which, after recrystallization from methanol, was obtained as dark green plates, mp 119–120°; $\lambda_{max}^{cyclohexane}$ 337.5 mμ (ε, 87,000), 377 (37,000), 463 (6000), 528 (58), 536 (58), 586 (110), 598 (150), 611 (210), 627 (230), 634 (210), and 641 (330); nmr, τ 1.33 (6 H), 1.43 (2 H), 1.77–2.02 (2 H), and 14.25 (6 H).

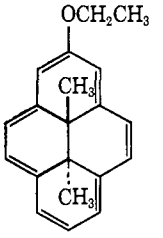
Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.82; H, 7.13.

B. By Dehydrogenation of 33 with DDQ. A mixture of 50 mg of **33** and 100 mg of 2,6-dichloro-3,5-dicyanoquinone (DDQ) in 25 ml of benzene was boiled under reflux for 2 hr. The solution was concentrated to dryness; the residue was taken up in a pentane–ether mixture (20:1) and chromatographed over neutral alumina (Woelm, No. 1). The green eluate fraction was concentrated to dryness, and the residue was recrystallized from methanol to give 48 mg (100%) of dark green plates, mp 119–120°, identical with the specimen obtained by procedure A.

***trans*-15,16-Dimethyl-2,7-dideuteriodihydropyrene (34).** In order to prepare the deuterio derivative **34** in which the 2- and 7-positions could be assigned to the deuterium atoms with certainty, it was necessary to devise a procedure of converting the quinone **30** to dimethyldihydropyrene (**1**) without using catalytic dehydrogenation. This was found to be possible by carrying out the reduction of the quinone at room temperature with inverse addition. Thus, to a solution of 300 mg of quinone **30** in 10 ml of benzene, 300 ml of ether was added, and then at room temperature the lithium aluminum hydride–aluminum chloride reagent (described under the preparation of **33**) was added dropwise with stirring. The resulting mixture was allowed to stir overnight before decomposing the excess reagent by addition of water. The ether layer was separated, washed with water, and concentrated. The residue was taken up in petroleum ether and chromatographed over Florisil. Elution with a petroleum ether–ether mixture (20:1) led to the separation of two dark green bands. The first of these bands was collected and then chromatographed again over neutral alumina (Woelm, No. 1). Concentration of the main eluate fraction gave 84 mg (32%) of dark green plates, mp 119–120°, identical in all respects with samples of **1** described previously.

When this experiment was repeated using lithium aluminum deuteride in place of lithium aluminum hydride, the corresponding 2,7-dideuterio-*trans*-15,16-dimethyldihydropyrene (**34**) was obtained in comparable yield. In the nmr spectrum, **34** showed two incompletely resolved singlets (4 H each) at τ 1.33 and 1.37 and a sharp singlet at τ 14.28.

The second dark green band from the original chromatography was also purified by rechromatography over neutral alumina (Woelm, No. 2) using a petroleum ether–ether mixture (20:1). This gave 60 mg of a dark green oil which could not be induced to crystallize. It was unstable toward light and air. Its visible and ultraviolet spectrum showed absorption maxima at 351, 382, 462, and 615 mμ, clearly showing it to be a dihydropyrene derivative. Its nmr spectrum showed signals at 0.95–2.40 (multiplet, 9 H), 5.45 (quartet, 2 H), 8.34 (triplet, 3 H), and 13.97 (singlet, 6 H).



37

The nmr spectrum strongly suggests structure **37**, although the mode of its formation is not apparent.

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

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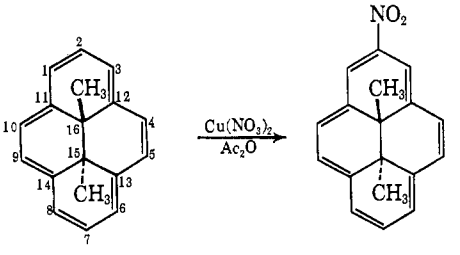
Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon. *Received October 19, 1966*

Abstract: It is shown that *trans*-15,16-dimethyldihydropyrene (**1**) undergoes bromination, deuteration, Friedel–Crafts alkylation and acylation, and nitration. These typical aromatic electrophilic substitution reactions occur more readily than with benzene, giving mono- and disubstitution products resulting from attack at the 2- and 7-positions.

