was dissolved in trifluoroacetic acid and treated under the same reaction conditions as in A, only pyrene was recovered. Pyrene was also allowed to react under the same conditions as in A with a solution of trifluoroacetic acid containing trifluoroperacetic acid. In this case the same two quinones, **29** and **30**, were isolated and identified as in A. The thin layer chromatogram of the oxidation product mixture indicated that there were numerous other products present of both lower and higher R_f values than those of the two quinones.

C. A small amount of the diene was dissolved in trifluoroacetic acid. It was observed that the solution rapidly became green reaching a maximum intensity after 30 to 40 min. The color faded very slowly requiring several days to become a light yellow and remain that color. The visible spectrum showed an intense band at 469 mμ with considerably weaker bands between 550 and 700 mμ. The appearance and disappearance of the band at 469 mμ was followed with time holding the reaction mixture at 30°. The band reached a maximum intensity at 22 min and then slowly faded in intensity. A plot of the log of absorption *vs.* time gave a good straight line for those values of absorption recorded for decay of the 469-mμ band from about 1 hr after maximum intensity until about 11 hr after the maximum intensity had been reached.

D. A solution of 4.228 mg of the diene in 100 g of trifluoroacetic acid was allowed to stand for 1 hr. To it was then added 100 ml of water. This was extracted with three portions of chloroform (a total of 250 ml) and the combined chloroform extracts were washed successively with two 100-ml portions of water, 100 ml of a 10% aqueous sodium bisulfite solution, and 100 ml of a saturated sodium bicarbonate solution. After the chloroform solution was dried, it was concentrated. From the residue pyrene was isolated by preparative tlc using the silica gel with a 5% solution of ethyl acetate in hexane as the eluent. The pyrene was dissolved in 500 ml of cyclohexane and a quantitative ultraviolet spectrum indicated that 0.931 mg (24%) of pyrene was present. There were two fluorescent bands directly below the pyrene band which were in the area where starting material would be present. Examination of the ultraviolet spectrum of these two bands indicated that essentially no starting material was present.

The two quinones were isolated by preparative tlc, using silica gel with ethyl acetate as eluent. The two quinones (together) were dissolved in 50 ml of methanol. Their ultraviolet spectrum indicated that 4.8% of 1,6-pyrenequinone (**29**) and 4.4% of 1,8-pyrenequinone (**30**) were present. The amount of each in the mixture was determined by measuring the absorption of the solution of the mixture at two different wavelengths for which the extinction coefficients were known for both compounds.[3,2]

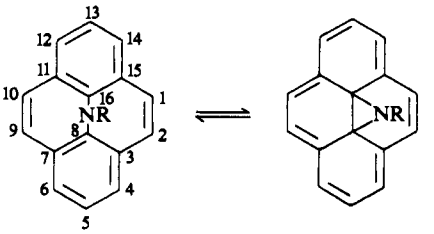
8,16-Imino[2.2]metacyclophane-1,9-diene. A Valence Tautomer of Pyren-*cis*-15,16-imine[1]

B. Andes Hess, Jr.,[2] and V. Boekelheide

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403. *Received September 23, 1968*

Abstract: A synthesis of 8,16-imino[2.2]metacyclophane-1,9-diene (**1**) and certain simple N-substituted derivatives is described. Although **1** is a valence tautomer of pyren-*cis*-15,16-imine (**4**), spectral examination of the compound at room temperature is in complete accord with structure **1** and provides no evidence for the presence of pyren-*cis*-15,16-imine. On the other hand, **1** and its N-substituted derivatives undergo rearrangement and expulsion reactions of the imine bridge which are best explained by invoking pyren-*cis*-15,16-imine as an intermediate. These rearrangement and expulsion reactions occur thermally in neutral solvents or may be initiated by solution in strong acid. The nature of the substituent on the imino nitrogen plays an important role in determining the ease with which these expulsion and rearrangement reactions occur.

In an accompanying paper,[3] the background and reasons for interest in *cis*-15,16-dihydropyrenes are discussed. Since *cis*-bridged [2.2]metacyclophane-1,9-dienes are valence tautomers of the corresponding *cis*-15,16-dihydropyrenes, a natural synthetic approach has been to prepare suitable *cis*-bridged [2.2]metacyclophane-1,9-dienes. In the previous paper a synthesis of 8,16-oxido[2.2]metacyclophane-1,9-diene is described,[3] and in this report the synthesis of 8,16-imino[2.2]metacyclophane-1,9-diene (**1**), a valence tautomer of pyren-*cis*-15,16-imine (**4**), is presented as well as certain aspects of its chemistry.[4]



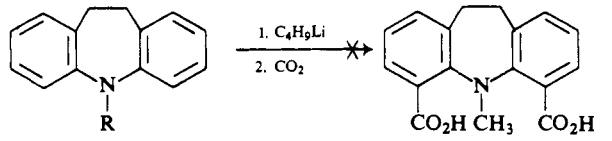
1, R = H
2, R = CH_3
3, R = CO_2Et

4, R = H
5, R = CH_3
6, R = CO_2Et

In undertaking a synthesis of 8,16-imino[2.2]metacyclophane-1,9-diene (**1**) we were hopeful that we could follow a reaction sequence similar to the successful route worked out for 8,16-oxido[2.2]metacyclophane-1,9-diene.[3] Therefore, the commercially available 10,11-dihydro-5H-dibenz[*b*,*f*]azepine (**7**) was methylated and the N-methyl derivative (**8**) was subjected to metalation with *n*-butyllithium followed by carbonation. Un-

(1) Aided in part by a grant from the National Science Foundation.
(2) National Institutes of Health Postdoctoral Fellow, 1966–1968.
(3) B. A. Hess, Jr., A. S. Bailey, B. Bartusek, and V. Boekelheide, *J. Am. Chem. Soc.*, **91**, 1665 (1969).
(4) The numbering system used for the [2.2]metacyclophanes is that recommended by B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, N. Y., 1964, p 8.

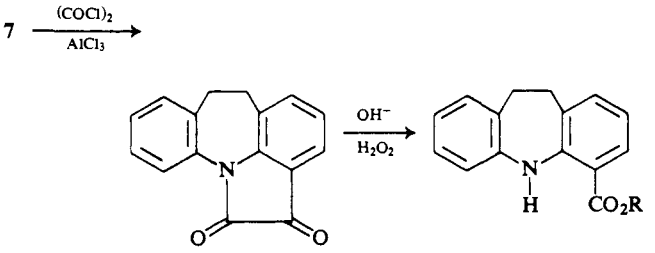
fortunately, though, the metalation and carbonation procedure proceeded badly giving only a monocarboxylic acid in poor yield and none of the desired dicarboxylic acid (**9**).



