30690-06-3; **24**, 30690-07-4; **25**, 30690-08-5; **26**, 30690-09-6; **28**, 30758-67-9; **29**, 30758-68-0; **30**, 30690-10-9; **31**, 30758-69-1; **35**, 30690-11-0; **36**, 30690-12-1; **37**, 30758-70-4; **39**, 30758-71-5; **41**, 30690-13-2; **42**, 30690-14-3; **45**, 30690-15-4; **46**, 30690-16-5; **47**, 30690-17-6; **48**, 30690-18-7; **49**, 30690-19-8; **50**, 18804-91-6; **51**, 30690-20-1; **53**, 23580-52-1.

Overcrowded Molecules. I. Substituted 8-*tert*-Butyl-1-(2-pyridyl)naphthalenes, Including a Thermodynamically Stable Ketonic Tautomer

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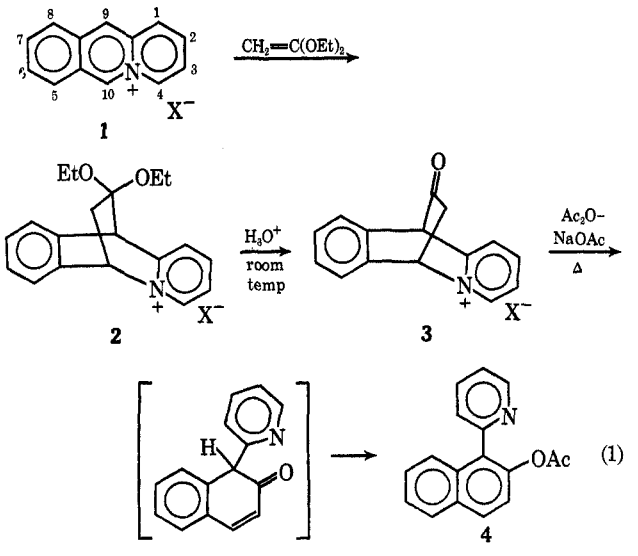
Condensation of appropriately substituted 4a-azoniaanthracene salts with ketene diethyl acetal followed by mild hydrolysis and then thermolysis in acetic anhydride has given several 8-*tert*-butyl-1-(2-pyridyl)naphthalenes. Their spectral properties and reactivity are adduced to indicate the high degree of steric strain present. Low-temperature nmr spectra of the *N*-methyl quaternary salt of 6-substituted 2,5-diacetoxy-8-*tert*-butyl-1-(2-pyridyl)naphthalenes indicate the existence of two isomers and are interpreted in terms of skewing of the naphthalene framework. 8-*tert*-Butyl-1-(2-pyridyl)naphthalenediol **13** is shown to exist exclusively as the thermodynamically stable keto tautomer **14**. 5-Acetoxy-8-*tert*-butyl-1-(2-pyridyl)-2-naphthol (**11**) has been oxidized (by Cu^{2+}) to give a novel intramolecular cyclization product formed by attack by N at the peri position to displace the *tert*-butyl group.

1-(2-Pyridyl)-2-naphthyl acetate (**4**) has recently been obtained by a three-step synthesis outlined in eq 1 involving the stereospecific 4 + 2 cycloaddition of ketene diethyl acetal to 4a-azoniaanthracene **1**, controlled hydrolysis of the resulting adduct (**2**) to ketone **3**, and sequential elimination, enolization, and acetylation reactions which occur as **3** is heated in acetic anhydride in the presence of sodium acetate.[1] Owing to the easy



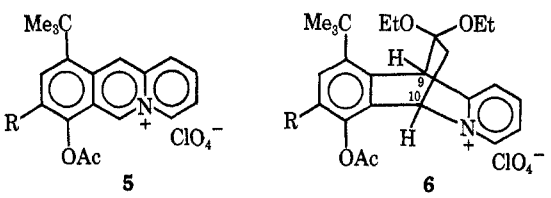
(1)

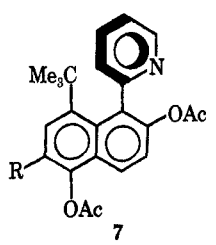
availability of a variety of types of substituted 4a-azoniaanthracene salts, especially those having substituents on the C_5–C_8 positions, this synthesis offers convenient access to 8-substituted 1-(2-pyridyl)naphthalenes, certain ones of which are of interest for peri-interaction studies. In succeeding papers we will describe some highly overcrowded pyridyl-substituted phenanthrenes and pentaphenes whose syntheses are based on this general approach. In this paper we report the synthesis of 8-*tert*-butyl-1-(2-pyridyl)naphthalenes and our observations of the consequences of steric strain on their physical and chemical properties.

