Overcrowded Molecules. II. 4,5-Bis(2-pyridyl)phenanthrene-3,6-diols

D. L. FIELDS* AND T. H. REGAN

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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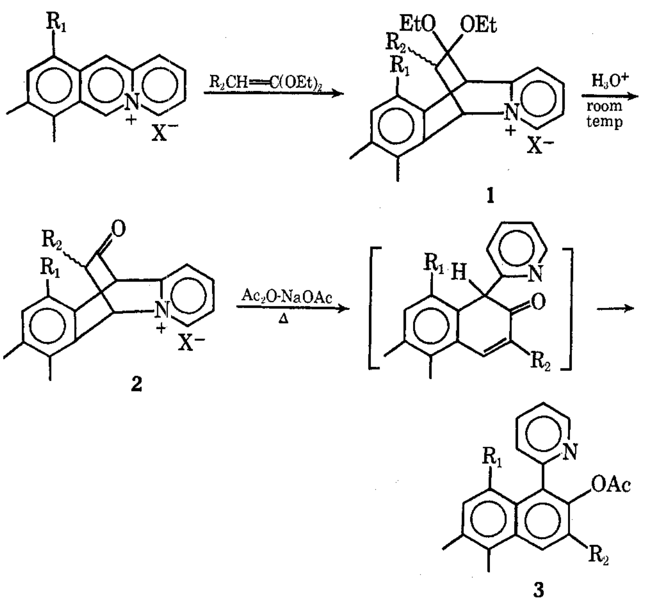
The ketene acetal adducts of several azoniaanthracene, azoniabenzanthracene, and diazoniapentaphene salts were used to prepare (2-pyridyl)naphthols **5**, (2-pyridyl)phenanthrols **7** and **9**, and bis(2-pyridyl)phenanthrenediols **11**, **13**, and **15**, respectively, by a modification of a known procedure. The phenanthrene-3,6-diols having pyridine substituents at the 4,5 positions (**11**) show a high degree of steric strain which strongly influences their uv, mass, and nmr spectra.

The synthetic route to 1-(2-pyridyl)-2-naphthols *via* the three-step process outlined in Scheme I has been utilized for the preparation of two new classes of molecules with exceedingly high steric strain. One set, the 8-*tert*-butyl-1-(2-pyridyl)naphthalenes, has already been described.[1]

SCHEME I



In this paper, some further observations on the synthetic pathway are noted, and the synthesis and basic spectral properties of the second class of sterically hindered compounds, the 4,5-bis(2-pyridyl)phenanthrene-3,6-diols, are described. An X-ray crystallographic structure determination of one of these compounds was undertaken by Smith and is discussed elsewhere.[2] The pyridine rings in these nonplanar, and therefore chiral, phenanthrenes have a spatial relationship similar to that of the phenyl groups in [2.2]-metacyclophanes,[3] being almost coplanar and held in face-to-face proximity. The combination of severe ring strain and unusual geometry has pronounced effects on their physical and chemical properties, some aspects of which are reported here; certain others are under current investigation.

Results and Discussion

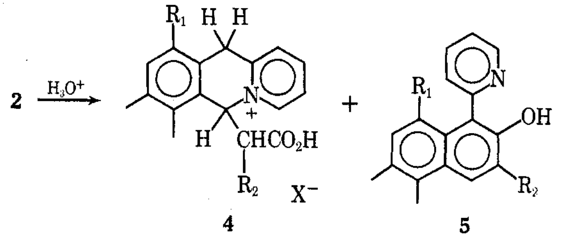
Synthesis.—Prior to this study, our envisioned adaptation of Scheme I to the synthesis of more complex polycyclic compounds was clouded by the knowledge that ketones **2**, generated from ketal precursors by acid treatment, are themselves acid labile, readily degrading to a mixture of **4** and **5**, with **4** often predominating.[4]

Accordingly, the success of this synthesis was thought to depend on the isolation of these rather elusive intermediate ketones in useful yields. Fortunately, however, the hydrolytic cleavage product **4** readily reverts to **2** in high yield on treatment with acetic anhydride–sodium acetate at room temperature. More importantly, this reagent at reflux temperature converts **4**, *via* **2**, to the desired product **3**, exclusively. Thus the initial hydrolysis of ketal **1** may be carried out in refluxing 6 *N* HCl without concern for the nature of the products, be they **2**, **4**, or **5**, since treatment of the resulting mixture with acetic anhydride–sodium acetate at reflux temperature will convert each of them to the same final product, **3**.[5]