7, R = H
8, R = CH_3

9

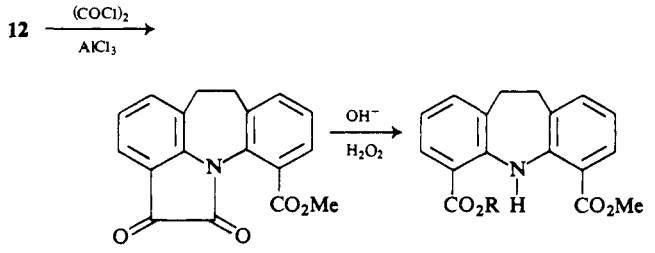
It was necessary, therefore, to devise a different synthetic approach. Starting again with **7**, we utilized the Stollé isatin procedure[5] to introduce carboxylic acid groups at both positions *ortho* to the imino nitrogen. Treatment of **7** with oxalyl chloride and aluminum chloride gave the isatin **10** in 80% yield. This was then dissolved in base and oxidized with hydrogen peroxide to yield the corresponding acid (**11**). The crude acid was directly esterified with diazomethane giving the methyl ester (**12**) in 89% over-all yield from the isatin **10**.



10

11, R = H
12, R = Me

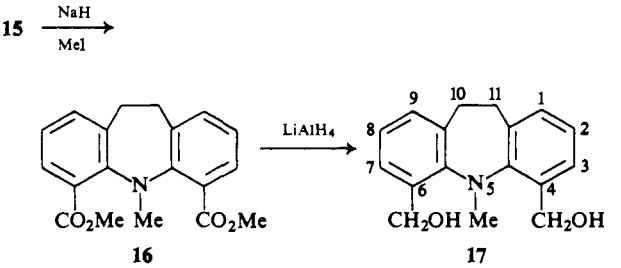
Repetition of the same sequence led to an excellent conversion of **12** to the corresponding isatin **13**. Treatment of **13** with base and hydrogen peroxide led to the crude acid (**14**) which, on esterification, gave the diester **15** in an over-all yield from **12** of 64%. The structure of **15** follows from its method of synthesis but its spectral properties are also in full accord with this assignment.



13

14, R = H
15, R = Me

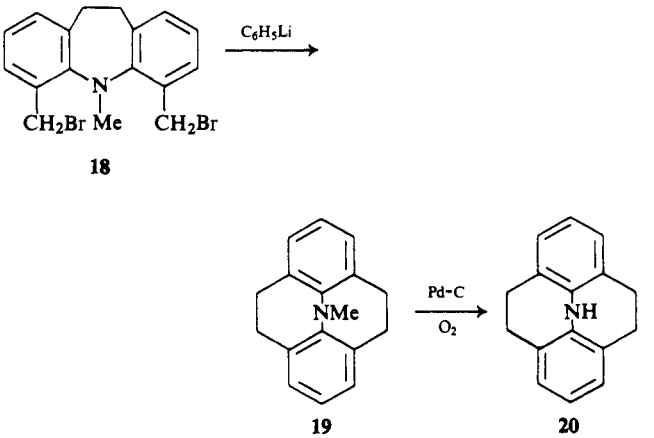
Since it was envisioned that the conversion of **15** to a metacyclophane would be accomplished by a Wurtz ring closure, it was necessary to introduce a protective group on nitrogen. Under the usual conditions for alkylating an amine, **15** was recovered unchanged. However, treatment of **15** with sodium hydride followed by prolonged heating with methyl iodide did give the desired N-methyl derivative (**16**) in 88% yield. That part of the difficulty in the alkylation reaction was due to steric hindrance seems evident from examination of molecular models and is borne out by the change in spectral properties effected through N-methylation. The crystals of **15** are a definite yellow and show a long-wavelength absorption band at 363 mμ (ε 10,780), whereas **16** is colorless showing only end absorption in the ultraviolet. Clearly, the ester carbonyls, which are coplanar and conjugated with the aromatic rings in **15**, are forced out of planarity by the presence of the N-methyl group leading to the loss of absorption in the visible region. The effects of this crowding by the N-methyl group are also apparent in the next product in the series, the diol **17**, obtained by lithium aluminum hydride reduction of **16**. In this case the crowding by the N-methyl group results in hindered rotation about the carbon–carbon bonds at the 4 and 6 positions so that the nmr signals for the methylene protons of the hydroxymethyl groups in **17** appear as AB quartets rather than singlets.



16

17

For the Wurtz ring closure, **17** was converted to the corresponding dibromide (**18**), and this was treated with a solution of phenyllithium. The desired 8,16-imino[2.2]-metacyclophane (**19**) was readily isolated in 75% yield. The spectral data corroborated the structure assigned to **19**. Its mass spectrum showed the expected parent molecular ion (*m/e* 235) and its nmr spectrum showed the bridging methylene protons as an AA′BB′ multiplet centered at τ 6.84.



18

19

20

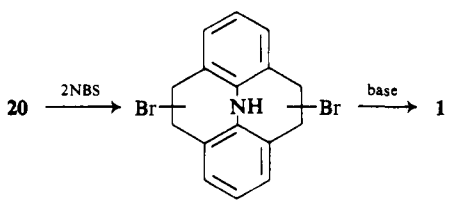
The remaining step in the synthesis was simply the introduction of double bonds into the bridging carbons of **19**. As had been shown in the analogous oxygen

(5) R. Stollé, *Ber.*, **46**, 3915 (1913).

series,[3] *cis*-bridged [2.2]metacyclophanes undergo substitution reactions at the benzylic positions even though *trans*-[2.2]metacyclophanes do not.[6] However, in contrast to the oxygen series, treatment of **19** with 2 mol of N-bromosuccinimide followed by reaction with base gave a complex mixture of products with no spectral indication that the desired diene **2** had been formed. The contrasting behavior of the two series is rather puzzling.

An attempt to introduce the necessary double bonds was then investigated using other reagents. Treatment of **19** with 2,3-dichloro-5,6-dicyanoquinone again gave a mixture of products from which the demethylated derivative **20** could be isolated in poor yield. Dehydrogenation was next tried using a palladium catalyst in an inert atmosphere.[7] Again, the demethylated derivative **20** was formed, but also in poor yield. However, by varying the conditions it was found that bubbling oxygen through a boiling methanolic solution of **19** in the presence of a 30% palladium-on-charcoal catalyst led in a smooth conversion to 8,16-imino[2.2]metacyclophane (**20**) in 75% yield. This appears to be a reaction of some generality and a useful new method for demethylating tertiary amines.[8] Presumably, the reaction proceeds through an intermediate methylene immonium ion.