(1) D. L. Fields and T. H. Regan, *J. Org. Chem.*, **35**, 1870 (1970).

Results and Discussion

The feasibility of the synthesis outlined in eq 1 to yield highly overcrowded naphthalenes was readily confirmed by the preparation of 8-*tert*-butyl-1-(2-pyridyl)naphthalenes **7a–c**. Some feeling for the high





a, R = H; **b**, R = Br; **c**, R = OAc

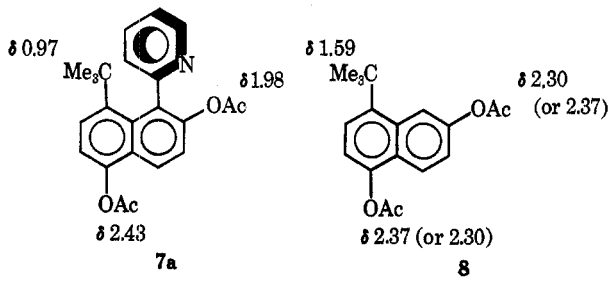
degree of overcrowding inherent in these compounds follows from the knowledge that even with the much less crowded 1,8-dimethylnaphthalene, peri interaction between the methyls is sufficient to cause distortion of the naphthalene skeleton as well as considerable bond-angle deformation.[2] Nonetheless, the syntheses of **7a–c** proved to be quite straightforward and free of complications.

As an example, adduct **6a** was obtained in quantitative yield following treatment of **5a** with an excess of ketene diethyl acetal for 10 min at room temperature. The stereochemistry of the addition was confirmed by

(2) A single-crystal X-ray analysis of 3-bromo-1,8-dimethylnaphthalene showed the normal C_1–C_8 distance in naphthalene of 2.44 Å extended to 2.56 Å, the methyls constrained to a 2.92-Å separation, a distance much less than the sum of their van der Waal's radii (4.0 Å) accompanied by some departure from planarity within the aromatic rings: M. D. Jameson and B. R. Penfold, *J. Chem. Soc.*, 528 (1965). The strain energy of 1,8-dimethylnaphthalene has been estimated at 7.9 kcal: J. Parker, J. Vaughan, and E. Wong, *J. Org. Chem.*, **23**, 1373 (1958).

nmr analysis, based on the multiplicities of the bridgehead hydrogens, *i.e.*, H_9 a singlet at δ 6.05 and H_{10} a broadened triplet at δ 6.67 (DMSO-d_6). Mild acid hydrolysis of **6a** afforded the corresponding bicyclic ketone which, in turn, was heated for 5 min in refluxing acetic anhydride in the presence of anhydrous sodium acetate. Work-up of the reaction mixture gave crystalline **7a** in 79% overall yield from **5a**.

The elemental analysis and molecular weight (mass spectrometry) of this product were satisfactory, and its infrared spectrum was consistent with the assigned structure. The salient features of its nmr spectrum include two AB quartets (3,4- and 6,7-naphthalene protons) in the aromatic region superimposed on the pyridyl proton absorptions, and the unusually high-field positions for the *tert*-butyl and one of the two acetoxymethyl signals (0.6 and 0.3 ppm higher field, respectively, than those of analogous groups in model compound **8**[3]). Such upfield shifts would result if the gross overcrowding is accommodated by bond-angle deformations so that the *tert*-butyl and pyridyl groups are bent away from one another above and below the naphthalene ring, with the pyridine rotated further out



7a **8** **9**

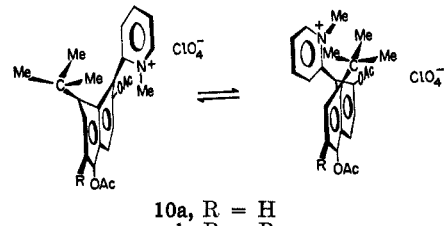
of the plane to a degree that helps minimize its interaction with the *tert*-butyl as well as the 2-acetoxy groups. In this conformation, the *tert*-butyl group would lie outside the zone of maximum deshielding of the naphthalene, and both it and the 2-acetoxy group would reside in the shielding zone of the pyridine as well.

The syntheses of **7b** and **7c** were accomplished in like manner, and analytical and spectral data for both were consistent with their assigned structures.

Low-temperature nmr spectra of **7** were examined with the expectation that the high degree of steric interference would lead to restricted rotation of the *tert*-butyl group, a phenomenon which has been observed in considerably less sterically crowded molecules.[4] At −86°, the absorption of the *tert*-butyl group of **7a** had broadened considerably ($W_{1/2}$ = 13 Hz compared to $W_{1/2}$ = 0.8 Hz for TMS at −100°) but was still symmetrical; *i.e.*, it showed no evidence for nonequivalence of the methyl groups. This was true also for **7b** and **7c**. That at least part of the broadening was due to restricted motion of the *tert*-butyl group was indicated by the fact that the acetate methyls were broadened only approximately one-third as much as the *tert*-butyl peak.

