# Cleavage Reactions of Bicyclic Ketones Derived from Azoniaanthracene–Ketene Acetal Adducts

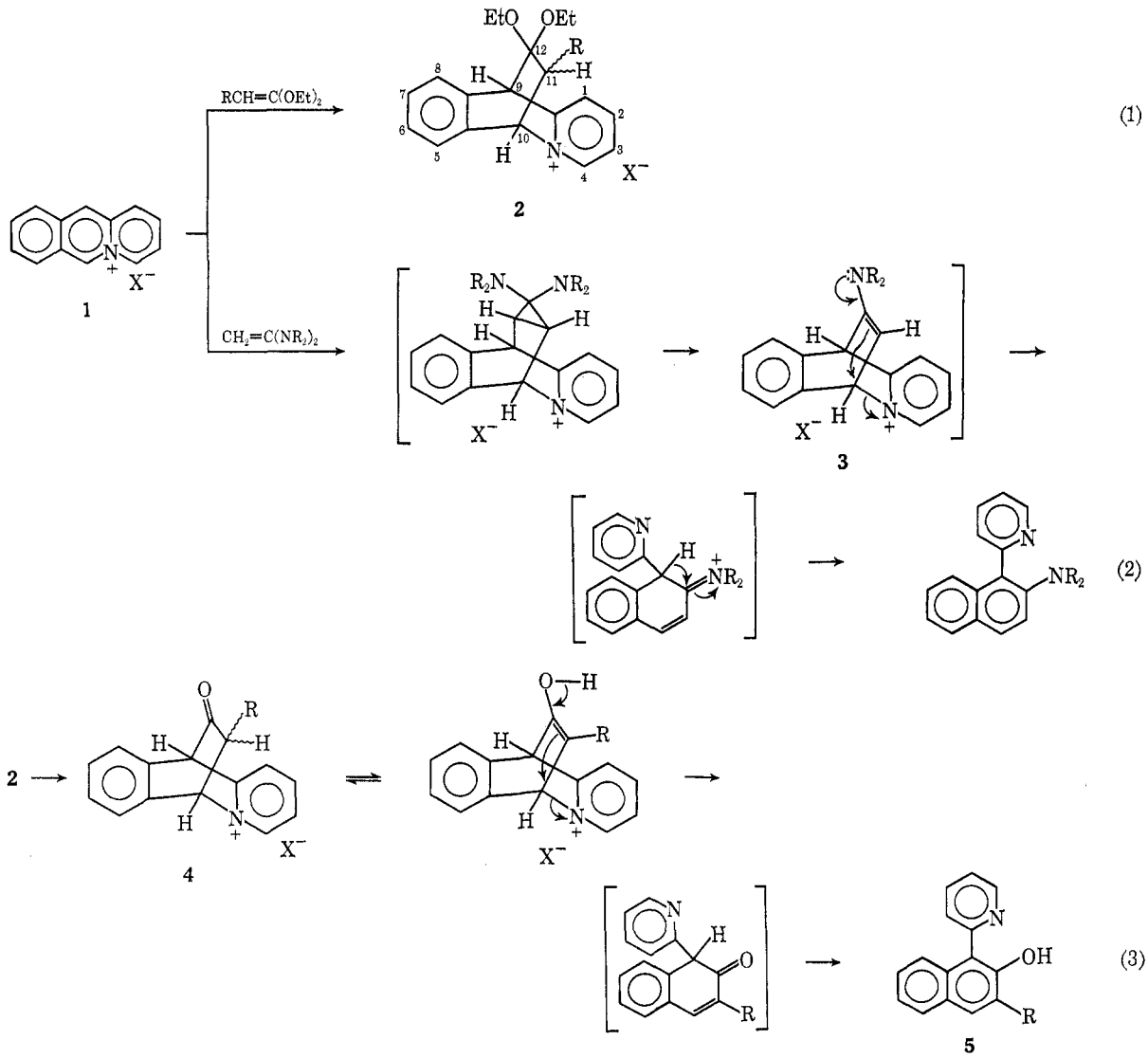
D. L. FIELDS AND T. H. REGAN

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

*Received September 25, 1969*

9,10-Dihydro-12-oxo-4a-azonia-9,10-ethanoanthracenes **4a–4c** were isolated following the mild acid hydrolysis of their respective ketals, **2a–2c**. Depending on the nature of the R group at C-11, **4** proved to be more or less labile to acidic as well as basic reagents, undergoing two distinctly different types of fragmentations to yield 1-(2-pyridyl)-2-naphthols (**5**) and/or 9,10-dihydro-10-(carboxymethyl)-4a-azoniaanthracene salts (**6**). Some structure–reactivity relationships were examined and a mechanism for these cleavages is suggested.