Application of this modified synthesis (eq 1) to the previously described azoniapolycyclic ketene acetal

$$1 \xrightarrow[\Delta]{H_3O^+} [2 \text{ and/or } 4 + 5] \xrightarrow[\Delta]{Ac_2O\text{-}NaOAc} 3 \xrightarrow{H_3O^+} 5 \qquad (1)$$

adducts[6] shown in Scheme II has provided the indicated naphthols and phenanthrols in 85–90% yields. In like manner, bis adducts **10a–e**, **12**, and **14** (Scheme III), obtained from stereoselective[7] cycloadditions of ketene diethyl acetals to 4a,8a-, 4a,12a-, and 12a,14a-diazoniapentaphene salts, were converted without difficulty to the desired phenanthrenediols **11a–e**, **13**, and **15**, respectively. The structural assignments of the new products were supported by elemental analyses



4 **5**

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[1] D. L. Fields and T. H. Regan, *J. Org. Chem.*, **36**, 2986 (1971).

[2] D. L. Smith and E. K. Barrett, *Acta Crystallogr., Sect. B*, **27**, 419 (1971).

[3] C. J. Brown, *J. Chem. Soc.*, 3278 (1953).

[4] (a) D. L. Fields and T. H. Regan, *J. Org. Chem.*, **35**, 1870 (1970). (b) For example, **1** (R_1, R_2 = H; X^- = ClO_4^-) gives on treatment with 6 *N* hydrochloric acid at 90° for 0.5 hr a mixture of **4** (84%) and **5** (9%); no **2** could be isolated.

[5] A minor limitation to this procedure exists when **4** possesses a 5-hydroxyl substituent, in that O-acylation–elimination leading to a coumarin by-product competes favorably with the desired C-acylation–elimination.

[6] D. L. Fields, T. H. Regan, and J. C. Dignan, *J. Org. Chem.*, **33**, 390 (1968).

[7] Adducts **10a–e**, **12**, and **14** each are believed to be a mixture of geometric isomers formed from bis cycloadditions in which the ketene acetal had added both to the same side and from opposite sides of the diazoniapentaphene ring (see ref 6) in a stereoselective or, when R_2 = H, a stereospecific manner. This is inconsequential in the preparation of **11**, **13**, and **15**.

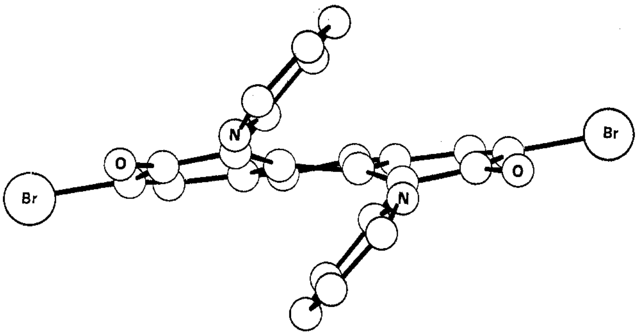
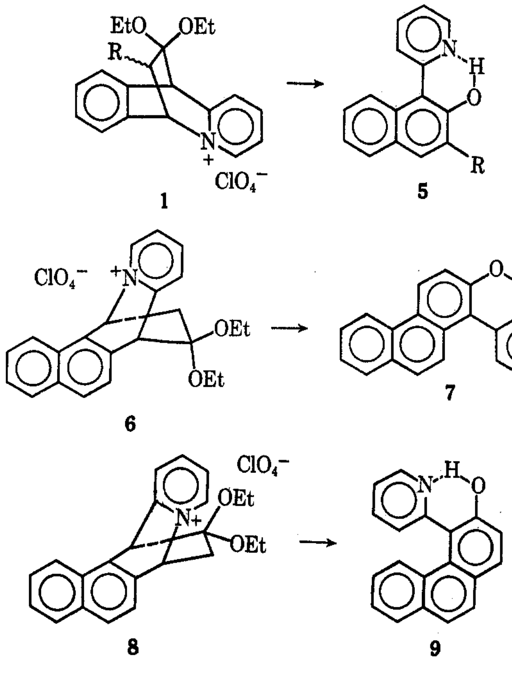


Figure 1.—View of **11b** along the twofold symmetry axis.