Careful examination of Dreiding models of compounds **7** shows that, while there is a very high degree of interference at the 1,8 positions, the methyls of the *tert*-butyl do not pass through an obvious energy minimum in the course of rotating past the face of the pyridyl ring. Thus, there is no energy well corresponding to a frozen position of the *tert*-butyl rotation, and, therefore, no preferred conformation in which the methyls would be nonequivalent.

Alkylation of **7a–c** with iodomethane followed by anion exchange produced the methyl quaternary salts **10a–c**. The nmr spectrum of **10a** again showed disproportionate broadening (symmetrical) of the *tert*-butyl signal with respect to the two acetate methyls as the temperature was lowered to −100°. Interestingly, the *N*-methyl signal showed the most broadening. This broadening was even more dramatic for **10b** and **10c** (their *N*-methyl signals collapsed and actually split into two peaks of unequal intensity below −53 and −86°, respectively). The appearance of two *N*-methyl signals is interpreted in terms of the previously mentioned ring deformation of the naphthalene system as depicted below. While the two conformational isomers are in rapid equilibrium above −50°, the rate of ring inversion slows sufficiently below this to allow the separate *N*-methyl resonances to be observed. An attempted line-shape analysis[5] of the *N*-methyl signal of **10b** over the range −80 to −40° was complicated, apparently by viscosity broadening below −65°. However, over the temperature range near coalescence (−64 to −40°), a constant $\Delta G^{\pm}$ = 12.0 ± 1.0 kcal/mol was obtained, and, from a plot of log k/T) *vs.* $1/T$, $\Delta H^{\pm}$ was found to be 19.5 ± 1.0 kcal/mol. The two configurations differ by only 220 cal/mol.



10a, R = H
b, R = Br
c, R = OAc

Ultraviolet and mass spectral data obtained for **7a–c** when compared with like data of several related compounds, **8**, **9**, and 1,6-diacetoxynaphthalene, also show abnormalities which are considered to be manifestations of ring strain. The uv spectrum of **7a** in such a comparison (Figure 1) shows pronounced bathochromic and hyperchromic shifts in its long-wavelength absorptions accompanied by loss of vibrational structure, which is indicative of the large perturbation present in its aromatic system. Analogous spectral characteristics for a number of other overcrowded

(3) D. L. Fields, *J. Org. Chem.*, **36**, 3002 (1971).

(4) As examples, see J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 27 (1967); F. A. L. Anet, M. St. Jacques, and G. N. Chmurny, *J. Amer. Chem. Soc.*, **90**, 5243 (1968); W. E. Heyd and C. A. Cupas, *ibid.*, **91**, 1559 (1969).

(5) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *ibid.*, **88**, 3185 (1966); J. Jonas, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3396 (1965).

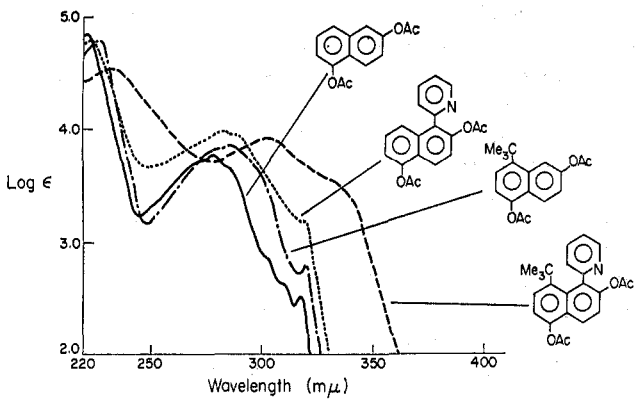


Figure 1.—Ultraviolet spectra of **7a**, **8**, **9**, and 1,6-diacetoxynaphthalene.

aromatic compounds have been documented in the literature and are usually attributed to a convergence of excited- and ground-state energy levels, the ground state having been destabilized by overcrowding.[6]

Low-resolution mass spectral data for **7a** and **8** are compared in Table I. The strongest signal displayed