In a previous communication[1] ketene acetals were shown to react rapidly and stereoselectively by Diels–Alder addition with a variety of types of azoniapolycyclic aromatic compounds, *i.e.*, **1** → **2** (eq 1). Without exception, the cycloadditions gave the positional isomers with the alkoxy groups nonadjacent to the quaternary nitrogens as a mixture, where possible, of two geometrical forms in which the R group resides either *syn* or *anti* to the quaternary nitrogen. It was also shown that the reaction of 1,1-dimorpholinoethylene with the 4a-azoniaanthracene ion (**1**) readily gives 2-morpholino-1-(2-pyridyl)naphthalene (eq 2, $R_2N$ = morpholino), probably resulting from an elimination reaction involving enamine **3** as an intermediate.



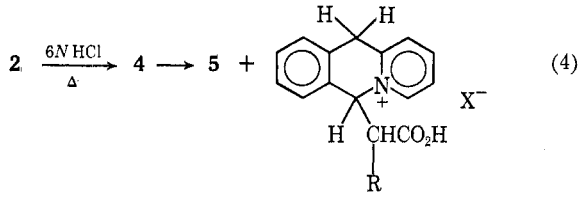
Noting the structural similarity of the enol of ketone **4**, a type of compound assumed to be available from **2** and enamine **3**, we thought it of interest to see if **4** would undergo an analogous elimination reaction, as indicated in eq 3, to give naphthol **5**. We now know that such a transformation is indeed quite feasible, and in fact it has been exploited in the syntheses of a number of highly overcrowded compounds to be described in several forthcoming publications. This

(1) D. L. Fields, T. H. Regan, and J. C. Dignan, *J. Org. Chem.*, **35**, 390 (1968).

paper deals with an investigation of an unexpected and undesired second type of fragmentation of **4**-type ketones which was encountered during their preparation.

## Results and Discussion

**Acid Cleavages.**—Treatment of the 4a-azoniaanthracene perchlorate–ketene diethyl acetal adduct, **2a**, with 6 *N* hydrochloric acid for 0.5 hr at reflux temperature afforded an easily separable mixture of two products (eq 4), neither of which was the expected bicyclo ketone, **4a**.



(4)

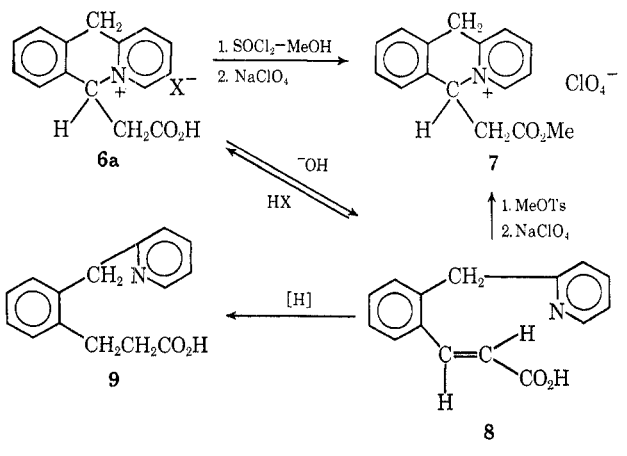
**6**

| | R | Yield, % 4 | 5 | 6 |
|---|---|---|---|---|
| a | H | 0 | 9 | 84 |
| b | Me | 0 | 58 | 32 |
| c | $C_6H_5$ | 15 | 80 | 0 |

The minor product, isolated in 9% yield, proved to be naphthol **5a**, based on elemental analyses of it and its O-acetyl derivative, and on the following spectral results. Its mass spectrum displayed a parent peak in agreement with the calculated molecular weight of 221. Its nmr spectrum ($CDCl_3$) consisted of a nine-proton multiplet at $\delta$ 7.17–8.35 (aromatic), a one-proton doublet of multiplets centered at $\delta$ 8.70 (pyridyl H $\alpha$ to N), and one exchangeable proton at $\delta$ 11.91 (–OH). The chemical shift of the hydroxyl proton is independent of concentration, indicative of intramolecular hydrogen bonding, consistent with the 1,2-substitution pattern assigned to **5a**. A comparison of the ultraviolet spectra of the acetyl derivative of **5a** and $\beta$-naphthyl acetate showed marked similarities.