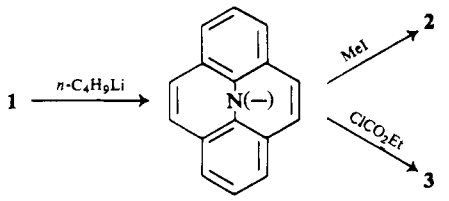
The availability of 8,16-imino[2.2]metacyclophane (**20**) through the palladium-catalyzed oxidation of **19** prompted us to investigate its behavior toward the bromination–dehydrobromination procedure. Treatment of **20** with 2 mol of N-bromosuccinimide gave a dibromide mixture whose nmr spectrum suggested it was a mixture of 1,9- and 1,10-dibromides (**21**) analogous to that obtained in the oxygen series.[3] Without further purification, the crude dibromide was heated with 1,5-diazabicyclo[4.3.0]-non-5-ene to effect elimination of hydrogen bromide. This gave 8,16-imino[2.2]metacyclophane-1,9-diene (**1**) as white crystals, mp 87–90°, in 66% yield. Although gratifying, it is not at all obvious why the bromination–dehydrobromination procedure should be so successful with the imino derivative (**20**) and fail completely with the N-methyl imino derivative (**19**).



21

That the product was the *cis*-bridged metacyclophane **1** and not its valence tautomer **4** was readily obvious from the spectral data. The ultraviolet spectrum of **1** showed a long-wavelength absorption band at 304 mμ (ε 12,600) as would be expected for this type of *cis*-stilbene and closely paralleling the band at 302 mμ in 8,16-oxido[2.2]-metacyclophane-1,9-diene.[3] The corresponding valence tautomer **4** should exhibit the typical emerald green color of the dihydropyrene system. Likewise, the nmr spectrum of **1** closely parallels that of its oxygen analog, showing an A_2B multiplet in the range of τ 2.38–3.08 with the four bridging vinyl protons appearing as a singlet at τ 2.58. The fact that the vinyl protons appear at such low field suggests that there is a reasonably strong peripheral ring current. The mass spectrum of **1** showed the expected parent molecular ion at 217 with a strong signal at *m/e* 202, corresponding to the loss of the imino bridge.

Although **1** was essentially nonbasic and unreactive toward the usual alkylating agents, it was of interest to see whether N-alkylation might be forced. Treatment of **1** with *n*-butyllithium in tetrahydrofuran produced a deep red solution containing the corresponding anion **22** and addition of methyl iodide then gave the N-methyl derivative **2**. Similarly, addition of ethyl chlorocarbonate to a solution of the anion gave the corresponding urethan **3**. Again, the spectral evidence clearly showed that these products exist as the metacyclophane derivatives **2** and **3** and not as their valence tautomers **5** and **6**. The fact that all of these derivatives show a sharp singlet in the nmr for the bridging vinyl protons requires that either the substituents on nitrogen are symmetrically placed or else the inversion of nitrogen occurs so rapidly that each of the vinyl protons sees the same time-average effect.



22

As discussed in the previous paper,[3] the chemical behavior of 8,16-oxido[2.2]metacyclophane-1,9-diene suggested that either thermally or by acid catalysis valence tautomerization to pyrene *cis*-15,16-epoxide could occur with resultant expulsion or rearrangement of the bridging oxygen. It remained to determine whether the imino derivatives would show a similar behavior. The thermal experiments are best discussed first.

When N-methyl-8,16-imino[2.2]metacyclophane-1,9-diene (**2**) was heated in benzene in a sealed tube at 200° for 20 hr, it was converted in essentially quantitative yield to pyrene. At temperatures below 200° the thermal decomposition in benzene was exceedingly slow. However, when **2** was heated in methanol at 100° for 44 hr it underwent conversion in quantitative yield to N-methyl-1-pyrenamine (**27**). The striking change in the course of the reaction with a change in the polarity of the solvent strongly suggests that the lower temperature reaction in polar solvent involves a heterolytic process whereas the higher temperature reaction in the nonpolar solvent is a homolytic process.

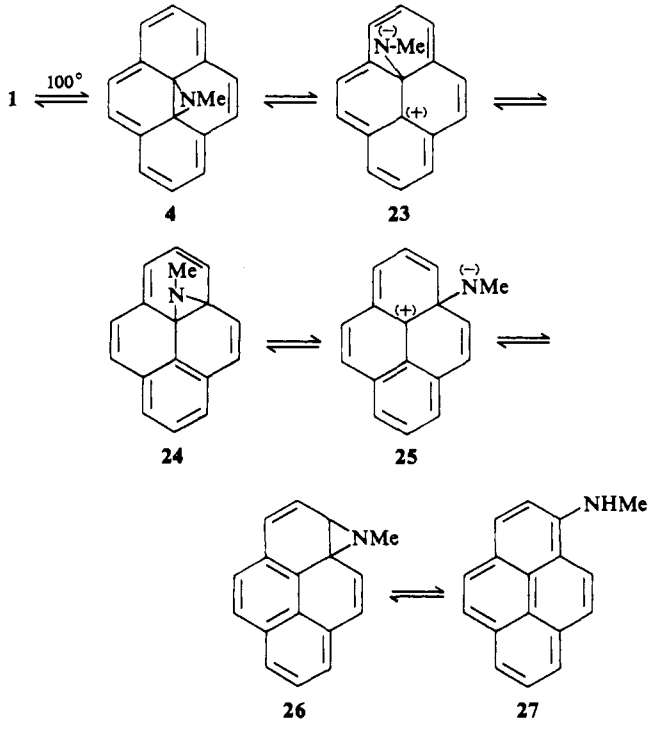
A reasonable interpretation of the reaction in methanol would be, as shown below, a thermally induced valence tautomerization of **1** to **4** which, by bond rupture, could lead to **23** and this by a guided-tour mechanism involving **24**, **25**, and **26** would yield N-methyl-1-pyrenamine (**27**). The intermediate ionic species would, of course, be highly

(6) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961).

(7) This experiment was inspired by a lecture given by Professor D. Arigoni at the University of Oregon, Oct 20, 1966, in which he described using a palladium catalyst for demethylating certain tertiary amines, although in poor yield.