TABLE I

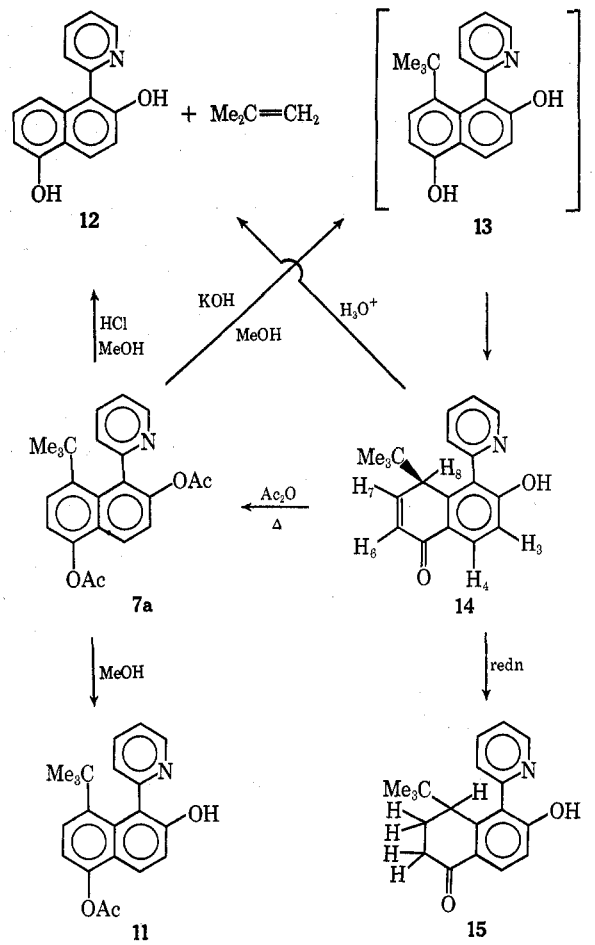
MASS SPECTRAL DATA (70 eV)

Fragment	Assignment	—% abundance— 7a	8
M	M	0.1	43
M − 42	M − CH_2CO	0.2	86
M − 84	M − $2CH_2CO$	0.05	67
M − 57	M − C_4H_9	63	19
M − 97	M − (CH_2CO + C_4H_9)	44	0
M − 141	M − ($2CH_2CO$ + C_4H_9)	100	100

by both compounds is a M − 141 peak, representing the parent ion minus the *tert*-butyl and two ketene fragments. The data indicate that, for the most part, the succession of fragmentations leading to the M − 141 species differs for **7a** and **8** in that **7a**, upon electron impact, expels the *tert*-butyl radical before, rather than after, ester fragmentation–rearrangement (-CH_2CO). We assume that relief of peri strain is responsible for this behavior.

One property of **7**, of a chemical nature, is particularly indicative of the high degree of resonance destabilization which characterizes these naphthalene derivatives. This was encountered during our attempt to deacetylate **7a** to the corresponding naphthalenediol **13** (Scheme I). In refluxing methanol, **7a** lost an acetyl group, presumably as a consequence of neighboring pyridyl group participation, to give naphthol **11**. When **7a** was treated with methanolic HCl under conditions permitting complete deacetylation, the *tert*-butyl group was lost as isobutylene in the process,[7] yielding diol **12**. On the other hand, deacetylation without accompanying loss of the *tert*-butyl substituent was easily achieved under basic conditions, and from a reaction of **7a** with methanolic KOH, we isolated a crystalline product which was analyzed satisfactorily as **13** and whose mass spectrum showed the

SCHEME I



correct parent ion at *m/e* 293, as well as strong signals at 257 (M − C_4H_8) and 256 (M − C_4H_9). However, other more meaningful spectral (ir, uv, nmr) and chemical evidence negates this structural assignment in favor of the tautomeric structure **14**. Its uv spectrum showed maxima at $\lambda_{max}^{CH_3CN}$ 213 nm (ε 15,800), 244 (17,000), and 283 (15,200), and its ir spectrum had a strong carbonyl absorption at 1661 cm^{-1}, both pieces of data consistent for structure **14** rather than **13**. More definitive is the spectral evidence derived from 90-MHz nmr measurements. The *tert*-butyl signal was observed as a sharp singlet at 0.55 ppm, a field position more in keeping with a *tert*-butyl group attached to an sp^3 than an sp^2 carbon. The remaining absorptions, completely consistent for **14**, were observed at δ 4.36 (d, 1 H, J = 5.5 Hz, H_8), 6.47 (d, 1 H, J = 10 Hz, H_6), 7.03 (d, 1 H, J = 8.5 Hz, H_3), 7.21 and 7.27 (d of d, J = 5.5, 10 Hz, H_7) superimposed on the H_5 pyridyl proton multiplet, two multiplets at 7.50 and 7.85 (2 H, H_3 and H_4 pyridyl protons, respectively), 8.15 (d, 1 H, J = 8.5 Hz, H_4), and 8.67 ppm (d of m, 1, H_6 pyridyl proton). The coupling assignments for H_6, H_7, and H_8 were confirmed by double irradiation experiments. Coupling between H_8 and H_6 is so small as to be barely observable.