In an accompanying paper,[2] the synthesis of *trans*-15,16-dimethyldihydropyrene (**1**) is described. All of the physical properties of **1** support the conclusion that this molecule is aromatic, having a 14-π-electron perimeter with methyl groups being inserted into the cavity of the π-electron cloud. The present investigation was undertaken to examine the chemical properties of *trans*-15,16-dimethyldihydropyrene to see whether it would exhibit the substitution reactions typically associated with benzene.

The first reaction to be investigated was nitration. Under the very mild conditions, cupric nitrate in acetic anhydride at 0°, previously used for nitration of azulene[3] and [3.2.2]cyclazine,[4,5] *trans*-15,16-dimethyldihydropyrene underwent nitration in essentially quan-



1 **2**

(1) We express our deep appreciation to the National Science Foundation for their support of this work.

(2) For the previous communication in this series, see V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **89**, 1695 (1967).

(3) A. G. Anderson, Jr., J. A. Nelson, and J. J. Tazuma, *ibid.*, **75**, 4980 (1953).

(4) R. J. Windgassen, W. H. Saunders, Jr., and V. Boekelheide, *ibid.*, **81**, 1459 (1959).

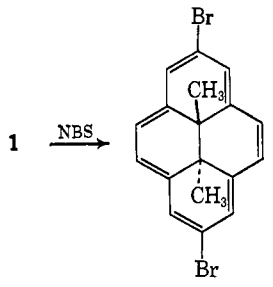
(5) V. Boekelheide and T. Small, *ibid.*, **83**, 462 (1961).

titative yield to give the corresponding 2-nitro derivative (**2**) as deep purple needles, mp 172–173°. Only a single isomer was formed and the assignment of structure is based on an interpretation of its nmr spectrum.

Of the ring protons in **1**, those at the 2- and 7-positions appear at highest field (τ 1.77–2.02), showing a distinctive AB_2 pattern. The highest field signal (τ 1.50–1.75) of the ring protons in **2** shows again this same AB_2 pattern, but the integrated area for this signal is reduced by one-half, as would be expected if only the 7-proton were present.

The signal for the 1- and 3-protons of **2** appear at lowest field (τ 0.37) as a singlet, whereas the 4,10- and 5,9-protons occur as overlapping doublets centered at τ 0.93 and 1.13 (J = 7.5 cps). Finally, the 6,8-protons show as a doublet centered at τ 1.22 (J = 7.5 cps). The signals for the protons of the internal 15- and 16-methyl groups are not resolved at 60 Mc and appear as a slightly broadened singlet at τ 14.03.

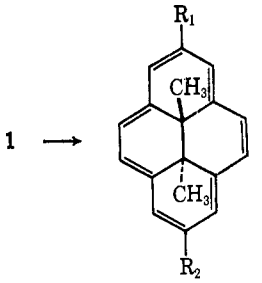
Treatment of **1** with a solution of bromine in carbon tetrachloride caused immediate decolorization of the bromine solution with evolution of hydrogen bromide. When **1** was titrated in this fashion there was an uptake of 5 moles of bromine before the bromine color persisted. Isolation experiments indicated the formation of a complex mixture of polysubstituted derivatives. However, when **1** was treated with 2 moles of N-bromosuccinimide, the reaction proceeded in a much cleaner fashion to give the 2,7-dibromo derivative (**3**). Because of the symmetry of **3**, its nmr spectrum is very simple and provides conclusive proof for the structural assignment. Thus, the 1-, 3-, 6-, and 8-protons of **3** appear as a singlet at τ 1.30, the 4-, 5-, 9-, and 10-protons as a singlet at τ 1.48, and the protons of the 15- and 16-methyls as a singlet at τ 14.02.



3

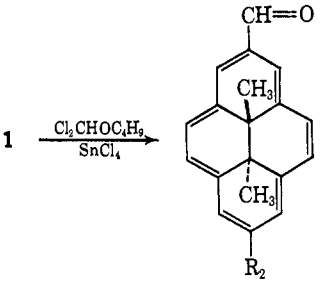
Friedel–Crafts acylation of **1** also proceeded readily under mild conditions. Acetylation of **1** with acetic anhydride and boron trifluoride etherate in methylene chloride at room temperature, conditions used by Gaoni and Sondheimer to acetylate 1,8-bisdehydro[14]-annulene,[6] proceeded smoothly in high yield to give the 2-acetyl derivative **4**. Similarly, the reaction of **1** with benzoyl chloride in methylene chloride at room temperature using aluminum chloride as catalyst gave the 2-benzoyl derivative **5**. In this case there was also isolated a small amount of the 2,7-dibenzoyl-*trans*-15,16-dimethyldihydropyrene (**6**). Again the assignment of structure of these acyl derivatives is based on their distinctive nmr spectra.