SCHEME II



a, R = H; **b**, R = CH$_3$; **c**, R = C$_6$H$_5$; **d**, R = Br

(Table III and IV, Experimental Section) and by the usual spectral means, selected results of which will be discussed in the following sections.

Molecular Structure of 11b.—The compounds of prime interest are, of course, the 4,5-dipyridyl derivatives **11a–e**, products which if completely planar and free of angle and bond deformations would have the two pyridyl rings occupying the same space. Obviously considerable altering of normal bond angles and lengths is necessary for **11** to have even the minimum-allowed ~3-Å separation between their pyridine rings.[8] The nature and extent of the deviations have been clarified through a single-crystal X-ray analysis of a representative member, **11b**. Although the details of this structure determination are being reported elsewhere,[2] a brief qualitative description of the results is warranted here.

In agreement with conclusions drawn from nmr data that will be commented on later, each pyridine of **11b** is found to be intramolecularly hydrogen bonded to the neighboring hydroxyl group, creating a twofold axis of symmetry. As can be inferred from Figure 1, the distortion is distributed over the entire framework of the molecule in such a way that the trigonal symmetry of the bonds around any particular carbon bond is not greatly disturbed. No major segment of the molecule is truly planar; yet all individual rings are approximately planar. The pyridyl rings have a stair-step relationship to one another (Figure 2) and are almost parallel, being inclined 11° to each other. The distance between vicinal nonbonded pyridyl carbon atoms varies from an extraordinary close 2.81 Å between C$_2$ of one pyridine and C$_{2'}$ of the second pyridine, to a more normal 3.34 at C$_6$–C$_{6'}$.

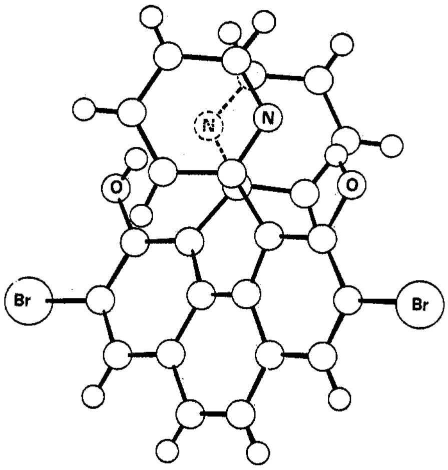
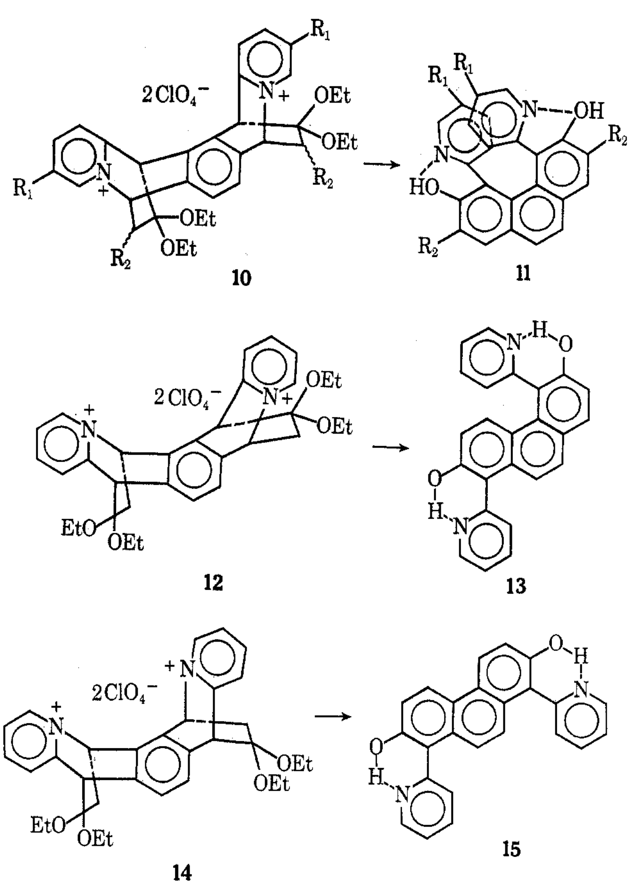


Figure 2.—Projection of **11b** normal to one of the pyridyl rings.