Supporting chemical evidence for this structural assignment includes the rearomatization of **14** to **7a** when treated at reflux temperature with acetic anhydride, and to **12** (plus isobutylene) when heated with 6 *N* HCl. Its reduction, either chemically ($LiAlH_4$ in ether) or catalytically (Pd/C, 40 psi of H_2), gave

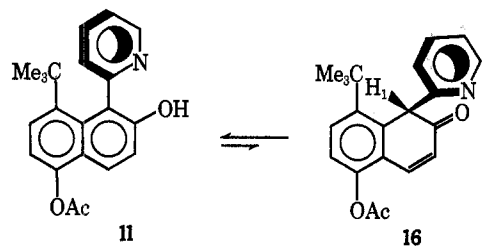
(6) See V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966), for leading references.

(7) This is not an uncommon phenomenon for strained *tert*-butyl aromatic compounds. For a recent example, see R. W. Franck and E. G. Leser, *J. Amer. Chem. Soc.*, **91**, 1577 (1969).

phenol **15**: $\nu_{C=O}$ 1671 cm^{-1}; partial nmr, four-proton multiplet centered at δ 2.52.

There is, of course, abundant evidence that, if a reagent requires it, certain phenolic substances react as if they existed in equilibrium with the keto form. Furthermore, isolable keto tautomers of several highly substituted phenols have been reported.[8] They were formed under kinetically controlled conditions, albeit by several different types of reactions, *i.e.*, thermal rearrangements,[8a,b] electrophilic substitution,[8c] and photochemical[8d,e,f] and oxidative coupling;[8g] with one exception,[9] each proved to be more or less labile, ultimately tautomerizing to the thermodynamically more stable phenol. In related naphthol systems, although a few rare examples of thermodynamically stable keto tautomers of naphthols are known,[10] the case under discussion is certainly a striking example of this phenomenon. Even the expected solution equilibrium between **14** and **13** is very slow to be established, since H_8 of **14** does not undergo detectable deuterium exchange over a 2-hr period in the presence of D_2O or D_2O plus a few drops of either 35% DCl or 40% KOD in D_2O (by nmr in DMSO-d_6).

Let us contrast these results with the behavior of naphthol **11**, which on first inspection might be expected to relieve *tert*-butyl–pyridine overcrowding by isomerizing to **16**. We found, however, that such a tautomerization does not occur to a measurable extent,



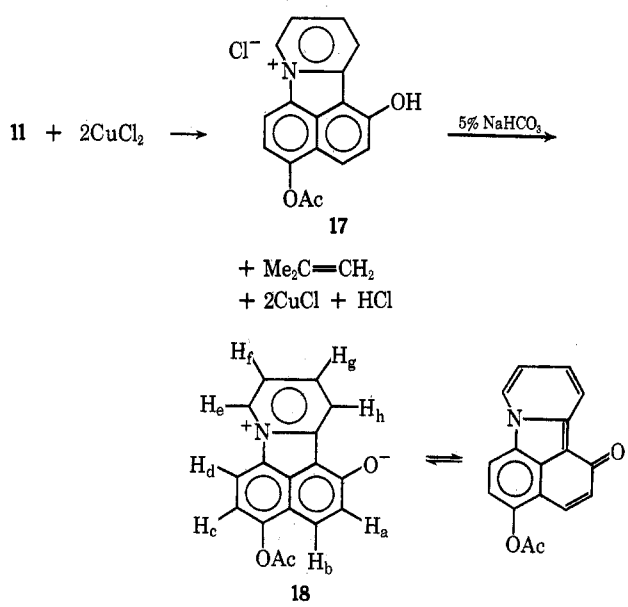
11 **16**

in that the amount of **16** present upon dissolution of **11** in $CDCl_3$ or DMSO-d_6 is less than that detectable by nmr means.

Examination of molecular models of **14** and **16** suggests a rationale for this marked difference in behavior. For the equilibrium between **13** and **14** to lie far toward **14** means that the energy gained in relief of steric strain must greatly overbalance the loss of naphthalene resonance energy associated with **13**; and indeed there appears to be a complete absence of steric interaction between the *tert*-butyl, pyridine, and H_8 substituents when **14** assumes a conformation having the *tert*-butyl in a quasiaxial position.

Such is not the case for the tautomerization of **11** to **16**. While the pyridine of **16**, in a quasiaxial conformation, is removed from interacting with the *tert*-butyl group, H_1 finds itself thrust directly into it. Ketonization of **11** to **16** thus produces at best only a partial relief of steric strain at the expense of resonance energy, evidently insufficient to make ketonization an energetically preferred process.