Attempts to effect a Vilsmeier reaction were unsuccessful, leading to recovery of **1**. The reason for this



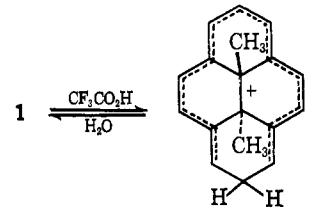
4, $R_1 = COCH_3$; $R_2 = H$
5, $R_1 = COC_6H_5$; $R_2 = H$
6, $R_1 = R_2 = COC_6H_5$

failure is not apparent, for the corresponding procedure for preparing aldehydes developed by Rieche[7] was quite successful. Thus, the reaction of **1** with dichloromethyl *n*-butyl ether at 0° in the presence of stannic chloride with methylene chloride as solvent gave the corresponding aldehyde **7** in 83% yield.



7

When **1** was treated with strong acid, solution occurred with a change in color to deep blue. The process is reversible, so that on dilution with water **1** was recovered unchanged. Solutions of **1** in trifluoroacetic acid could be examined directly by nmr, and the spectrum is in good accord with the carbonium ion structure **8**. Thus, the high-field signal for the 15- and 16-methyl protons disappears on solution, and the two different methyl groups of **8** appear as separate singlets at τ 9.37 (3 H) and 9.77 (3 H). The vinyl protons of **8** appear as a multiplet centered around τ 3 (9 H) and the allylic protons as a multiplet centered at τ 7.40 (2 H). When a solution of **1** in CF_3CO_2D was allowed to stand at room temperature for 2 min and was then diluted with deuterium oxide, the recovered **1** showed almost a complete absence of aromatic protons, indicating a very rapid exchange of hydrogen for deuterium.



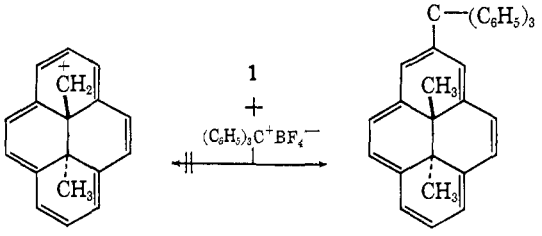
8

The development of carbonium ions within the cavity of the π-electron cloud is a problem of much interest in the dihydropyrene series. An attempt was made to accomplish this directly by hydride abstraction. However, treatment of **1** with triphenylmethyl fluoroborate gave only the 2-triphenylmethyl derivative **9**, and there

(6) Y. Gaoni and F. Sondheimer, *J. Am. Chem. Soc.*, **86**, 521 (1964).

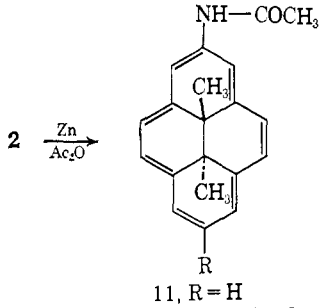
(7) A. Rieche, H. Gross, and E. Höft, *Chem. Ber.*, **93**, 88 (1960).

was no evidence for the presence of the desired carbonium ion **10**. The formation of **9** is analogous, of course, to the behavior of azulene toward triphenylmethyl fluoroborate.[8]



10 **9**

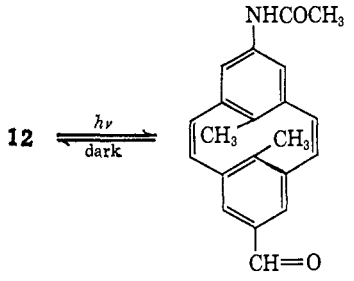
Reduction of the 2-nitro derivative **2** was investigated in the hope that the availability of the corresponding amine would make possible a wide range of aromatic diazonium ion reactions. With metals and acid, the 2-nitro derivative was readily reduced to the corresponding ammonium ion, as inferred from spectral data, but liberation of the free base led to extensive polymerization. In this respect the behavior of 2-amino-*trans*-15,16-dimethyldihydropyrene is analogous to that of various other aromatic compounds such as the aminopyrroles and aminothiophenes. With 1-nitroazulene[3] and 1-nitro[3.2.2]cyclazine,[5] reduction with zinc in the presence of acetic anhydride led smoothly to the corresponding acetamido derivative. This proved to be true also with **2** and 2-acetamido-*trans*-15,16-dimethyldihydropyrene (**11**) was obtained in excellent yield.