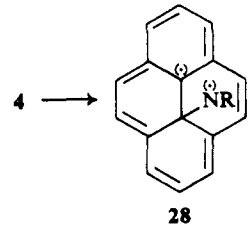
(8) After this investigation was completed, a publication by G. T. Davis and D. H. Rosenblatt (*Tetrahedron Letters*, 4085 (1968)) appeared in which they describe the platinum-catalyzed air oxidation of N-methyl tertiary amines to the corresponding N-formyl derivatives as a general method.

solvated. The same argument explaining why N-methyl-1-pyrenamine is formed with the complete exclusion of N-methyl-4-pyrenamine can be used as that employed previously to explain why in the oxygen series there is exclusive formation of 1-pyrenol with 4-pyrenol being absent.[3]

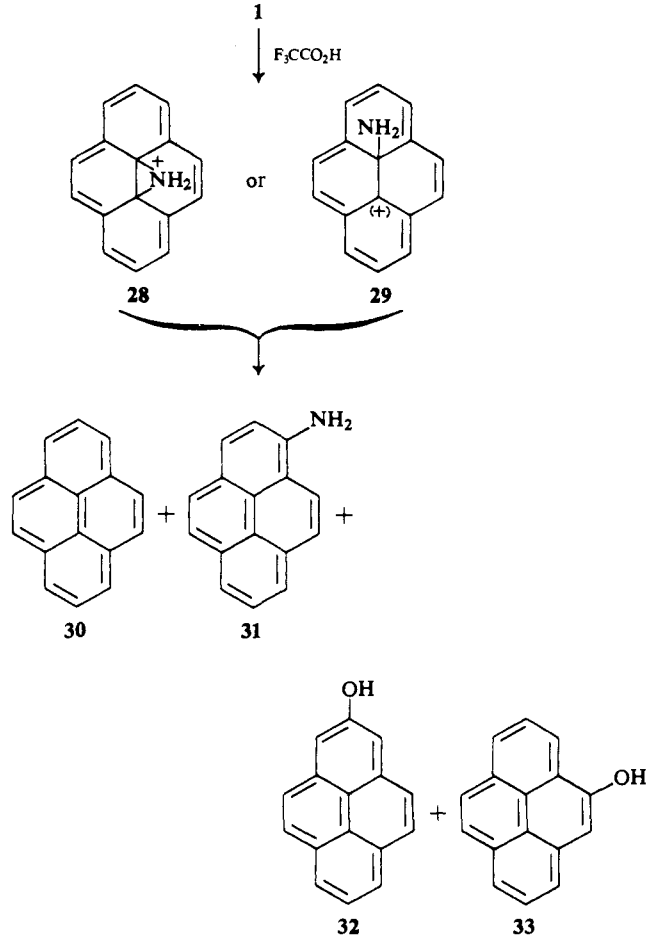


The contrasting behavior in benzene, though, suggested that either the imine bridge was being expelled as a nitrene or that a multistep radical process was involved. Various possibilities for trapping a nitrene intermediate were considered. A great deal of study has been devoted recently to the chemistry of nitrenes and, in particular, Lwowski has studied the behavior of nitrenes derived from ethyl azidoformate in reaction with cyclohexene.[9] The compound which might provide a nitrene whose behavior could be compared directly with that encountered by Lwowski was **3** and this, of course, was the reason for its preparation. Unfortunately, **3** proved to be thermally much more stable than **2**, requiring a temperature of 275° before decomposition to pyrene occurred at a reasonable rate. Although an experiment was tried in which **3** was decomposed in the presence of cyclohexene at 275°, the products, aside from pyrene, were a complex mixture and appreciable polymeric material was formed. The fact that no N-carbethoxy-7-azabicyclo[4.1.0]heptane was isolated is not significant since a control run established that it also is thermally decomposed under these conditions.

The most significant observation relative to these thermal decompositions in nonpolar solvents appears to be that the urethan **3** is very much more stable thermally than the N-methyl derivative **2**. If one assumes that an N-acyl radical is of considerably higher energy than an N-alkyl radical,[10] this difference in thermal stability is in accord with a multistep process in which the pyren-*cis*-15,16-imine (**4**) is first formed and then undergoes bond fission to the diradical **28**. Subsequent reaction of **28** with solvent (cyclohexene) could then yield pyrene plus an aminoalkyl radical.



In the case of 8,16-oxido[2.2]metacyclophane-1,9-diene, solution in strong acid produced a deep green color which slowly faded on standing and from which pyrene plus two pyrene quinones were isolated.[3] When 8,16-imino[2.2]-metacyclophane-1,9-diene (**1**) was dissolved in trifluoroacetic acid, an analogous development of color occurred but fading proceeded so rapidly that the same depth of color was not observed as in the oxygen series. The N-methyl derivative **2** behaved in a very similar fashion, but the urethan **3** was unaffected by solution in trifluoroacetic acid and could be recovered unchanged.



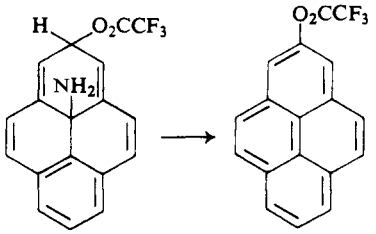
(9) W. Lwowski and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **87**, 1947 (1965).

(10) Professor T. W. Koenig has informed us that he has preliminary evidence suggesting that this is a valid assumption.

An investigation of the reaction of **1** with trifluoroacetic acid revealed four main products: pyrene (**30**), 1-pyrenamine (**31**), 2-pyrenol (**32**), and 4-pyrenol (**33**). The formation of these products can best be explained by assuming that there is first an acid-catalyzed valence tautomerization to give a protonated colored species, either **28** or **29**. The lack of reactivity of the urethan **3** would be in harmony with this postulation since its lowered bascicity would adversely affect the acid-catalyzed valence tautomerization.

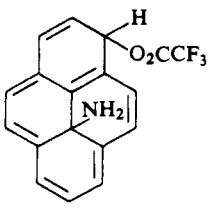
The formation of pyrene from **28** or **29** would be analogous to the oxygen series with the by-product in this case being hydroxylamine trifluoroacetate. Also, the formation of 1-pyrenamine (**31**) could be explained in an analogous fashion to that used to explain the formation of N-methyl-1-pyrenamine (**27**) during the thermal rearrangement in methanol.

The formation of the 2- and 4-pyrenols is likewise readily understandable. In the case of 2-pyrenol, for example, attack of trifluoroacetate anion on either **28** or **29** would give **34** which, by protonation on nitrogen followed by loss of a proton and ammonia, would give the trifluoroacetate of 2-pyrenol (**35**). Hydrolysis of **35** to give 2-pyrenol would be expected under the conditions used for working up the reaction mixture. A similar explanation would apply, of course, for the formation of 4-pyrenol (**33**).



34 **35**

Authentic samples of 1-, 2-, and 4-pyrenol were prepared and, as discussed previously,[3] they are readily distinguished from each other by their nmr spectra and from their behavior on thin layer chromatography. Also, each of these pyrenols is readily detected in the presence of the others even when present in a minute quantity. Thus, we feel the absence of 1-pyrenol in the reaction mixture is genuine. At first this might seem puzzling but the comparable intermediate **36** needed to give 1-pyrenol would be of higher energy than **34** since it does not retain an aromatic ring.