The second product, obtained in 84% yield, was assigned structure **6a** based on elemental and spectral analyses of it and its derivatives shown in Scheme I.

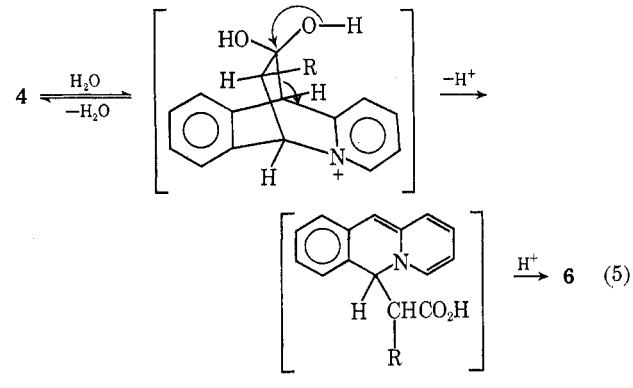
SCHEME I



Its nmr spectrum (DMSO-$d_6$) displayed the methylene protons $\alpha$ to the carboxyl group and adjacent to an asymmetric center (>CHC**H**$_2$CO$_2$H) as four peaks centered at $\delta$ 4.68, representing the center strong peaks of the AB portion of an ABX pattern. The remaining absorptions appeared as a two-proton singlet at $\delta$ 4.77 ($\alpha$-picolinium methylene), a poorly resolved one-proton triplet centered at $\delta$ 6.50 (>C**H**CH$_2$CO$_2$H, X part of ABX), a seven-proton multiplet at $\delta$ 7.41–8.80 (aromatic), and a one-proton doublet of multiplets centered at $\delta$ 9.25 (pyridyl H $\alpha$ to N$^+$). Esterification of **6a** with methanol gave **7**. Treatment of **6a** with 0.5 *N* sodium hydroxide for 5 min at 100° followed by neutralization to pH 6.7 produced the *trans*-cinnamic acid (**8**), which in turn was catalytically reduced to **9**. Cinnamic acid (**8**), incidentally, was found to undergo cyclization to regenerate **6**-type products with particular ease. Its hydrochloride reverted without melting within 2 min at 175° to **6a** ($X^-$ = $Cl^-$), and **7** was isolated following an attempted quaternization of **8** using 1 molar equiv of methyl *p*-toluenesulfonate in refluxing acetonitrile.

Similar fragmentations to **6**- and/or **5**-type products also resulted when the 11-methyl and 11-phenyl adducts, **2b** and **2c**, respectively, were treated with refluxing 6 *N* hydrochloric acid, although, as indicated by the yield data accompanying eq 4, the product distribution showed a considerable dependence on the nature of the R group at C-11.

A reasonable mechanism which will explain these results involves two competitive fragmentations of the intermediate bicyclic ketone **4**. As suggested earlier, **4** may cleave by an elimination sequence to give naphthol **5** (eq 3). Alternatively, **4** may suffer fragmentation by acid-catalyzed hydration of its carbonyl to give a 12,12-diol and cleavage of the 9,12 bond (eq 5). This