11, R = H
12, R = CH=O

In view of the reversible photochromic behavior encountered in the dihydropyrene series,[2] it was of interest to prepare a derivative in which one *peri* position held an electron-donating substituent and the other an electron-withdrawing substituent. It would be predicted that for such a derivative the reverse dark reaction would become very much faster than for the unsubstituted or monosubstituted derivatives. Subjection of **11** to the Rieche formylation procedure readily gave the formyl derivative **12** in good yield. When **12** was irradiated, it was found, as expected, that the reverse dark reaction was very fast. The dark reaction by which **13** reverts to **12** follows first-order kinetics with a half-life at room temperature of a few seconds.[9]

It was of interest to compare the change in chemical shift for the protons of the internal 15,16-methyls as substituents were introduced into the perimeter. The signal occurring at highest field (τ 14.25) is that for the



13

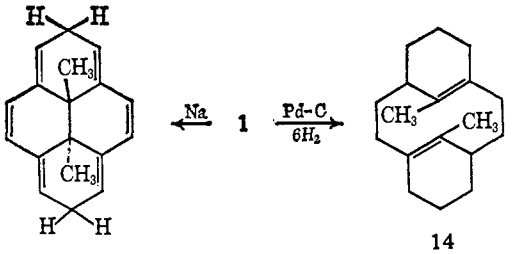
methyl groups in *trans*-15,16-dimethyldihydropyrene (**1**) itself. Introduction of either electron-donating or electron-withdrawing substituents on the aromatic perimeter causes the signal for the internal methyls to appear at lower field. This suggests that the inductive effect of the substituent is pretty much insulated from the internal methyls but that all substituents by resonance interaction with the aromatic π cloud cause a decrease in the ring current, and thus the chemical shift of the internal methyl protons moves to lower field.

The question of why electrophilic substitution occurs preferentially at the *peri* positions is not clear. Naively one might expect internal alkyl groups to show similar inductive and directive effects as when the same groups are externally substituted. However, on this basis the 1- and 4-positions would be predicted to be favored over the *peri* positions. Likewise, the Hückel molecular orbital calculations of **1** are not very helpful in explaining the orientation in electrophilic substitution. The usual reactivity indices (electron density, localization energy, and superdelocalizability) predict either random orientation or a slight preference for the 1- and 4-positions. The preference for *peri* orientation during electrophilic substitution, although unexpected, parallels the behavior encountered during electron spin resonance studies of the radical anion and radical cation of **1**.[10]

Reduction of **1** leads to different products depending upon the reagent and reaction conditions. Microhydrogenation of **1** using a palladium-on-charcoal catalyst showed a rapid uptake of 6 moles of hydrogen. When the experiment was repeated on a preparative scale, the product could be isolated as white crystals, mp 129–131°. Tentatively we assign structure **14** to this product. Its nmr spectrum shows no vinyl hydrogen and has only a broad complex signal between τ 7.4 and 9.1. Its mass spectrum shows a parent molecular ion at 242 with a major fragmentation peak at 227, corresponding to the loss of a methyl group.[11] Also, the hydrogenation product gives a yellow color with tetranitromethane, indicating that unsaturation is still present. Although these data are in accord with structure **14**, they do not distinguish, of course, between **14** and an alternate structure in which the double bonds are unsymmetrically placed.

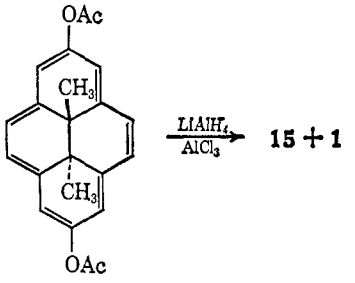
Under the condition of the Birch reduction, **1** was reduced smoothly to the bis-triene **15**, identical in all respects with an authentic sample of **15** prepared during the original synthesis of **1**.[2]

(8) E. C. Kirby and D. H. Reid, *Tetrahedron Letters*, No. 27, 1 (1960).
(9) A detailed description of the photochemical studies will be presented elsewhere.
(10) F. Gerson, E. Heilbronner, and V. Boekelheide, *Helv. Chim. Acta*, 47, 1123 (1964).
(11) We are indebted to Professor David Nelson of the University of Wyoming for the mass spectral determination.