One other interesting point related to **11** concerns its behavior upon oxidation. Naphthol **11** in solution is fairly labile to oxidation, as substantiated by a polarographic study which showed that it undergoes a facile one-electron oxidation at $E_{1/2}$ = 1.00 V. When **11** was treated with anhydrous $CuCl_2$ in refluxing ethanol, a yellow crystalline chloride salt separated from solution, and isobutylene collected as a gaseous by-product within 15 min. Basification of the chloride salt with 5% sodium bicarbonate gave a red crystalline diamagnetic zwitterion, which was purified by Florisil chromatography. Elemental, nmr, and mass spectral analyses support the assigned structures as **17** and **18** for the chloride salt and zwitterion, respectively. The overall reaction is a two-electron oxidation process involving a novel intramolecular naphthalene peri



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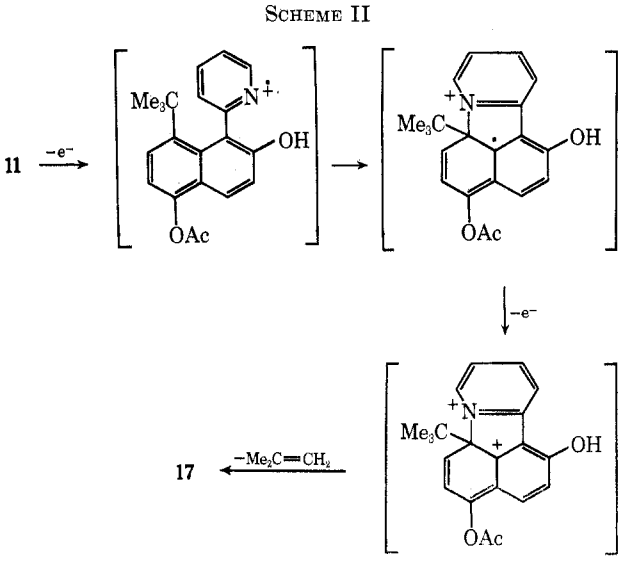
cyclization. A reasonable mechanism for this transformation is suggested in Scheme II. The oxidative

SCHEME II



(8) (a) B. Miller, *ibid.*, **89**, 1685 (1967); (b) J. C. Floyd, D. A. Plank, and W. H. Starnes, Jr., *Chem. Commun.*, 1237 (1969); (c) V. V. Ershov and A. A. Volod'kin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 680 (1962); *Chem. Abstr.*, **57**, 12337c (1962); (d) T. Matsuura and K. Ogura, *J. Amer. Chem. Soc.*, **89**, 3846 (1967); (e) *Tetrahedron*, **24**, 6167 (1968); (f) *ibid.*, **24**, 6157 (1968); (g) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).

(9) Major amounts of both 2,4,6-tri-*tert*-butylresorcinol and its diketo tautomer are present at solution equilibrium; see ref 8b.

(10) Certain dihydroxynaphthalenes have been partly isomerized in the molten state to the corresponding diketone form: D. B. Bruce and R. H. Thomson, *J. Chem. Soc.*, 2759 (1962). The monoanion of 1,3-naphthalenediol exists as a keto tautomer: E. S. Hand and R. M. Horowitz, *J. Org. Chem.*, **29**, 3088 (1964).

coupling of a pyridyl radical through N rather than C is, to our knowledge, unprecedented in the literature. We have examined its occurrence in a different system, which we shall describe in a future paper.

Experimental Section[11]

5-Acetoxy-8-*tert*-butyl-4a-azoniaanthracene–Ketene Diethyl Acetal Adducts 6a–c.—These adducts were isolated in quantitative yields following a procedure described previously[12] involving cycloaddition of ketene diethyl acetal to 4a-azoniaanthracene perchlorates **5a–c**,[13] respectively.

Adduct **6a** had mp 219–221° dec after one recrystallization from acetonitrile–ether.

Anal. Calcd for $C_{25}H_{32}ClNO_8$: C, 58.9; H, 6.3; N, 2.8. Found: C, 58.6; H, 6.0; N, 2.6.

Adducts **6b** and **6c** were isolated as amorphous white powders.

2,5-Diacetoxy-8-*tert*-butyl-1-(2-pyridyl)naphthalenes 7a–c.—As a representative example, a suspension of adduct **6a** (2.00 g, 3.9 mmol) in 10 ml of 12 *N* hydrochloric acid was shaken on a wrist-action shaker for 2 hr at room temperature.[14] The resulting heterogeneous mixture was diluted with 5 ml of cold water and then treated with sodium perchlorate to complete the crystallization of the desired bicyclic ketone, 8-*tert*-butyl-9,10-dihydro-5-hydroxy-12-oxo-4a-azonia-9,10-ethanoanthracene perchlorate, 1.30 g (84%). An analytical sample, crystallized as white needles from acetonitrile–ether, had mp 170–174° dec, ir 1750 cm^{-1} (C=O).