SCHEME III



a, R$_1$, R$_2$ = H; **b**, R$_1$ = H, R$_2$ = Br; **c**, R$_1$ = H, R$_2$ = CH$_3$; **d**, R$_1$ = CH$_3$, R$_2$ = H; **e**, R$_1$ = CH$_3$, R$_2$ = CH$_3$

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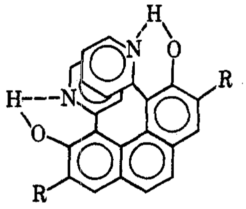
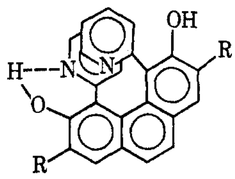
[8] When aromatic rings are held face to face and are not constrained, they have a normal "van der Waal" separation of ~3.4 Å; see J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953, pp 157, 174, 206, 270.

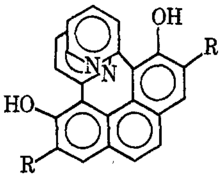
Under such steric constraint, it seems reasonable that the pyridines would suffer restricted rotation, making possible two diastereoisomers other than that known from the X-ray study. The three isomers would differ solely in the orientation of the pyridines with respect to one another as indicated for **11**, **11-I** and **11-II**. However, we have no experimental evidence suggesting the presence of the latter two possibilities. Each of **11a–e** appeared homogeneous based on melting point behavior and tlc analysis. More significant is the fact that the position of the hydroxyl proton signals in their nmr spectrum ($CDCl_3$) was concentration independent, located as a two-proton broadened singlet at a low-field position (~12.5 ppm). This result is only consistent for the energetically preferred, intramolecularly hydrogen-bonded isomer **11**.



11



11-I



11-II

Spectral Properties.—Some effects of overcrowding on the spectral properties of **11** are easily recognized through a comparison of uv and mass spectral data of **11a** with like data obtained for the lesser strained isomeric phenanthrenediols **13** and **15**.

Perturbations resulting from distortion of the phenanthrene nucleus are known to produce bathochromic and hyperchromic shifts of the longer wavelength absorptions,[9] and such shifts are apparent in comparison with the uv spectra of the diacetyl derivatives of **11a**, **13**, **15**, and the parent 3,6-dihydroxyphenanthrene (Figure 3). Spectra of the diacetates rather than the parent diols are compared to eliminate unknown contributions resulting from hydroxyl–pyridine hydrogen bonding.

The mass spectral fragmentation of **11a** also shows abnormalities attributable to overcrowding. The initial and major fragmentation of **11a** involves loss of a pyridyl group, a fragmentation of minor importance in the lesser strained **13** and **15** (Table I). This mode of cleavage appears to be characteristic of these 4,5-dipyridylphenanthrene derivatives and has proved valuable in structure elucidation of reaction products derived from free radical oxidation processes which will be reported at a later time.

TABLE I

IMPORTANT IONS IN THE MASS SPECTRA OF **11a**, **13**, AND **15**

		Rel intensity, %		
m/e	Assignment	**11a**	**13**	**15**
364	M	21.0	65.0	100.0
363	M − 1	0.6	100.0	96.0
286	M − Py	100.0	1.7	8.6

