H, 8.42.

***trans*-15,16-Diethyldihydropyrene (2).** An activated 20% palladium-on-charcoal catalyst was prepared following the procedure described by Pfau and Plattner.[14] A mixture of 300 mg of the bis-triene **17** and 300 mg of the 20% palladium-on-charcoal catalyst in a solution of 8 ml of methanol and 2 ml of ether was stirred at room temperature for 30 hr. After removal of the catalyst, the filtrate was concentrated under reduced pressure. The deep green, crystalline residue was taken up in a 9:1 mixture of petroleum ether and methylene chloride and chromatographed over silica gel. The first yellow eluate contained 30 mg of the starting bis-triene **17**. The green eluate coming off next was concentrated under reduced pressure to give 181 mg (61%) of deep green crystals, mp 148–149°. A sample recrystallized from methylene chloride at −80° by adding petroleum ether formed deep green pillars, mp 148–151°; $\lambda_{\max}^{\text{cyclohexane}}$ 345 mμ (ϵ 61,000), 349 (63,900), 367 (18,400), 386 (28,180), 391 (36,850), 428 (4870), 493 (4620, inflection), 545 (97), 554 (78), 606 (100), 619 (140), 633 (246), 649 (255), and 655 (376); infrared, $\nu_{\max}^{\text{KBr}}$ 1440, 1308, 1283, 1252, 1220, 833, 744, 686, and 644 cm^{-1}; nmr, τ 1.33 (doublet (J = 7 cps), 4 H), 1.36 (singlet, 4 H), 2.05 (triplet (J = 7 cps), 2 H), 11.86 (triplet (J = 7.5 cps), 6 H), and 13.96 (quartet (J = 7.5 cps), 4 H).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.12; H, 7.73.

2-Nitro-*trans*-15,16-diethyldihydropyrene (19). To an ice-cold solution of 100 mg of *trans*-15,16-diethyldihydropyrene (**2**) in 2 ml of acetic anhydride there was added 51 mg of cupric nitrate trihydrate with stirring. The green color of the solution quickly changed to purple and, after 20 min of stirring, the solution was poured onto 5 ml of ice water. When the excess acetic anhydride had reacted with the water, the solution was extracted with three 10-ml portions of methylene chloride. The methylene chloride extracts were washed with water, dried, and, after concentration to a small volume, chromatographed over silica gel using methylene chloride for elution. The deep purple fraction of eluate was concentrated to dryness, and the solid residue was recrystallized from methylene chloride in the cold by addition of petroleum ether to give 62 mg (53%) of deep purple plates, mp 135–137°; $\lambda_{\max}^{\text{cyclohexane}}$ 355 mμ (38,500), 394 (17,000), 398 (17,000), 419 (31,000), 544 (10,100), 615 (1560), 658 (48), 669 (120), and 683 (650); infrared, $\nu_{\max}^{\text{KBr}}$ 1540, 1375, 882, 828, and 646 cm^{-1}; nmr, τ 0.44 (singlet, 2 H), 1.09 (doublet (J = 7.5 cps), 2 H), 1.30 (doublet (J = 7.5 cps), 2 H), 1.35 (doublet (J = 7.5 cps), 2 H), 1.83 (triplet (J = 7.5 cps), 1 H), 11.73 and 11.80 (two overlapping triplets, 6 H), and 13.72 (two slightly separated quartets, 4 H).

Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27. Found: C, 78.28; H, 6.42.

Thermal Rearrangement of *trans*-15,16-Diethyldihydropyrene. A solution of 50 mg of *trans*-15,16-diethyldihydropyrene (**2**) in 100 ml of cyclohexane was boiled under reflux. The concentration of hydrocarbon **2** was followed by taking aliquots at regular intervals and measuring their ultraviolet and visible absorption spectra. With the passage of time the absorption maxima of **2** fell in a regular fashion, and a new absorption appears at 350 mμ which grows in a regular fashion. After 12 hr the values of the extinction coefficients for the various absorption maxima of **2** had fallen to one-half their original value. When the boiling solution had become colorless, it was concentrated to a volume of 5 ml under reduced pressure. It was then transferred to a silica gel and eluted with cyclohexane. The main eluate fraction was concentrated to 0.5 ml and then cooled in a Dry Ice–acetone bath, causing the separation of 25 mg of fine, white crystals; mp 130–135°. These crystals appeared to react readily with oxygen and were difficult to handle, so that with the limited quantity of sample available an analytically pure sample was not obtained. The absorption spectrum of the sample taken in cyclohexane showed a main band at 253 mμ with a small band, almost as a shoulder, at 270 mμ. Its nmr spectrum exhibited a quartet (J = 7 cps) centered at τ 9.25 corresponding to the methylene protons of the ethyl group, a triplet (J = 7 cps) centered at τ 9.43 (methyl groups), a singlet at τ 3.67 (vinyl protons), and a multiplet centered at τ 3.05 (aromatic protons).

A solution of 10 mg of these crystals in 1 ml of acetic anhydride was cooled to 0°, and 10 mg of cupric nitrate trihydrate was added. After about 10 min the solution turned purple. It was allowed to stand for an additional 2 hr and then was poured into 5 ml of ice water. After the acetic anhydride had decomposed, the mixture was extracted by three 5-ml portions of methylene chloride. The methylene chloride extracts were concentrated and the residue was chromatographed over silica gel using methylene chloride for elution. Concentration of the main fraction of purple eluate followed by addition of petroleum ether (bp 30–68°) gave 7 mg of purple crystals, mp 135–137°, undepressed by admixture of an authentic sample of 2-nitro-*trans*-15,16-diethyldihydropyrene. Also its ultraviolet and visible spectra, as well as its nmr spectrum, were identical with those of authentic 2-nitro-*trans*-15,16-diethyldihydropyrene.

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(14) A. S. Pfau and P. A. Plattner, *Helv. Chim. Acta*, **23**, 768 (1940).