Anal. Calcd for $C_{19}H_{20}ClNO_6$: C, 57.9; H, 5.1; Cl, 9.0; N, 3.6. Found: C, 57.5; H, 5.0; Cl, 9.2; N, 3.7.

A mixture of 0.90 g (2.3 mmol) of this product, 0.30 g of anhydrous sodium acetate, and 20 ml of acetic anhydride was heated under reflux for 5 min and concentrated to a syrup; the syrup was triturated in 75 ml of 5% aqueous sodium bicarbonate solution, giving 0.81 g (94%) of crude **7a**. One recrystallization from methylcyclohexane gave analytically pure **7a** as white plates: mp 182–184°; nmr ($CDCl_3$) δ 0.97 (s, 9, *tert*-butyl), 1.98 (s, 3, 2-acetoxy), 2.43 (s, 3, 5-acetoxy), doublets at 7.20 (H_3) and 8.01 (H_4), J = 9 Hz, and 7.20 (H_7) and 7.70 (H_6), J = 8 Hz, superimposed on H_3, H_4, and H_5 pyridyl multiplets, 8.73 ppm (d of m, 1, H_6 pyridyl proton).

Anal. Calcd for $C_{23}H_{23}NO_4$: C, 73.2; H, 6.1; N, 3.7. Found: C, 73.1; H, 6.2; N, 3.7.

Pyridinium perchlorate **10a**, prepared by treating **7a** with excess iodomethane for 18 hr at 40° followed by anion exchange, had mp 111–113°.

Anal. Calcd for $C_{24}H_{26}ClNO_8$: C, 58.6; H, 5.3; Cl, 7.2. Found: C, 58.4; H, 5.5; Cl, 7.0.

Naphthalenes **7b**, mp 154–156°, and **7c**, mp 198–200°, and their respective *N*-methyl derivatives **10b**, mp 134–137°, and **10c**, mp 237–238°, were prepared in a similar manner.

Anal. Calcd for $C_{23}H_{22}BrNO_4$ (**7b**): C, 60.6; H, 4.8; N, 3.1. Found: C, 60.6; H, 5.1; N, 3.1.

Anal. Calcd for $C_{25}H_{25}NO_6$ (**7c**): C, 69.0; H, 5.7. Found: C, 69.3; H, 6.0.

Anal. Calcd for $C_{24}H_{25}BrClNO_8$ (**10b**): C, 50.5; H, 4.4. Found: C, 50.6; H, 4.7.

Anal. Calcd for $C_{26}H_{28}ClNO_{10}$ (**10c**): C, 56.7; H, 5.1; N, 2.5. Found: C, 56.7; H, 5.1; N, 2.5.

5-Acetoxy-8-*tert*-butyl-1-(2-pyridyl)-2-naphthol (11).—A mixture of **7a** (5.00 g, 0.0133 mol) and 100 ml of methanol was refluxed for 3 hr. Naphthol **11** (4.04 g, 91%) crystallized from solution during this period and was collected after refrigerating the mixture for 2 hr at 5°. The product had mp 194–195° after one recrystallization from methylcyclohexane; nmr ($CDCl_3$) δ 1.15 (s, 9, *tert*-C_4H_9), 2.55 (s, 3, OAc), 6.22–7.17 (2 AB quartets, J = 8 and 9 Hz, superimposed on multiplets, 7, H_3, H_4, H_6, H_7 of naphthalene and H_3, H_4, H_5 of pyridine), 8.60 ppm (d of m, 1, H_6 of pyridine).

Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.3; H, 6.3; N, 4.2. Found: C, 74.9; H, 6.3; N, 4.4.

5-(2-Pyridyl)naphthalene-1,6-diol (12).—The yellow crystalline hydrochloride salt of **12** separated from solution and isobutylene evolved as an off-gas (identified by mass spectrometry) when a mixture of **7a** (0.60 g, 1.6 mmol) in 12 ml of 6 *N* hydrochloride acid was heated for 30 min at reflux temperature. The chloride salt was collected after being refrigerated at 5° for 2 hr and converted directly into its diacetyl derivative **9** (0.44 g, 88%): mp 145–147° (from methylcyclohexane); nmr ($CDCl_3$) δ 2.00 (s, 3, 2-acetoxy), 2.40 (s, 3, 5-acetoxy), 7.17–7.50 (m, 6), 7.70 (d of d, 1, H_8), 8.00 (d, 1, J = 8 Hz, H_4), 8.78 ppm (d of m, 1, H_6 of pyridine).

Anal. Calcd for $C_{19}H_{15}NO_4$: C, 71.1; H, 4.7; N, 4.4. Found: C, 70.7; H, 5.1; N, 4.1.