36

In summary, several 8,16-imino[2.2]metacyclophane-1,9-diene derivatives have been prepared and it has been shown that they do not undergo valence tautomerization to the corresponding pyren-*cis*-15,16-imines to a measurable degree at room temperature. However, either thermally or in the presence of strong acid these 8,16-imino[2.2]metacyclophane-1,9-dienes undergo rearrangement and expulsion reactions which are most readily explained by invoking the corresponding pyren-*cis*-15,16-imines as intermediate species.

Experimental Section[11]

Isatin of 10,11-Dihydrodibenz[*b*,*f*]azepine (10). A solution of 40.0 g of 10,11-dihydrodibenz[*b*,*f*]azepine (**7**) in 250 ml of ether was added dropwise over a 30-min period to a boiling solution of 30 ml of oxalyl chloride in 150 ml of ether. After the addition was complete, the reaction mixture was boiled under reflux for 3.5 hr and then concentrated under reduced pressure. The resultant green solid was dissolved in 1.0 l. of boiling carbon disulfide and 50.0 g of aluminum chloride was added in portions over a 5-hr period. The reaction mixture was boiled under reflux an additional 15 hr, before cooling and decanting off of the carbon disulfide solution. To the remaining solid residue a careful addition of 200 ml of concentrated hydrochloric acid followed by 200 ml of water was made. Then, 1.0 l. of chloroform was added with vigorous stirring and the two phases were separated. The chloroform layer was washed with water, dried, and concentrated to give 50 g of a red solid. Recrystallization of this from ethanol gave 36.0 g of red crystals. However, concentration of the mother liquor followed by chromatography over silica using benzene for elution provided another 5 g of red crystals, making a total yield of 41.0 g (80%) of isatin of satisfactory purity for further experiments. A sample recrystallized from ethanol gave red needles, mp 180–181°; uv, λ_{max}^{EtOH} 249 (22,600), 284 (sh, 4410), and 430 mμ (ε 446); ir, $\lambda_{max}^{CHCl_3}$ 5.73 μ (–C=O); nmr ($CDCl_3$), multiplet at τ 2.10–3.13 (7 H, Ar*H*) and singlet at 6.98 (4 H, $-CH_2CH_2-$).

Anal. Calcd for $C_{16}H_{11}O_2N$: C, 77.09; H, 4.45; N, 5.62. Found: C, 76.92; H, 4.42; N, 5.78.

4-Carbomethoxy-10,11-dihydrodibenz[*b*,*f*]azepine (12). A mixture of 41.0 g of **10** in 420 ml of water containing 44.0 g of sodium hydroxide was stirred at room temperature for 1 hr when solution was complete. There was then added dropwise with stirring over a period of 10 min a solution of 40 ml of 30% hydrogen peroxide and 400 ml of water. After the addition was complete and the solution had been stirred for an additional 2 hr at room temperature, it was acidified with concentrated hydrochloric acid. The resultant slurry was stirred for 0.5 hr and then the yellow solid was collected by filtration. After it had been washed with water and then dried, the yellow solid, corresponding to the acid **11**, weighed 34.4 g. This was dissolved in 1400 ml of ether and treated with an excess of diazomethane in ether at 0°. After the solution had stood at 0° for 15 min, the excess diazomethane was decomposed by addition of acetic acid. The ether solution was then washed successively with water, aqueous bicarbonate, aqueous bisulfite, and again with water before drying. Concentration under reduced pressure gave 37 g (89%) of an oil that solidified on standing and was satisfactory for use in the next experiment. A sample recrystallized from methanol gave yellow crystals, mp 63–64°; uv, λ_{max}^{EtOH} 223 (sh, 17,500), 293 (16,800), and 367 mμ (ε 8450); ir, $\lambda_{max}^{CHCl_3}$ 2.91 (–NH) and 5.82 μ (–C=O); nmr ($CDCl_3$), broad singlet at τ −0.71 (1 H, –N*H*–), doublet of doublets at 2.20 (1 H, Ar*H ortho* to ester), multiplet at 2.82–3.58 (6 H, Ar*H*), singlet at 6.20 (3 H, $-OCH_3$), and singlet at 7.03 (4 H, $-CH_2CH_2-$).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.75; H, 6.00; N, 5.68.

Isatin of 4-Carbomethoxy-10,11-dihydrodibenz[*b*,*f*]azepine (13). A solution of 36 g of **12** in 250 ml of ether was added dropwise to a boiling solution of 55 ml of oxalyl chloride in 150 ml of ether. After the addition was complete, the reaction mixture was boiled under reflux for 5 hr and then was concentrated under reduced pressure. The resultant oil was taken up in 450 ml of carbon disulfide and added dropwise with stirring to a slurry of 40 g of aluminum chloride in 450 ml of carbon disulfide over a period of 1 hr. It was then boiled under reflux with stirring for an additional 12 hr. The carbon disulfide solution was removed from the solid precipitate by decantation through glass wool. To the residue was added 200 ml of concentrated hydrochloric acid at 0 followed

(11) Microanalyses by Microtech Laboratories and A. Bernhardt Microanalytical Laboratories. Spectral measurements were made with a Cary Model 15, a Beckman IR-5A, and a Varian A-60. Mass spectra were determined by Morgan and Schaffer Corp. We are indebted to the National Science Foundation for funds for the purchase of the Varian A-60.

by an additional 200 ml of water. The mixture was vigorously stirred while 400 ml of chloroform was added. After separation of the two phases, the chloroform layer was washed with water and dried. Concentration of the chloroform extract gave 43.0 g (99%) of red crystals of satisfactory purity for use in the next experiment. A sample recrystallized from ethanol gave red crystals, mp 192–193°; uv, λ_{max}^{EtOH} 247 (18,000), 284 (sh, 6370), and ($CHCl_3$) 440 mμ (ε 250); ir, $\lambda_{max}^{CHCl_3}$ 5.86 μ (–C=O); nmr ($CDCl_3$), multiplet at τ 2.14–3.09 (6 H, Ar*H*), singlet at 6.1 9 (3 H, $-OCH_3$), and broad singlet at 6.94 (4 H, $-CH_2CH_2-$).

Anal. Calcd for $C_{18}H_{13}NO_4$: C, 70.35; H, 4.26; N, 4.56. Found: C, 70.51; H, 4.41; N, 4.61.