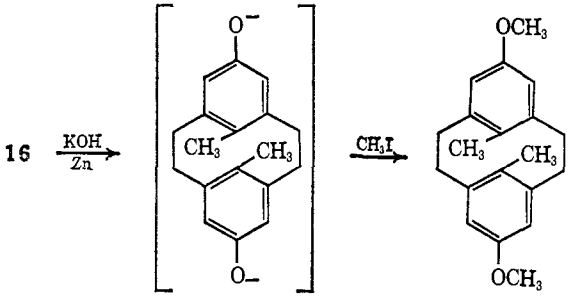
15 14

When 2,7-diacetoxy-*trans*-15,16-dimethyldihydropyrene[2] (**16**) was reduced with a mixture of lithium aluminum hydride and aluminum chloride, the product was a mixture of the bis-triene **15** and the aromatic hydrocarbon **1**. Treatment of this mixture with a palladium-on-charcoal catalyst in boiling cyclohexene gave **1** in 65% over-all yield from **16**.



16

On the other hand, when **16** was treated with aqueous base and zinc dust, the reaction mixture became colorless. Addition of methyl iodide and work-up in the usual way gave the corresponding metacyclophane **18**. Presumably, the hydrolysis and metal reduction are accompanied by valence tautomerism resulting in the formation of the intermediate **17**. The metacyclophane **18** was identical in all respects with an authentic sample prepared previously.[2]



17 18

Attempts to form complexes of **1** with trinitrobenzene and similar reagents were unsuccessful. Presumably, the internal methyl groups sterically interfere in the formation of such complexes. Also, attempts to effect a reaction between **1** and maleic anhydride in boiling benzene led to recovery of **1**.

In summary, the chemical properties of **1** fully support its description as an aromatic compound. Its electrophilic substitution reactions are quite analogous to those of benzene. However, its photochemical behavior, as well as its behavior on reduction, present properties peculiar to the dihydropyrene system.

Experimental Section[12]

2-Nitro-*trans*-15,16-dimethyldihydropyrene (2). To a stirred solution of 15 mg of *trans*-15,16-dimethyldihydropyrene[2] (**1**) in 3.0 ml of acetic anhydride held at 0° there was added 15 mg of powdered cupric nitrate trihydrate. In about 20 min the color of the solution had changed from emerald green to deep purple. The reaction mixture was stirred at 0° for 2 hr before adding 5 g of ice and 10 ml of ether. When the reaction of the acetic anhydride with the water was complete, the ether layer was separated, washed with water, dried, and concentrated. The residual purple crystals were sublimed at 120° (0.01 mm) and then recrystallized from a 1:1 mixture of chloroform and petroleum ether (bp 30–60°) to give 18 mg (99%) of deep purple needles, mp 172–173°; $\lambda_{max}^{cyclohexane}$ 348 mμ (ε 59,200), 382 (18,000), 406 (28,100), 516 (13,000), 598 (1200), and 662 (500); nmr, τ 0.37 (singlet, 2 H), 0.93 (doublet (J = 7.5 cps), 2 H), 1.13 (doublet (J = 7.5 cps), 2 H), 1.28 (doublet (J = 7.5 cps), 2 H), 1.50–1.75 (multiplet, 1 H), and 14.03 (6 H).

Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.57; H, 5.45; N, 5.53.

2,7-Dibromo-*trans*-15,16-dimethyldihydropyrene (3). A solution containing 50 mg of *trans*-15,16-dimethyldihydropyrene, 80 mg of recrystallized N-bromosuccinimide, and 5 mg of benzoyl peroxide in 150 ml of carbon tetrachloride was boiled under reflux for 4 hr. After removal of the solvent under reduced pressure, the residue was transferred to a neutral alumina column (Woelm, No. 1) and developed by elution with a 1:20 mixture of ether and petroleum ether. The eluate fraction containing the deep green band was concentrated, and the crystalline residue was subjected to repeated crystallization from a mixture of chloroform and methanol. This gave 16 mg of green needles, mp 213–214°; $\lambda_{max}^{cyclohexane}$ 342 mμ (ε 110,000), 378 (84,600), 480 (14,700), 647 (760), and 654 (1100); nmr, τ 1.30 (singlet, 4 H), 1.48 (singlet, 4 H), and 14.02 (singlet, 6 H).

Anal. Calcd for $C_{18}H_{14}Br_2$: C, 55.42; H, 3.62. Found: C, 55.08; H, 3.73.