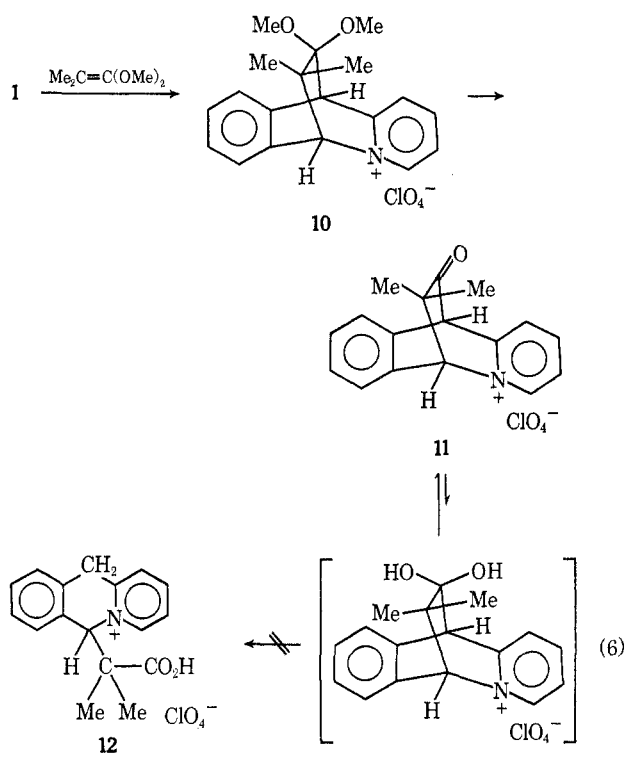


(5)

suggests that increasing the steric requirement of the R group at C-11 might well disfavor the production of **6**, since this would further enhance unfavorable steric interaction between the R group and the neighboring 12-hydroxyl groups, which are being held in an eclipsed conformation. This may at least partially account for the variation in yield of **6** from 84% when R = H (**6a**) to 32% when R = $CH_3$ (**6b**), and the concomitant increase in naphthol from 9 to 58% for **5a** and **5b**, respectively. On the other hand, if the enol of eq 3 plays an important role in the formation of the naphthol, then 11-phenyl substitution should favor naphthol formation owing to conjugative stabilization of the enol, as well as the aforementioned steric eclipsing effect. Experimentally, the fragmentation was considerably slower when R = $C_6H_5$ than when R = H or $CH_3$, and afforded, after 0.5-hr reflux in 6 *N* hydrochloric acid, naphthol **5c** and uncleaved **4c** in 80 and

15% yields, respectively, while **6c**, if formed, was not detected.

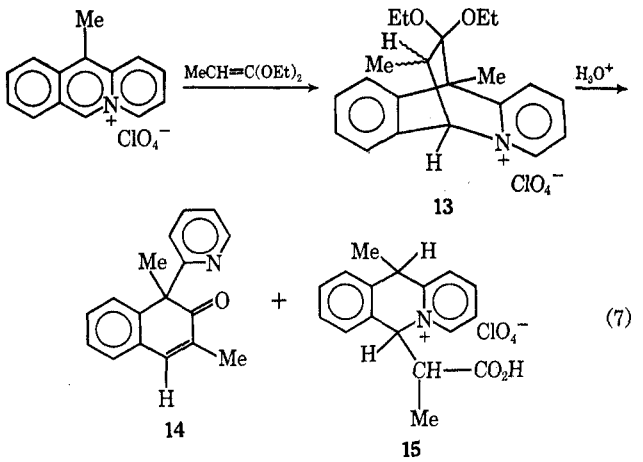
Introduction of two alkyl substituents at C-11 will, of course, prevent naphthol formation, and an eq 5 type of cleavage would also be expected to be more difficult to effect based on steric considerations. This was substantiated in that bicyclo ketone **11** (eq 6), produced by heating for 0.5 hr at reflux a mixture of **10** and 6 *N* hydrochloric acid, proved to be completely stable to prolonged treatment (4 hr) under those same conditions. The steric strain inherent in the eclipsed geminal methyl–geminal hydroxyl intermediate leading to **12** should be reflected in a higher energy barrier for an **11** → **12** transformation than is encountered in the successful eq 5 type fragmentation of **4a** and **4b**, and it is evidently sufficient to prevent this type of cleavage under our reaction conditions. Ketal **10** has a similar eclipsed conformation, and indeed the Diels–Alder reaction that produced it was very sluggish compared with those involving less highly substituted ketene acetals.



(6)

One other question briefly examined was whether or not the formation of an aromatic product, *i.e.*, naphthol **5**, provided the sole driving force for the elimination reaction. To this end adduct **13** was treated with 6 *N* hydrochloric acid for 1 hr at reflux temperature. A small amount (4%) of cyclic $\alpha,\beta$-unsaturated ketone **14** was isolated in addition to **15** (89%) (eq 7).