4,6-Dicarbomethoxy-10,11-dihydrodibenz[*b*,*f*]azepine (15). A mixture of 42.0 g of **13** in 500 ml of water containing 61 g of sodium hydroxide was allowed to stand at room temperature until complete solution occurred. It was then diluted with 750 ml of water and a solution of 45 ml of 30% hydrogen peroxide and 500 ml of water was added dropwise with stirring over a period of 0.5 hr while the reaction mixture was maintained between 25 and 30°. It was stirred an additional 2 hr at 25° before acidification with concentrated hydrochloric acid. The yellow precipitate was collected, washed with water, and dried to give 28 g of a yellow powder. This was taken up in 1400 ml of ether and treated with excess diazomethane at 0°. After the solution had stood at 0° for 15 min, the excess diazomethane was decomposed by addition of acetic acid. The ether solution was then washed successively with water, aqueous bicarbonate, and again with water before drying. Concentration under reduced pressure gave 29.0 g of an orange solid. This, on recrystallization from methanol, gave 23.0 g of orange crystals, mp 109–112°. Concentration of the mother liquor followed by chromatography of the residue over silica gel using benzene for elution yielded an additional 4.0 g of yellow crystals, making a total of 27.0 g (64%). A sample recrystallized from hexane gave yellow crystals, mp 114–115°; uv, λ_{max}^{EtOH} 224 (24,500), 250 (sh, 9940), 291 (11,500), and 363 mμ (ε 10,780); ir, $\lambda_{max}^{CHCl_3}$ 3.03 (–NH) and 5.84 μ (–C=O); nmr ($CDCl_3$), a broad singlet at τ −0.40 (1 H, –N*H*), doublet of doublets (2 H, Ar*H ortho* to esters, J = 7.5, J' = 2 cps), doublet of doublets at 2.91 (2 H, Ar*H para* to esters, J = 7.5, J' = 2 cps), triplet at 3.31 (2 H, Ar*H meta* to esters, J = 7.5, J' = 7.5 cps), singlet at 6.10 (6 H, $-OCH_3$), and singlet at 6.99 (4 H, $-CH_2CH_2-$).

Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.54; H, 5.50; N, 4.46.

N-Methyl-4,6-dicarbomethoxy-10,11-dihydrodibenz[*b*,*f*]azepine (16). A mixture of 5.0 g of **15**, 3.0 g of a 55% sodium hydride dispersion in hexane, and 125 ml of methyl iodide in 375 ml of dry dioxane was boiled under reflux with stirring for 26 hr. The cold reaction mixture was then diluted with 300 ml of water. The two phases were separated and the aqueous phase was extracted with ether. The combined organic phase and ether extract were washed with water, dried, and concentrated to give 6.0 g of solid. This was taken up in a 1:1 mixture of benzene and hexane and chromatographed over silica gel. The main eluate fraction gave 4.6 g (88%) of pale yellow crystals, mp 122–124°. A sample recrystallized from hexane yielded colorless crystals, mp 123–124°; uv, λ_{max}^{EtOH} end absorption only; ir, $\lambda_{max}^{CHCl_3}$ 5.76 (–C=O); nmr ($CDCl_3$), multiplet at τ 2.60–3.12 (6 H, Ar*H*), singlet at 6.02 (6 H, $-OCH_3$), singlet at 6.70 (3 H, $-NCH_3$), and broad singlet at 6.92 (4 H, $-CH_2CH_2-$).

Anal. Calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31. Found: C, 70.29; H, 5.81; N, 4.49.

N-Methyl-4,6-bis(hydroxymethyl)-10,11-dihydrodibenz[*b*,*f*]azepine (17). A solution of 4.6 g of **16** in 500 ml of ether was added dropwise with stirring to a slurry of 3 g of lithium aluminum hydride in 100 ml of ether over a period of 0.5 hr. The resulting mixture was boiled under reflux for 1 hr and cooled and a saturated aqueous sodium sulfate solution added until the metallic hydroxides formed as a granular precipitate. After filtration, the filtrate was dried and concentrated to give 3.7 g (97%) of a white solid, mp 131–135°. A sample recrystallized from benzene gave white crystals, mp 138–139°; uv, λ_{max}^{EtOH} 214 (21,400) and 250 mμ (ε 5000); ir, $\lambda_{max}^{CHCl_3}$ 2.90 μ (–OH); nmr ($CDCl_3$), multiplet at τ 2.66–2.97 (6 H, Ar*H*), quartet at 5.20 (4 H, $-CH_2OH$, J = 12 cps), singlet at 5.30 (2 H, –OH), multiplet at 6.52–7.32 (4 H, $-CH_2CH_2-$), and singlet at 6.89 (3 H, $-NCH_3$).

Anal. Calcd for $C_{17}H_{15}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.79; H, 7.20; N, 5.17.

N-Methyl-8,16-imino[2.2]metacyclophane (19). A mixture of 3.5 g of **17** and 6 ml of phosphorus tribromide in 130 ml of benzene was boiled under reflux for 1 hr. After the mixture had been cooled to 0°, 75 ml of cold water was added with stirring and the two phases were separated. The aqueous phase was extracted once with benzene and the benzene extract was combined with the organic phase. This was washed with water and then concentrated to give 5.0 g of a yellow oil whose nmr spectrum was in accord with structure **18** for the dibromide. The dibromide appeared to be somewhat unstable and so was used directly in the next experiment.

A solution of 4.8 g of the yellow oil (**18**) in 2.0 l. of ether was added over a period of 10 min to a boiling solution of 40 ml of a 0.9 *N* solution of phenyllithium. After the addition was complete, the mixture was boiled under reflux for another 30 min. Then water was added and the ether phase was separated. After the ether phase had been washed with water, it was dried and concentrated to give an orange oil. This was dissolved in 50 ml of hexane, boiled, and filtered. The filtrate was concentrated and the residue chromatographed over silica gel using hexane for elution. The main eluate fraction gave 1.81 g of white crystals, mp 80–83°, whose nmr spectrum indicated it to be virtually pure **19**. A sample recrystallized from methanol gave white crystals: mp 95–97°; uv, $\lambda_{max}^{cyclohexane}$ 248 mμ (ε 6640); nmr ($CDCl_3$), multiplet at τ 3.12–3.30 (6 H, Ar*H*), singlet at 6.72 (3 H, $-NCH_3$), and an AA′BB′ multiplet at 6.84 (8 H, $-CH_2CH_2-$); *m/e* 235.

Anal. Calcd for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.72; H, 7.14; N, 5.81.