2-Acetyl-*trans*-15,16-dimethyldihydropyrene (4). The acetylation conditions followed those used by Gaoni and Sondheimer.[6] To a solution of 25 mg of *trans*-15,16-dimethyldihydropyrene (**1**) in 10 ml of methylene chloride was added 0.25 ml of acetic anhydride and a few drops of boron trifluoride etherate. The resulting deep blue-green solution was allowed to stand at room temperature for 1.5 hr before adding 10 ml of water. The organic layer was separated and concentrated under reduced pressure. The oily residue was taken up in 20 ml of ether and washed successively with dilute aqueous potassium carbonate solution and water. After the ether solution had been dried, it was concentrated and the residue was distilled in a molecular still at 110° (0.1 min). This gave 27.4 mg (93%) of a red viscous oil; infrared, $\nu_{max}^{CHCl_3}$ 6.0 μ; nmr, τ 0.77 (singlet, 2 H), 1.12–1.50 (complex multiplet, 6 H), 1.87 (triplet, 1 H), 6.97 (singlet, 3 H), and 14.03 (split peak, 6 H).

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.36; H, 6.70.

2-Benzoyl-*trans*-15,16-dimethyldihydropyrene (5). To a solution of 20 mg of *trans*-15,16-dimethyldihydropyrene (**1**) in 10 ml of methylene chloride there was added successively 0.25 ml of benzoyl chloride and sufficient anhydrous aluminum chloride (about 20 mg) to produce a deep blue color. After the solution had stood at room temperature for 6 hr, 10 ml of ice water was added with stirring. The red organic layer was separated, washed successively with aqueous 0.25 N potassium hydroxide solution and water, dried, and concentrated. The residue was taken up in benzene and chromatographed over neutral alumina (Woelm, No. 3). The green band which eluted first was concentrated to give 9 mg of the starting hydrocarbon **1**. The second eluate fraction containing a deep red band was collected and concentrated. The solid residue, on recrystallization from aqueous methanol, gave 13.3 mg (84%, based on unrecovered **1**) of dull red needles, mp 142–144°; $\lambda_{max}^{cyclohexane}$ 280 mμ (ε 11,000), 347 (60,000), 372 (16,000), 393 (23,000), 508 (13,000), 598 (460), and 663 (320); infrared, $\nu_{max}^{CHCl_3}$ 1640 cm^{-1}; nmr, τ 0.91 (singlet, 2 H), 1.13–1.80 (multiplet, 7 H), 1.80–2.75 (typical benzoyl multiplet, 5 H), 13.83 and 13.93 (split peak, 6 H).

Anal. Calcd for $C_{25}H_{20}O$: C, 89.25; H, 5.99. Found: C, 89.26; H, 6.00.

From the chromatography described in the experiment above, a second, slower moving red band could be separated. The amount of material present in this band was quite small. However, by combining this fraction from three separate preparations, sufficient

(12) Microanalyses are by Micro-Tech Laboratories and 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 thank the National Science Foundation for the funds allowing the purchase of the Varian A-60.

material for investigation was obtained. The residue from these combined fractions was rechromatographed over neutral alumina (Woelm, No. 3) using benzene for elution and only a single band developed. The eluate fraction containing this band was concentrated, and the solid residue was recrystallized from a mixture of chloroform and petroleum ether to give 10 mg of purple needles, mp 194–195°. The assignment of these crystals as **2,7-dibenzoyl-*trans*-15,16-dimethyldihydropyrene** (**6**) is based primarily on their nmr spectrum which has signals at τ 0.94 (singlet, 4 H), 1.22 (singlet, 4 H), 1.75–2.70 (typical multiplet of the benzoyl group, 10 H), and 13.68 (singlet, 6 H).

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.24; H, 5.49. Found: C, 87.30; H, 5.55.

2-Formyl-*trans*-15,16-dimethyldihydropyrene (**7**). To a stirred solution of 50 mg of *trans*-15,16-dimethyldihydropyrene (**1**) in 10 ml of methylene chloride held at 0° there was added 0.05 ml of stannic chloride and 45 mg of *n*-butyl dichloromethyl ether, following the procedure of Rieche, Gross, and Höft.[7] The mixture was then stirred at room temperature for 1 hr before being poured into 100 ml of water. The aqueous suspension was then extracted with three 25-ml portions of methylene chloride. The methylene chloride extracts were then washed with water, dried, and concentrated. The red solid residue was taken up in benzene and chromatographed over neutral alumina (Woelm, No. 3). The main eluate fraction gave 45 mg (83%) of red crystals, mp 129–131°. Recrystallization from 5% aqueous methanol gave red plates, mp 131–132°; λ_{max}^{EtOH} 235 mμ (ϵ 6060), 255 (4120), 342 (28,200), 374 (13,000), 395 (14,500), and 506 (5200); nmr, τ −0.67 (singlet, 1 H), 0.90 (singlet, 2 H), multiplet centered at 1.33 (6 H), and 13.92 (singlet, 6 H).