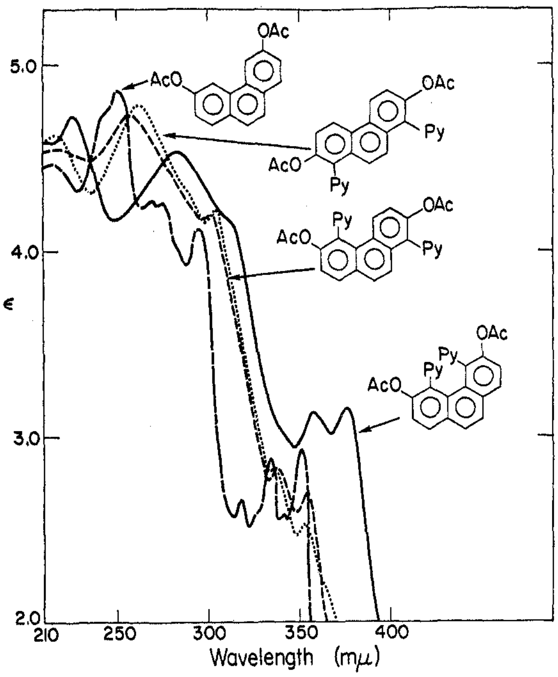
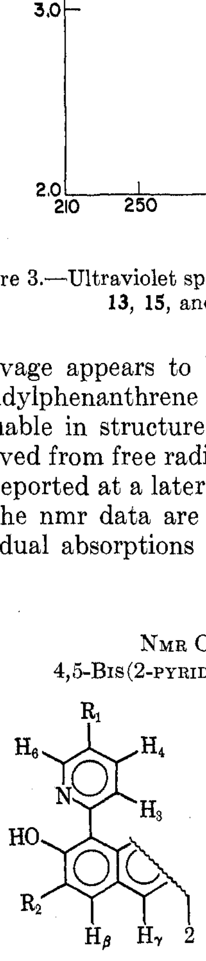


Figure 3.—Ultraviolet spectra of the diacetyl derivatives of **11a**, **13**, **15**, and phenanthrene-3,6-diol.

The nmr data are contained in Table II. The individual absorptions in the spectrum of **11e** were unambiguously assignable since the positions of the methyl substituents were unequivocal from the synthesis, and the "apparent" coupling constants in this and the other compounds ($|J_{34}| \simeq$ 8–9 Hz, $|J_{45}| \simeq$ 7.5 Hz, and $|J_{46}| \simeq$ 2 Hz) defined the positions of the protons with respect to one another. Using these assignments, absorptions of the remaining compounds could be readily identified, since the chemical shifts were such that no serious second-order perturbations appeared to be present.

TABLE II

NMR CHEMICAL SHIFTS[a] OF 4,5-BIS(2-PYRIDYL)PHENANTHRENE-3,6-DIOLS



	R_1	R_2
11a	H_5	H_α
11b	H_5	Br
11c	H_5	CH_3
11d	CH_3	H_α
11e	CH_3	CH_3

Compd	R_2	H_β	H_γ	H_3	H_4	R_1	H_6	OH
11a	7.24	7.77	7.54	6.83	7.39	6.97	8.03	12.5
11b		8.06	7.48	6.85	7.47	7.04	8.04[b]	
11c	2.42	7.63	7.49	6.84	7.39	6.96	8.01	13.0
11d	7.18	7.74	7.52	6.72	7.22	2.26	7.84	12.5
11e	2.29	7.59	7.46	6.74	7.20	2.23	7.82	12.6

[a] δ values in ppm downfield from internal TMS. Obtained with a Varian HA-100 spectrometer using 1–4% solutions in $CDCl_3$. Accuracy ±0.01 ppm. [b] Partially obscured by H_β.

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[9] For example, see G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael, and A. I. Scott, *J. Chem. Soc.*, 2326 (1950); H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, pp 384–449.

TABLE III

PYRIDYL-SUBSTITUTED 2-NAPHTHOLS AND PHENANTHROLS

Compd	Yield, %	Mp, °C	Uv, $\lambda_{max}^{CH_3CN}$ (log ε)	Calcd, %			Found, %		
				C	H	N	C	H	N
5a[a]	91								
5b[a]	95								
5c[a]	87								
5d[b]	93	98–100	232 (4.67) 250 (4.38) 318 (3.98) 351 (3.90)	60.1	3.3	4.7	59.8	3.1	4.6
7[b]	86	194–195	259 (4.69), 315 (4.00) 353 (3.50), 367 (3.48)	84.1	4.8	5.2	84.5	5.0	5.2
9[b]	88	126–127	226 (4.59), 246 sh (4.44) 281 (4.31), 361 (3.49) 383 (3.46)	84.1	4.8	5.2	84.2	4.9	5.1

[a] Reference 4. [b] Recrystallized from methylcyclohexane.