8,16-Imino[2.2]metacyclophane (20). A. Use of Palladium-on-Charcoal with Oxygen. A solution of 300 mg of **19** in 30 ml of absolute ethanol containing 300 mg of a 30% palladium-on-charcoal catalyst was boiled under reflux while bubbling oxygen through the mixture from a fritted gas inlet tube. After 4 hr, the mixture was cooled and filtered and the filtrate concentrated to give 277 mg of a white solid. This was taken up in a 1:1 mixture of benzene–cyclohexane and chromatographed over silica gel to give 210 mg (75%) of white crystals, mp 152–159°. A sample recrystallized from methanol gave white crystals, mp 160–164°; uv, $\lambda_{max}^{cyclohexane}$ 248 mμ (ε 5870); ir, $\lambda_{max}^{CHCl_3}$ 2.93 μ (–NH); nmr ($CDCl_3$), singlet at τ 3.21 (6 H, Ar*H*), a broad singlet at 5.78 (1 H, –NH), and an AA′BB′ multiplet at 6.82 (8 H, $-CH_2CH_2-$); *m/e* 221.

Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.81; H, 6.92; N, 6.34.

B. Use of DDQ. A mixture of 65 mg of **19** and 126 mg of 2,3-dichloro-4,5-dicyanoquinone (DDQ) in 20 ml of benzene was boiled under reflux for 2 hr. The reaction mixture was filtered through a silica gel column, and the first eluate fraction gave 20 mg of a white solid. This, after rechromatographing over silica gel with benzene for elution, yielded 15 mg of white crystals, mp 155–160°. These were shown to be identical with the crystals obtained in A by a mixture melting point determination plus a comparison of spectral data.

8,16-Imino[2.2]metacyclophane-1,9-diene (1). A mixture of 100 mg of **20** and 161 mg of N-bromosuccinimide in 50 ml of carbon tetrachloride containing a small amount of azobisisobutyronitrile was boiled under reflux. In 10 min the solution had turned yellow but after 30 min it was colorless. The mixture was cooled and filtered. Concentration of the filtrate gave a solid residue which was taken up in 30 ml of benzene, 130 mg of 1,5-diazabicyclo-[4.3.0]non-5-ene was added, and the solution was boiled under reflux for 15 min. It was then washed with water and concentrated. The residual yellow oil was taken up in a 1:1 benzene–cyclohexane mixture and chromatographed over silica gel. The main eluate fraction gave 64 mg (66%) of white crystals, mp 87–90°; uv, $\lambda_{max}^{cyclohexane}$ 230 (sh, 28,200), 250 (sh, 14,200), and 304 mμ (ε 12,600); nmr ($CDCl_3$), A_2B multiplet at τ 2.38–3.08 (6 H, Ar*H*), singlet at 2.58 (4 H, $-CH{=}CH-$), and a broad singlet at 6.61 (1 H, –N*H*); *m/e* 217 with a strong signal at 202.

Anal. Calcd for $C_{15}H_{11}N$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.29; H, 5.14; N, 6.63.

N-Acetyl-8,16-imino[2.2]metacyclophane. A solution of 500 mg of **20** in 50 ml of acetic anhydride was heated at 110° for 10 hr. The solution was then cooled and diluted with 300 ml of water. Solid sodium bicarbonate was added to the resultant slurry until no further effervescence occurred. The slurry was extracted with chloroform using vigorous stirring. The chloroform extract was washed with water, dried, and concentrated. The residual solid was taken up in a 1:1 benzene–chloroform mixture and chromatographed over silica gel to give 535 mg (90%) of colorless crystals. A sample recrystallized from cyclohexane yielded white crystals, mp 172–174°; uv, λ_{max}^{EtOH} 264 (7210) and 280 mμ (sh, ε 789); ir, $\lambda_{max}^{CHCl_3}$ 6.03 μ (C=O); nmr ($CDCl_3$), multiplet at τ 2.70–3.35 (6 H,

ArH), AA'BB' multiplet at 6.85 (8 H, $-CH_2CH_2-$), and singlet at 7.91 (3 H, $-NCH_3$).

Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.41; H, 6.59; N, 5.44.

N-Methyl-8,16-imino[2.2]metacyclophane-1,9-diene (2). To a solution of 273 mg of **1** in 50 ml of dry tetrahydrofuran under nitrogen there was added 1.0 ml of a 1.6 *N* solution of *n*-butyllithium in hexane. A deep burgundy color developed immediately. Then 4.0 ml of methyl iodide was added, causing a rapid disappearance of the red color. After the mixture had been stirred at room temperature for 0.5 hr, 100 ml of water was added and the resultant mixture was extracted with two 50-ml portions of chloroform. The combined chloroform extracts were washed with water, dried, and concentrated to give 330 mg of an oil. This was chromatographed over silica gel using a 1:1 benzene–hexane mixture for elution. The main fraction of eluate gave 74 mg (26%) of yellow crystals. A sample recrystallized from methanol yielded colorless crystals, mp 149–151°; uv, $\lambda_{max}^{cyclohexane}$ 228 (sh, 31,400), 253 (sh, 15,050), and 304 mμ (ε 12,500); nmr ($CDCl_3$), A_2B multiplet at τ 2.42–3.16 (6 H, ArH), singlet at 2.72 (4 H, $-CH{=}CH-$), and singlet at 7.60 (3 H, $-NCH_3$).

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.18; H, 5.48; N, 6.20.

N-Carbethoxy-8,16-imino[2.2]metacyclophane-1,9-diene (3). To a solution of 234 mg of **1** in 20 ml of dry tetrahydrofuran under nitrogen there was added 0.700 ml of a 1.6 *N* solution of *n*-butyllithium in hexane. The resultant burgundy-red solution was added dropwise over a period of 10 min to a solution of 2.0 g of ethyl chlorocarbonate in 25 ml of dry tetrahydrofuran. After the mixture had stirred at room temperature for 10 min, it was cooled to 0°, and 50 ml of water was added. The mixture was then extracted with two 50-ml portions of chloroform. The combined chloroform extracts were washed with water, dried, and concentrated to give 322 mg of a dark oil. This was taken up in benzene and percolated through a silica gel column. Concentration of the eluate gave a white solid which was recrystallized from a 1:1 benzene–hexane mixture to give 95 mg (30%) of white crystals, mp 231–232°; uv, λ_{max}^{EtOH} 227 (sh, 28,400), 247 (sh, 17,100), and 298 mμ (ε 13,460); ir, $\lambda_{max}^{CHCl_3}$ 5.81 μ (–C=O); nmr ($CDCl_3$), A_2B multiplet at τ 2.47–3.03 (6 H, ArH), singlet at 2.75 (4 H, $-CHCH-$), quartet at 5.99 (2 H, $-CH_2CH_3$, J = 7 cps), and triplet at 8.92 (3 H, $-CH_2CH_3$, J = 7 cps); *m/e* at 289 with strong signals at 217 and 202.

Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.84; H, 5.27; N, 4.98.