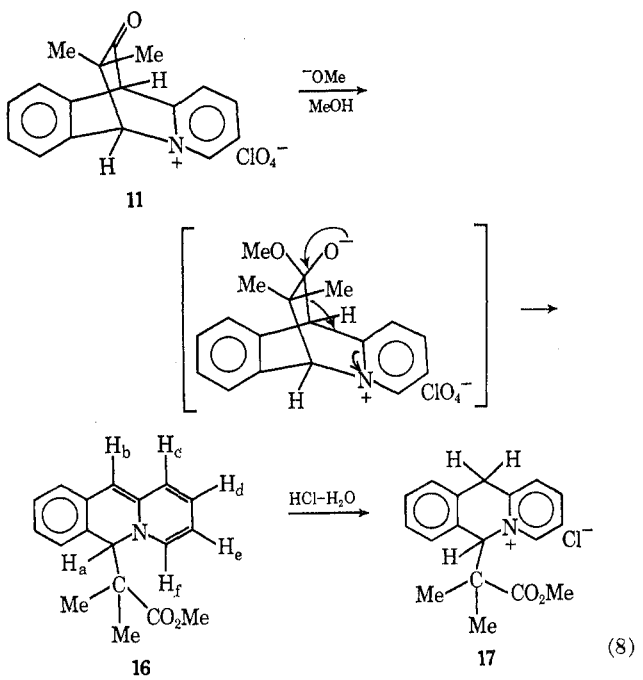
**Base Cleavages.**—While our original hydrolysis experiments with **2a–2c** in refluxing 6 *N* hydrochloric acid resulted primarily in the fragmentation of initially formed **4a–4c**, these ketones were later obtained by employing milder hydrolysis conditions. We were thus able to examine their chemical behavior under basic conditions as well. The most obvious difference in behavior is that there is a much greater tendency to



(7)

fragment by cleavage of the 9,12 carbon–carbon bond than is operative under acidic conditions.

Our best demonstration of this was observed starting with bicyclic ketone **11**. Although **11** is stable to refluxing 6 *N* hydrochloric acid, it suffered immediate ring opening upon treatment with methanolic sodium methoxide at room temperature to give the red, crystalline anhydro base **16** (eq 8). Acidification of **16** with dilute hydrochloric acid produced pyridinium salt **17**.

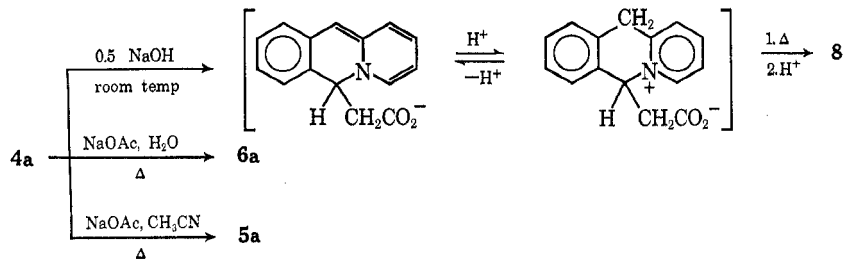


(8)

Incidentally, the fact that **16** and **17** were derived from **11** provides chemical proof that the cycloaddition of 1,1-diethoxy-2-methylpropene with **1** occurred, giving the structure depicted for **10**. The method used in elucidating the structure of **2a–2c** and **13**, based on noting in their nmr spectra the multiplicities of the bridgehead hydrogens, was inapplicable to **10**, since there are no spin-coupling possibilities for either of its bridgehead hydrogens.

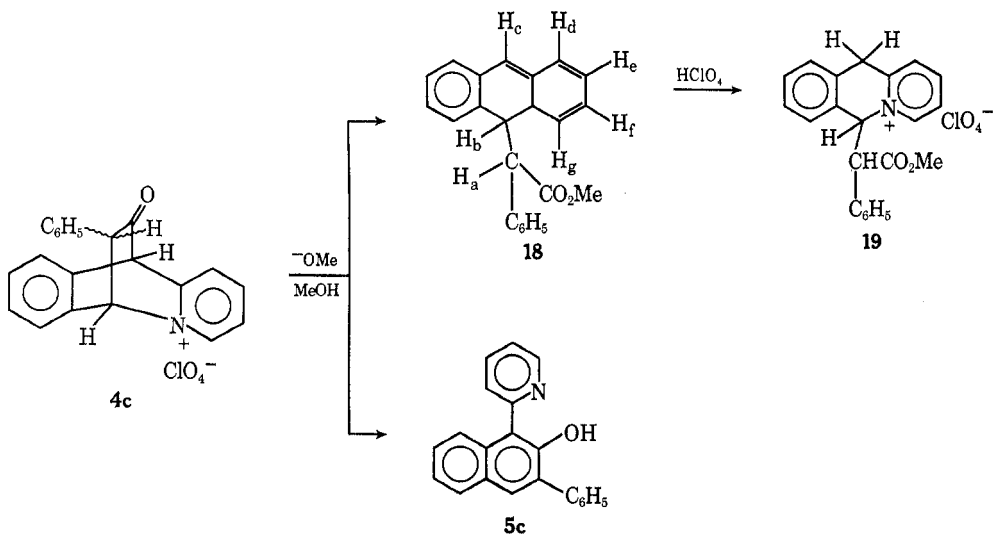
Cleavage of **4c** with methanolic sodium methoxide also occurred rapidly at room temperature to give anhydro base **18** and naphthol **5c** in 70 and 10% yields,