TABLE IV

DIPYRIDYL-SUBSTITUTED PHENANTHRENEDIOLS

Compd	Yield, %	Mp, °C	Uv, $\lambda_{max}^{CH_3CN}$ (log ε)	Calcd, %			Found, %		
				C	H	N	C	H	N
11a[a,b]	88	221–223	239 (4.66), 295 (4.49), 312 sh (4.40) 402 (3.60), 420 (3.63)	79.1	4.4	7.7	78.8	4.7	7.7
11b[c]		290 dec		55.2	2.7	5.4	55.1	2.8	5.2
11c[d]	86	274–277 (with dec)		78.7	5.2	7.1	78.9	5.4	7.2
11d		231–233		79.6	5.1	7.1	79.4	5.0	7.2
11e		267–269 (with dec)		80.0	5.7	6.7	79.6	5.7	6.7
13[a,e]	70	134–135	239 (4.59), 321 (4.39), 390 sh (3.45)	79.1	4.4	7.7	78.8	4.5	7.6
15[a,f]	92	236–237	241 (4.46), 273 (4.62), 310 (4.35), 380 (3.73)	79.1	4.4	7.7	78.7	4.8	7.9

[a] Recrystallized from methylcyclohexane. [b] Diacetyl derivative, mp 237–241°. [c] Recrystallized from CH_2Cl_2–ligroin (bp 30–60°). [d] Solvated: $0.25H_2O$. Recrystallized from ethanol–H_2O. [e] Diacetyl derivative, mp 176–179°. [f] Diacetyl derivative, mp 254–256°.

The nmr data combined with the nonbonded internuclear distances from the X-ray data provide an unusual opportunity to test the widely used "ring current" model for diamagnetic anistropy of aromatic compounds. This material is discussed in detail in another report.[10] The results show good agreement between the experimentally observed shifts and those calculated from theory.

Experimental Section[11]

Azoniapolycyclic Ketene Acetal Adducts.—Adducts **1a–d**, **6**, **8**, and **10a** have been described previously.[6] The following new adducts were prepared by the same general procedure. In each case the nmr spectrum was consistent with the assigned structure.

Adducts 10b and 10c were isolated as amorphous white powders in quantitative yields following treatment of 4a,8a-diazoniapentaphene diperchlorate[12] with 1-bromo-2,2-diethoxyethylene[13] and with 1,1-diethoxypropene,[14] respectively.

The synthesis of **10d** and of **10e** necessitated beginning with rudimentary starting materials. 2,5-Lutidine was converted by known procedures[15] to 5-methyl-2-(1,3-dioxolan-2-yl)pyridine [bp 55° (110 mm), n^{25}D 1.5215], which was further characterized as its methoperchlorate, mp 107–109°.

Anal. Calcd for $C_{10}H_{14}ClNO_6$: C, 42.8; H, 5.0; N, 5.0. Found: C, 42.8; H, 5.4; N, 5.3.

This pyridine acetal was then employed in the Bradsher diazoniapentaphene synthesis[11] to give 3,10-dimethyl-4a,8a-diazoniapentaphene diperchlorate: uv max (CH_3CN) 217 nm (log ε 4.69), 253 (4.02), 256 sh (4.01), 286 (4.24), 298 (4.32), 340 (4.51), 353 (4.56), 364 (4.38), 384 (4.51), 418 (3.66), 444 (3.61).

Its reaction with excess 1,1-diethoxyethylene[16] and 1,1-diethoxypropene[14] afforded **10d** and **10e**, respectively, as amorphous white solids. Adducts **10b–e** were not fully characterized other than to establish in each case the absence of absorbances longer than 270 nm in their uv spectra.

Adduct 12, mp 217° (with dec), and **adduct 14**, mp 270° dec, were obtained as crystalline solids from bis cycloadditions of 1,1-diethoxyethylene with 4a,12a- and 12a,14a-diazoniapentaphene perchlorates,[12] respectively.

Anal. Calcd for $C_{32}H_{38}Cl_2N_2O_{12}$: C, 53.8; H, 5.3; N, 3.9. Found (for **12**): C, 53.4; H, 5.3; N, 4.0. Found (for **14**): C, 53.6; H, 5.3; N, 3.9.