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.35; H, 6.25.

Reaction of *trans*-15,16-Dimethyldihydropyrene with Trifluoroacetic Acid. A solution of 40 mg of *trans*-15,16-dimethyldihydropyrene (**1**) in 0.4 ml of trifluoroacetic acid was prepared in an nmr tube under nitrogen. Its spectrum showed no high-field signal above that of tetramethylsilane but instead showed separate singlets at τ 9.37 and 9.77 (3 H each), a multiplet centered at 7.40 (2 H), and a multiplet centered around 3 (9 H). The ultraviolet spectrum of this solution showed absorption maxima at 277, 354, 535, and 705 mμ. When the solution was poured into 100 ml of water and the resulting dark green suspension was extracted with ether, concentration of the ether followed by sublimation of the residue led to the recovery of 35 mg (88%) of **1**.

Repetition of this experiment using deuteriotrifluoroacetic acid and 1 ml of deuterium oxide for dilution after the solution had stood for 2 min yielded a sample of **1** whose nmr spectrum showed only the high-field signal of the internal methyls at τ 14.26.

2-Triphenylmethyl-*trans*-15,16-dimethyldihydropyrene (**9**). To a solution of 20 mg of *trans*-15,16-dimethyldihydropyrene (**1**) in 2 ml of dry acetonitrile at room temperature was added a solution of 29 mg of triphenylmethyl fluoroborate in 2 ml of acetonitrile. The solution was allowed to stand for 15 min before adding 25 ml of ether. No precipitation occurred. After removal of the solvent under reduced pressure, the residual solid was taken up in a 1:20 mixture of ether–petroleum ether and chromatographed over neutral alumina (Woelm, No. 1). The first bright green band to be eluted contained 9 mg of the starting hydrocarbon **1**. The next fraction of eluate containing a dull green band was concentrated to dryness, and the residual solid was recrystallized from methanol to give 6 mg of green needles, mp 187–189°; nmr, multiplet centered around τ 1.53 (9 H), multiplet centered at 2.53 (15 H), and a split peak at 13.92 and 14.03 (6 H).

Anal. Calcd for $C_{37}H_{30}$: C, 93.63; H, 6.37. Found: C, 93.33; H, 6.45.

2-Acetamido-*trans*-15,16-dimethyldihydropyrene (**11**). To a solution of 30 mg of 2-nitro-*trans*-15,16-dimethyldihydropyrene (**2**) and 100 mg of sodium acetate in 5 ml of acetic anhydride there was added 250 mg of zinc dust with swirling over a 5-min period. The reaction mixture rapidly changed from purple to green as it was stirred at room temperature for 1 hr. Then, 100 ml of water was added and the aqueous suspension was extracted with three 25-ml portions of ether. The combined ether extracts were washed successively with aqueous ammonia and water, dried, and concentrated. The resulting green solid was taken up in benzene and chromatographed over neutral alumina (Woelm, No. 1), adding ether for elution. Concentration of the eluate fraction containing the green band gave a green solid which, after recrystallization from methanol, yielded 18 mg (58%) of lustrous green plates, mp 178–180°; λ_{max}^{EtOH} 235 mμ (ϵ 4280), 262 (3990), 342 (35,900), 382 (10,400), and 486 (4980); infrared, ν_{max}^{KBr} 1690 cm^{-1}; nmr, τ 1.06 (singlet, 2 H), multiplet centered at 1.43 (6 H), multiplet centered at 1.97 (1 H), 7.57 (singlet, 3 H), and 14.11 and 14.14 (split peak, 6 H).

Anal. Calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.81; H, 6.86; N, 5.01.