SCHEME II




respectively. This result also provides an interesting contrast to the incomplete fragmentation of **4c** by 6 *N* hydrochloric acid, which proceeded slowly even at 100° and gave only naphthol **5c**.

at room temperature by the very reactive potassium *t*-butoxide–water (10:3)–dimethyl sulfoxide reagent recently described by Gassman and coworkers.[2] However, this fragmentation was only two-thirds complete

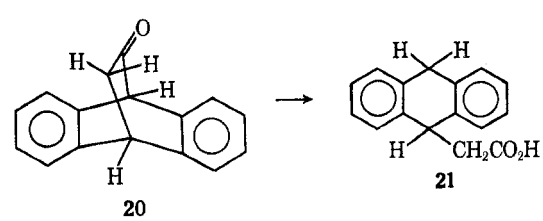



(9)

Weaker bases, including aqueous sodium hydroxide and even sodium acetate solutions, will produce these same types of results (see Scheme II). Treatment of **4a** with 0.5 *N* sodium hydroxide at room temperature immediately gave a blood-red solution characteristic of anhydro bases. This discolored to a pink solution upon warming, and afforded cinnamic acid **8** upon work-up of the reaction mixture. One molar sodium acetate solution, adequate for the cleavage reaction but not a strong enough base to effect a similar elimination, gave **6a** rather than **8** in 97% yield within 3 min at 100°.

Interestingly, since **6a** cannot be produced from **4a** under aprotic conditions, heating **4a** in a solvent such as acetonitrile or diglyme in the presence of anhydrous sodium acetate afforded naphthol **5a** in greater than 75% yield within 3 min at 80°, and the acetyl derivative of **5a** in quantitative yield within 3 min in refluxing acetic anhydride.

Undoubtedly, the extraordinary ease of cleavage of the 9,12 carbon–carbon bond of 9,10-dihydro-12-oxo-4a-azonia-9,10-ethanoanthracene salts such as **4a** by acidic and basic reagents is directly related to the ability of the pyridinium ring to stabilize a developing negative charge at C-9. A comparison of the ease of base cleavage of **20**, the hydrocarbon analog of **4a**, with cleavage results just cited for **4a** further emphasizes this fact. Ketone **20** was cleaved to **21** within 30 min after a 1-hr reflux period in the presence of sodium hydroxide in a diglyme–water mixture, and failed to




occur at all in the presence of either refluxing methanolic sodium methoxide or 6 *N* hydrochloric acid–diglyme solutions.

## Experimental Section[3]

**9,10-Dihydro-12-oxo-4a-azonia-9,10-ethanoanthracene Perchlorate (4a).**—A heterogeneous mixture of **2a** ($X^- = ClO_4^-$

(2) P. G. Gassman, J. T. Lumb, and F. V. Zalar, *J. Amer. Chem. Soc.*, **89**, 946 (1967).

(3) Melting points (uncorrected) were determined on a Thomas–Hoover apparatus. Ultraviolet absorption spectra were recorded on a Perkin-Elmer Model 202 spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrometer. Nmr spectra were determined with a Varian A-60 spectrometer on samples, unless otherwise stated, in dimethyl sulfoxide-$d_6$ solution with tetramethylsilane (TMS) as internal standard. Chemical shifts are recorded as parts per million to lower field from TMS ($\delta$ 0), followed by multiplicity, relative area, and assignment.