N-Methyl-1-pyrenamine (27). To a solution of 300 mg of 1-pyrenamine (Aldrich) in 40 ml of dry tetrahydrofuran there was added 0.865 ml of a 1.6 *N* solution of *n*-butyllithium causing the formation of a deep red color. Then, 1.0 ml of methyl iodide was added and the mixture was boiled under reflux for 5 min. The reaction mixture was cooled and diluted with 50 ml of water. It was then extracted with chloroform and the chloroform extract was washed with water and dried. Concentration of the chloroform extract gave 260 mg of an oil that solidified on standing. This was taken up in a 1:1 benzene–hexane mixture and chromatographed over silica gel to give 160 mg of crystals. This was dissolved in hot hexane, treated with charcoal, and cooled, causing the separation of 100 mg of yellow crystals, mp 94–96°;[12] uv, $\lambda_{max}^{cyclohexane}$ 231 (33,800), 243 (41,800), 277 (sh, 16,900), 292 (18,100), 320 (sh, 4220), 367 (17,300), 382 (16,600), 386 (16,700), 404 (sh, 17,100), and 407 mμ (ε 18,300); ir, $\lambda_{max}^{CHCl_3}$ 2.89 μ (NH); nmr ($CDCl_3$), multiplet at τ 1.74–2.35 (8 H, ArH), doublet at 2.76 (1 H, ArH), broad singlet at 5.50 (1 H, –NH), and singlet at 6.99 (3 H, $-NCH_3$) (nmr spectrum very concentration dependent).

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.35; H, 5.79; N, 6.18.

Thermolysis of N-Methyl-8,16-imino[2.2]metacyclophane-1,9-diene (2) in Methanol. A solution of 60 mg of **2** in 50 ml of absolute methanol was heated in a sealed tube at 100° for 44 hr. Concentration gave 60 mg of material which was shown to be essentially pure N-methyl-1-pyrenamine by comparison with an authentic sample (see above for the preparation of N-methyl-1-pyrenamine).

Thermolysis of N-Methyl-8,16-imino[2.2]metacyclophane-1,9-diene (2) in Benzene. A solution of 57 mg of **2** in 5 ml of benzene in a sealed tube was heated at 200° for 20 hr. After the tube was opened, the solution was concentrated leaving 50 mg of a crystalline solid. This was shown by comparison with an authentic sample to be identical with pyrene.

Thermolysis of N-Methyl- and N-Carbethoxy-8,16-imino[2.2]-metacyclophanes in Cyclohexene. In both cases 100 mg of the material (**2** or **3**) was placed in a Carius tube with 15 ml of purified cyclohexene. After careful degassing of the mixture, the tubes were sealed under vacuum and then placed in a single tube oven with the temperature controlled at ±1°. In the case of the N-methyl derivative 20 hr at 200° was required in order to get complete reaction (disappearance of starting material). The N-carbethoxy derivative required 20 hr at 275°. After the tubes were cooled, they were broken open, and the solvent and volatile products were collected by distillation under vacuum. The remaining residue in both cases was identified as pyrene.

In the case of the N-methyl compound (**2**) the distillate was examined by vapor phase chromatography. Only cyclohexene and a small amount of material of shorter retention time were found in the distillate. A sample of N-methyl-7-azabicyclo[4.1.0]heptane was prepared.[13] It had a retention time longer than that of cyclohexene and therefore was not present in the distillate from the thermolysis.

The distillate which was collected in the N-carbethoxy case (**3**) was also examined by vapor phase chromatography. However, only a very small amount of a complex mixture other than cyclohexene was present. It was later determined in a control run that N-carbethoxy-7-azabicyclo[4.1.0]heptane does not survive under these conditions but is decomposed to a complex mixture of products as evidenced by vapor phase chromatography.

Reaction of 8,16-Imino[2.2]metacyclophane-1,9-diene (1) with Trifluoroacetic Acid. A solution of 150 mg of **1** and 200 g of trifluoroacetic acid was prepared and allowed to stand at room temperature for 48 hr. The solution initially became light yellow and then turned darker as the reaction progressed. It was then boiled under reflux for 14 hr and cooled and 100 g of trifluoroacetic acid was removed by distillation. To the remaining solution was added 300 ml of water, and the mixture was neutralized with solid sodium bicarbonate. The neutral mixture was extracted with two portions of chloroform. The combined chloroform extracts were washed once with water and dried. Concentration gave 170 mg of a dark oil. Thin layer chromatography of this oil showed five distinct spots. The residual oil was dissolved in 20 ml of methanol containing 1 g of potassium hydroxide. After the solution had been stirred for 30 min, the solution was diluted with 120 ml of a 5% aqueous solution of potassium hydroxide. The resultant mixture was extracted with two portions of chloroform (extract A).

The aqueous phase was acidified with concentrated hydrochloric acid and extracted with two portions of ether. The ether solution was concentrated to give 25 mg of a dark oil. The oil was identified as a mixture of 4-pyrenol and 2-pyrenol by a comparison of its nmr spectrum to the nmr spectrum of a known mixture of the two pyrenols.[3] Analysis of the nmr spectrum of the mixture showed it to contain approximately 67% of the 2-pyrenol and 33% of the 4-pyrenol.

Extract A was washed once with water. It was then washed with three portions of 3 *N* hydrochloric acid. The combined aqueous acidic washings were neutralized with sodium bicarbonate and extracted with two portions of ether. Evaporation of the dried ether extract gave 16 mg of a dark oil which was shown to be 1-aminopyrene by comparison of its ultraviolet and nmr spectra with an authentic sample of 1-aminopyrene.

Extract A was then dried and concentrated to give 123 mg of a dark oil. A thin layer chromatogram showed that it still contained pyrenol. It was therefore redissolved in chloroform and washed with three portions of a 10% sodium hydroxide solution. The combined basic extracts were acidified with concentrated hydrochloric acid and extracted with three portions of ether. Concentration of the dried ether extracts gave 28 mg of oil which was shown by comparison with an authentic specimen to be exclusively 2-pyrenol.

The above chloroform solution, which had been extracted with base, was dried and concentrated to give 88 mg of a dark oil. Thin layer chromatography indicated that it no longer contained any of the pyrenols. There remained two distinct spots. These were isolated by preparative tlc using silica gel and one (4 mg) was shown to be pyrene. The other (5 mg) was not identified. The remainder of the material appeared to be all of lower R_f than any of the above materials, the bulk of which appeared to remain at the origin.

(12) H. Lund and A. Berg (*Kgl. Danske Videnskab. Selskab., Math-Fys. Medd.*, **22**, 1 (1946); *Chem. Abstr.*, **40**, 6072 (1946)) have reported that N-methyl-1-pyrenamine melts at 82–83°.

(13) T. Taguchi and M. Eto, *J. Am. Chem. Soc.*, **80**, 4075 (1958).