Ketonic Tautomer 14.—A mixture of **7a** (1.50 g, 4.0 mmol) and potassium hydroxide (0.40 g) in 20 ml of 50% aqueous methanol was stirred at room temperature for 10 min. The solution was diluted with 40 ml of water and then 5% HCl solution until the resulting amphoteric precipitate began to redissolve. The mixture was made alkaline with 5% aqueous sodium bicarbonate solution, and the product was collected, dried, and recrystallized as white needles (0.70 g, 60%) from methylcyclohexane, mp 194–196°; see text for spectral data.

Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.9; H, 6.5; N, 4.8. Found: C, 77.6; H, 6.5; N, 4.9.

Phenol 15.—A mixture of 0.60 g of **14**, 0.20 g of 10% palladium on charcoal, and 100 ml of ethanol was hydrogenated at 40 psi (initial pressure) for 3 hr in a Parr shaker, giving (after work-up of the reaction mixture) 0.54 g (90%) of **15** as white needles (from methylcyclohexane): mp 205–206°; nmr ($CDCl_3$) δ 0.62 (s, 9), 2.27–2.77 (m, 4), 3.50 (m, 1), 6.98 (d, 1, J = 9 Hz), 7.10–7.90 (m, 3), 8.09 (d, 1, J = 9 Hz), 8.67 ppm (d of m, 1).

Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.3; H, 7.1; N, 4.7. Found: C, 77.0; H, 7.2; N, 4.6.

The same product was obtained from a $LiAlH_4$ reduction of **14** in ether.

Zwitterion 18.—A solution of **11** (0.67 g, 2.0 mmol) and 0.67 g of anhydrous cupric chloride in 20 ml of ethanol was refluxed for 15 min, during which time isobutylene gas was evolved (identified by mass spectrometry) and **17** (0.45 g, 73%) crystallized from solution.

The zwitterion **18** was prepared by dissolving **17** in 10 ml of DMSO and basifying with 50 ml of 5% aqueous sodium bicarbonate solution. The resulting orange crystals were collected, dried, dissolved in a minimum amount of acetone, and introduced onto a column of Florisil magnesium silicate. The chromatogram was developed with acetone–ethanol (10:1 v/v) and the eluted product recovered and crystallized as red needles from ethanol–ligroin (bp 30–60°): mp 212–215° dec; uv max (CH_3CN) 242 nm (log ϵ 4.62), 264 (4.42), 330 (3.97), 345 (3.94), 410 (3.66), 431 (3.98), 457 (4.31), 489 (4.38); nmr (DMSO-d_6) δ 2.50 (s, 3, acetoxymethyl), 6.75 (d, 1, J = 10 Hz, H_a), 7.60 (d, J = 9 Hz, H_c), 7.60 (m, H_f or H_g), 7.80 (d, J = 10 Hz, H_b), 7.81 (m, H_f or H_g), 8.38 (d of m, H_h), 8.37 (d, J = 9 Hz, H_d), 9.22 ppm (d of m, 1, H_e); mass spectrum (70 eV) m/e (rel intensity) of major peaks 277 (32) (M^+), 235 (100) ($M - CH_2CO$).

Anal. Calcd for $C_{17}H_{11}NO_3$: C, 73.7; H, 4.0; N, 5.1. Found: C, 73.4; H, 4.0; N, 5.2.

Registry No.—**6a**, 30319-50-7; **7a**, 30310-01-1; **7b**, 30310-02-2; **7c**, 30310-03-3; **8**, 30310-04-4; **9**, 30310-05-5; **10a**, 30275-77-5; **10b**, 30275-78-6; **10c**, 30310-06-6; **11**, 30310-07-7; **14**, 30310-08-8; **15**, 30310-09-9; **18**, 30310-10-2; 8-*tert*-butyl-9,10-dihydro-5-hydroxy-12-oxo-4a-azonia-9,10-ethanoanthracene perchlorate, 30310-11-3.

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(11) Melting points (uncorrected) were determined on a Thomas-Hoover apparatus. Ultraviolet absorption spectra were recorded on a Cary Model 14 spectrophotometer. Infrared spectra were obtained with either a Beckman IR-12 or a Perkin-Elmer Infracord spectrometer. Nmr spectra were determined with either a Varian A-60 or Bruker HX-90 spectrometer. Peak positions are reported in parts per million downfield from tetramethylsilane, followed by (in parenthesis) multiplicity, relative area, and assignment.

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

(13) D. L. Fields and J. B. Miller, *J. Heterocycl. Chem.*, **7**, 91 (1970).

(14) More stringent conditions, using elevated temperatures, will degrade ketone-**8**-type intermediates; see ref 1.