Naphthol–Phenanthrol Synthesis.—The following procedure for the preparation of 4,5-bis(2-pyridyl)phenanthrene-3,6-diol (**11a**) is typical of that used in the syntheses of the products listed in Tables III and IV.

A solution of **10a**[5] (23.9 g, 0.032 mol) in 100 ml of 6 *N* hydrochloric acid was heated under reflux for 1 hr and then concentrated on a rotary evaporator to a viscous syrup. A mixture of this syrup, 10 g of anhydrous sodium acetate, and 200 ml of acetic

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(10) P. I. Rose, unpublished results.

(11) Melting points (uncorrected) were determined on a Thomas-Hoover apparatus. Ultraviolet absorption spectra were recorded by a Cary Model 14 recording spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrometer. Nmr spectra were determined at ambient probe temperature with either a Varian A-60 or HA-100 spectrometer. Peak positions are reported in parts per million downfield from internal tetramethylsilane. In a few cases $CHCl_3$ was used as a secondary reference. The mass spectra were determined on a Consolidated 21-110 instrument operating at nominal resolution.

(12) C. K. Bradsher and J. C. Parham, *J. Org. Chem.*, **29**, 856 (1964).

(13) F. Beyersted and S. M. McElvain, *J. Amer. Chem. Soc.*, **72**, 1661 (1950).

(14) S. M. McElvain and W. R. Davie, *ibid.*, **73**, 1400 (1951).

(15) V. Boekelheide and W. J. Linn, *ibid.*, **76**, 1286 (1954); C. K. Bradsher and J. C. Parham, *J. Org. Chem.*, **28**, 83 (1963).

(16) S. M. McElvain, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 506.

anhydride was refluxed for 1 hr. The residue obtained upon concentrating the reaction mixture was triturated in 250 ml of 5% sodium bicarbonate solution, giving 14.3 g of the diacetyl derivative of **11a**, as light tan crystals.

An analytical sample had mp 237–241° after two recrystallizations from methylcyclohexane; uv, Figure 3; nmr δ 1.88 (s, 6 H, $COCH_3$), 6.35 (d of m, 2, two pyridine H), 6.90–8.20 (m, 12, H_α, H_β, H_γ, and remaining pyridine H with H_γ appearing as a singlet at 7.80; H_β, d, $J = 9$ Hz at 7.98; H_α, d, $J = 9$ Hz at 7.30); mass spectrum (70 eV) *m/e* 448 (M^+), 406, 370, 364, 328, 286.

Anal. Calcd for $C_{28}H_{20}N_2O_4$: C, 75.0; H, 4.5; N, 6.2. Found: C, 75.0; H, 4.9; N, 6.3.

The above product was deacetylated by heating a solution of it in 100 ml of 6 *N* hydrochloric acid for 0.5 hr at reflux temperature. The resulting crystalline dihydrochloride was isolated after concentrating the reaction mixture to dryness; its neutralization with 5% sodium bicarbonate solution gave 10.2 g (88%) of essentially pure (tlc) **11a** as fine yellow needles.

Registry No.—**5d**, 30309-81-0; **7**, 30309-82-1; **9**, 30309-83-2; **11a**, 26244-86-0; **11a** diacetyl derivative, 26244-85-9; **11b**, 30309-86-5; **11c**, 30309-87-6; **11d**, 30309-88-7; **11e**, 30309-89-8; **12**, 30259-90-6; **13** diacetyl derivative, 30309-90-1; **14**, 30259-91-7; **15** diacetyl derivative, 30309-91-2; 3,6-diacetylphenanthrene, 30309-92-3; 5-methyl-2-(1,3-dioxolan-2-yl)pyridine, 30309-93-4, 30309-94-5 (methoperchlorate); 3,10-dimethyl-4a,8a-diazoniapentaphene diperchlorate, 30309-95-6.

Acknowledgment.—We wish to thank Mr. D. P. Maier for supplying the mass spectral data and Dr. P. I. Rose for technical assistance in recording some of the nmr spectra and for helpful discussions regarding their interpretation.