$^3/_4H_2O$)[1] (10.0 g, 0.0245 mol) in 40 ml of 6 *N* hydrochloric acid was allowed to shake for 3 hr at room temperature on a wrist-action shaker. A first crop of product (3.90 g) was collected by filtration and 3.50 g of additional crystalline product was obtained after diluting the filtrate with 40 ml of cold water and then treating it with solid sodium perchlorate. The combined product was washed with 5% sodium bicarbonate, dried, and then recrystallized from acetonitrile–ether as white needles, which proved to be an acetonitrile solvate of **4a**: mp 78–81°; ir 1740 $cm^{-1}$ (C=O); nmr $\delta$ 2.10 (s, 3, $CH_3CN$), 3.00 (m, 2, C-11 methylene), 5.90 (s, 1, 9-bridgehead proton), 6.98 (broadened t, 1, 10-bridgehead proton), 7.45–9.03 (m, 7, aromatic H), and 9.45 (d, 1, pyridyl H $\alpha$ to $N^+$). This spectrum changed within 20 hr at room temperature to that of the ring-opened **6a**, after treatment of the sample in the nmr tube with a few drops of $D_2O$ and 2 drops of 35% DCl.

*Anal.* Calcd for $C_{15}H_{12}ClNO_5 \cdot CH_3CN$: C, 56.3; H, 4.1; Cl, 9.8; N, 7.7. Found: C, 56.5; H, 4.0; Cl, 9.6; N, 7.5.

**9,10-Dihydro-12-oxo-11-phenyl-4a-azonia-9,10-ethanoanthracene perchlorate** (**4c**), mp 201–203°, was prepared in similar manner in 93% yield by treating 8.00 g of **2c**[1] with 75 ml of 6 *N* hydrochloric acid for 18 hr at room temperature on a wrist-action shaker. It was obtained as white needles after one recrystallization from nitromethane–ether: ir 1745 $cm^{-1}$ (C=O); nmr $\delta$ 4.62 (s, 1, C-9 bridgehead), 6.10 (d, 1, C-10 bridgehead), 6.50–6.75 (m, 2, *ortho* hydrogens of 11-phenyl), 6.95 (d, 1, C-11 H), 7.18–8.77 (m, 1, aromatic H), and 9.34 (d, 1, H $\alpha$ to $N^+$).

*Anal.* Calcd for $C_{21}H_{16}ClNO_5$: C, 63.4; H, 4.0; Cl, 8.9; N, 3.5. Found: C, 63.0; H, 4.0; Cl, 9.3; N, 3.7.

**Acid Cleavages of 2a–2c to 5- and 6-Type Products.**—In a typical experiment a mixture of **2a** ($X^- = ClO_4^- \cdot {}^3/_4H_2O$) (5.00 g, 0.0123 mol) in 6 *N* hydrochloric acid was refluxed for 0.5 hr and the solution was then concentrated *in vacuo* to give a crystalline solid. The solid was dissolved in a mixture of 200 ml of 5% aqueous sodium bicarbonate solution and 100 ml of ether and the two layers were separated. The aqueous layer was acidified with concentrated hydrochloric acid and then treated with solid sodium perchlorate to yield 3.40 g (84%) of **6a**. An analytical sample melted at 201–203° after one recrystallization from water.

*Anal.* Calcd for $C_{15}H_{14}ClNO_6$: C, 53.0; H, 4.1; Cl, 10.4; N, 4.1; neut equiv, 340. Found: C, 53.1; H, 4.5; Cl, 10.3; N, 4.0; neut equiv, 336.

Concentration of the ether extract and recrystallization of the residue from methanol–water furnished 0.24 g (9%) of $\beta$-naphthol **5a** as white needles: mp 139–140°; uv max ($CH_3CN$) 228 m$\mu$ (log $\epsilon$ 4.88), 300 (sh, 3.83), 310 (383), and 349 (3.87); mass spectrum (70 eV) *m/e* 221 $(M)^+$, 220 $[(M - H)^+]$, and 192 $[(M - COH)^+]$.

*Anal.* Calcd for $C_{15}H_{11}NO$: C, 81.5; H, 5.0; N, 6.3. Found: C, 81.4; H, 4.8; N, 6.3.

Its O-acetyl derivative was obtained from ligroin (bp 60–90°): mp 113–114°; uv max ($CH_3CN$) 223 m$\mu$ (log $\epsilon$ 4.76), 270 (sh, 3.87), 279 (3.93), 287 (sh, 3.90), and 320 (3.10); ir 1750 $cm^{-1}$ (C=O); nmr ($CDCl_3$) $\delta$ 2.00 (s, 3, $-OCOCH_3$), 7.19–8.03 (m, 9, aromatic H), and 8.83 (doublet of multiplets, 1, pyridyl H $\alpha$ to N).