2-Acetamido-7-formyl-*trans*-15,16-dimethyldihydropyrene (**12**). To a solution of 40 mg of 2-acetamido-*trans*-15,16-dimethyldihydropyrene (**11**) in 7 ml of methylene chloride held at 0° there was added with stirring 56 mg of anhydrous aluminum chloride followed immediately by the addition of 28 mg of *n*-butyl dichloromethyl ether. The reaction mixture was stirred at room temperature for 1.5 hr and then poured into 100 ml of water. The aqueous suspension was extracted with three 25-ml portions of methylene chloride. These were combined, washed with water, dried, and concentrated. The purple residue was taken up in benzene and chromatographed over neutral alumina (Woelm, No. 2) adding methylene chloride for elution. The eluate fraction containing the purple band was concentrated and the residue recrystallized from a mixture of benzene and petroleum ether to give 18 mg of purple needles, mp 202–203°; λ_{max}^{EtOH} 258 mμ (ϵ 18,900), 335 (shoulder, 49,400), 348 (78,800), 392 (19,400), 416 (24,200), 551 (17,600), and 600 (13,400); infrared, $\nu_{max}^{CHCl_3}$ 1653 and 1669 cm^{-1}; nmr, τ −0.58 (singlet, 1 H), 1.00 (singlet, 4 H), 1.28 (AB doublet (J = 8 cps), 2 H), 1.57 (AB doublet (J = 8 cps), 2 H), 7.50 (singlet, 3 H), 13.68 (singlet, 3 H), and 13.73 (singlet, 3 H).

Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03. Found: C, 79.25; H, 6.20.

Hydrogenation of *trans*-15,16-Dimethyldihydropyrene. A mixture of 25 mg of *trans*-15,16-dimethyldihydropyrene (**1**) and 100 mg of a 5% palladium-on-charcoal catalyst in 10 ml of ethanol was subjected to hydrogenation at room temperature and at atmospheric pressure of hydrogen. Hydrogen uptake was rapid with 6 moles of hydrogen being absorbed in 10 min. After removal of the catalyst and solvent, there remained a white solid which was recrystallized from methanol to give 12 mg of white needles, mp 129–131°. These crystals gave a yellow color with tetranitromethane and showed no absorption in the ultraviolet above 220 mμ. Their nmr spectrum showed no absorption in the vinyl hydrogen region but only general absorption in the τ 7.4–9.1 region. A sharp spike is present at τ 8.85 which we interpret as being due to the methyl protons having been shifted to higher field by interaction with the double bond of the opposite ring. The mass spectrum shows a parent molecular ion at 242 with a major fragmentation peak at 227.[11] These data suggest structure **14** for the reduction product.

Anal. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.96; H, 11.12.

Birch Reduction of *trans*-15,16-Dimethyldihydropyrene. A solution of 63 mg of *trans*-15,16-dimethyldihydropyrene (**1**) in 50 ml of dry tetrahydrofuran was added dropwise to the blue solution of 10 mg of sodium in 50 ml of liquid ammonia. The blue of the solution faded, leaving a light green color. Another small piece of sodium was added to regenerate the blue color showing an excess of sodium. After the ammonia had evaporated, an excess of methanol was added and the mixture was concentrated under reduced pressure. The residue was taken up in ether, washed with water, and dried. After concentration of the ether solution, the residue was dissolved in a 1:20 mixture of ether and petroleum ether and chromatographed over neutral alumina (Woelm, No. 1). The first eluate fraction containing a yellow band was concentrated to give 33 mg of yellow needles, mp 168–170°, identical with the bis-triene **15** reported previously.[2] As further identification, the sample of yellow needles was dehydrogenated over palladium on charcoal to give back the hydrocarbon **1**, as described previously.[2]

Lithium Aluminum Hydride Reduction of 2,7-Diacetoxy-*trans*-15,16-dimethyldihydropyrene. A solution of 60 mg of 2,7-diacetoxy-*trans*-15,16-dimethyldihydropyrene[2] (**16**) in 20 ml of dry ether was added dropwise with stirring to a solution of 1.9 g of lithium aluminum hydride and 6.6 g of powdered anhydrous aluminum chloride in 100 ml of ether. The resulting green mixture was stirred at room temperature for 12 hr with little change in color. It was then poured into 100 ml of ice water. The ether layer was separated, washed with water, dried, and concentrated. An nmr spectrum of the residue in deuteriochloroform indicated it was approximately a 1:1 mixture of the bis-triene **15** and the aromatic hydrocarbon **1**. The residue was then dissolved in 20 ml of cyclohexene containing 100 mg of a 5% palladium-on-charcoal catalyst, and the mixture was boiled under reflux for 2 hr. After removal of the catalyst and solvent, the residual green solid was taken up in petroleum ether and chromatographed over neutral alumina (Woelm, No. 2). Concentration of the dark green eluate

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]

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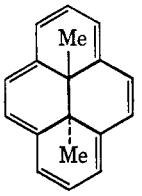
Abstract: The synthesis of *trans*-15,16-diethyldihydropyrene (**2**) is described. The molecule shows typical aromatic properties.

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.



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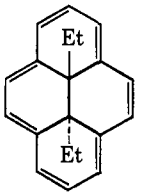

2

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**

(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.