Overcrowded Molecules. III. 13,14-Bis(2-pyridyl)pentaphene and Related Compounds

D. L. FIELDS,* T. H. REGAN, AND R. E. GRAVES

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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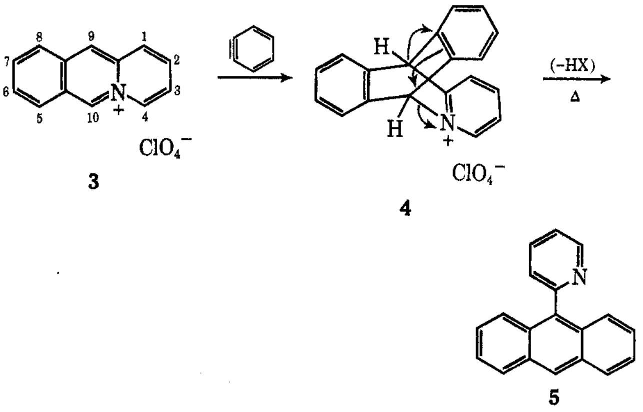
The reaction of benzyne with 4a-azoniaanthracene and 4a,8a- and 4a,12a-diazoniapentaphene salts produces, in good yields, azoniatriptycene-type adducts, which are thermolyzed in boiling acetic anhydride to 9-(2-pyridyl)-anthracene (**5**), 5,13- (**15**), and 13,14-bis(2-pyridyl)pentaphenes (**18**), respectively. The nmr spectrum of **19**, the bis-*N*-methyl quaternary salt of **15**, displays each of its *N*-methyl resonances as two sharp peaks of equal intensity up to 130°, indicative that both pyridine rings are suffering restricted rotation giving rise to a pair of geometric isomers. The nmr spectrum of the mono-*N*-methyl quaternary salt of **18** shows the presence of at least two of the four possible geometrical isomers; these, however, begin to interconvert at room temperature and are equilibrated above 80° ($\Delta F^{\ddagger} \sim 17$ kcal/mol). The bis-*N*-methyl quaternary salt of **18** shows its *N*-methyl absorptions as two singlets (2:1 area ratio) at 70°. The major peak is temperature independent, whereas the minor peak broadens as the temperature is lowered, finally separating into two singlets of equal area at 20°. These results are interpreted in terms of an unexpectedly facile pentaphene ring inversion accompanied by a synchronous rotation of both pyridines.

Previously it has been shown that, in marked contrast to the low order of reactivity that azonia polycyclic aromatic compounds display toward conventional electrophilic dienophiles, a variety of these compounds will readily undergo stereoselective 4 + 2 cycloadditions with nucleophilic olefins including enamines and ketene acetals to give adducts in high yields.[1] The ketene diethyl acetal adduct of 5-acetoxy-8-*tert*-butyl-4a-azoniaanthracene perchlorate and the bis adduct of 4a,8a-diazoniapentaphene diperchlorate have been particularly useful, serving as precursors to the interesting, highly overcrowded naphthalene **1**[2] and phenanthrene **2**,[3] respectively, *via* the synthesis shown in Scheme I.

Benzyne is considered to be an electrophilic reagent. Nevertheless, we have now found that it too will undergo cycloaddition efficiently with azonia polycyclics to afford azoniatriptycene-type adducts (**4**). Our interest in these types of compounds has been twofold. First, they serve as precursors to substituted anthracenes and related hydrocarbons in a synthesis to be described in a separate publication. Second, and relevant to this paper, is the discovery that their thermolysis usually leads to pyridyl-substituted polycyclic aromatic hydrocarbons, the simplest of these being 9-(2-pyridyl)anthracene (**5**). Exploitation of this reaction sequence as a new synthetic approach to overcrowded molecules has been profitably investigated



3 **4** **5**

in the synthesis of highly strained nonplanar, and therefore chiral, 13,14-bis(2-pyridyl)pentaphene. Manifestations of the ring strain and unusual geometry associated with this compound parallel those previously observed with 4,5-dipyridylphenanthrene **2** in several ways. One interesting and distinctive difference is discussed, related to conformational isomerism.

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[1] D. L. Fields, T. H. Regan, and J. C. Dignan, *J. Org. Chem.*, **33**, 390 (1968).

[2] D. L. Fields and T. H. Regan, *ibid.*, **36**, 2986 (1971).

[3] D. L. Fields and T. H. Regan, *ibid.*, **36**, 2991 (1971).