*Anal.* Calcd for $C_{17}H_{13}NO_2$: C, 77.8; H, 5.1; N, 5.3. Found: C, 78.1; H, 5.5; N, 5.2.

In similar manner acid cleavage of **2b** gave **6b** and **5b** in 32 and 58% yields, respectively, while **2c** afforded the naphthol **5c** in 80% yield, plus *ca.* a 15% yield of **4c**.

Pyridinium salt **6b** was recrystallized from acetonitrile–ether: mp 189–192°; nmr $\delta$ 1.08 (d, 3, methyl), 2.77–3.30 (m, 1, $>CHCO_2H$), 4.77 (s, 2, $\alpha$-picolinium methylene), 6.23 (d, 1, $>CHCHRCO_2H$), and 7.40–9.41 (m, 8, aromatic H).

*Anal.* Calcd for $C_{16}H_{16}ClNO_6$: C, 54.3; H, 4.5; Cl, 10.0; N, 4.0. Found: C, 54.3; H, 4.5; Cl, 10.3; N, 3.8.

**Naphthol 5b**, mp 62–64°, was obtained as yellow plates from petroleum ether: uv max ($CH_3CN$) 234 m$\mu$ (log $\epsilon$ 4.78), 310 (sh, 3.96), 318 (3.99), and 348 (3.91); nmr ($CDCl_3$) $\delta$ 2.40 (d, $J$ = 1 Hz, 3, 3-methyl, long-range spin coupled to C-4 hydrogen), and 6.90–8.60 (m, 9, aromatic H).

*Anal.* Calcd for $C_{16}H_{13}NO$: C, 81.7; H, 5.5; N, 6.0. Found: C, 81.4; H, 5.1; N, 6.2.

**Naphthol 5c** was recrystallized as yellow plates from methylcyclohexane, mp 111–115°.

*Anal.* Calcd for $C_{21}H_{15}NO$: C, 84.9; H, 5.1; N, 4.7. Found: C, 84.5; H, 5.0; N, 4.9.

**Methyl ester 7**, mp 158–160°, was prepared by adding 1.0 g of **6a** to a cooled mixture of 2 ml of thionyl chloride and 15 ml of methanol. The resulting solution was allowed to stand at room temperature for 1 hr, heated at reflux for 1 hr, and concentrated to dryness. The residue was recrystallized as white needles from water: ir 1740 $cm^{-1}$ (C=O); nmr $\delta$ 3.25 (4 peaks, 2, the center peaks of the AB part of ABX), 3.60 (s, 3, $OCH_3$), 4.77 (s, 2, $\alpha$-picolinium $CH_2$), 6.53 (t, 1, X part of ABX), and 7.37–9.34 (m, 8, aromatic H).

*Anal.* Calcd for $C_{16}H_{16}ClNO_6$: C, 54.3; H, 4.5; Cl, 10.0; N, 4.0. Found: C, 54.3; H, 4.9; Cl, 10.2; N, 3.9.

***trans*-Cinnamic Acid (8).**—The deep red solution initially formed upon dissolving **4a** (30.0 g, 0.11 mol) in 400 ml of 0.5 *N* sodium hydroxide solution discolored to a light pink during a 15-min reflux. Acidification of the solution to pH 6.7 with 0.5 *N* hydrochloric acid gave **8** as an oil, which crystallized upon scratching. The product was collected and recrystallized from acetone–water as white needles (14.8 g, 57%): mp 133–134.5°; nmr $\delta$ 4.27 (s, 2), 6.40 (d, 1, $J$ = 16 Hz), 7.65 (d, 1, $J$ = 16 Hz), 7.03–8.55 (m, 8), and one acidic proton, as shown by its rapid deuterium exchange.

*Anal.* Calcd for $C_{15}H_{13}NO_2$: C, 75.3; H, 5.4; N, 5.8; mol wt, 239. Found: C, 75.3; H, 5.8; N, 5.8; mol wt, 239.

Reduction of an ethanolic solution of **8** in a Parr hydrogenation apparatus in the presence of 5% palladium on charcoal gave **9**, mp 121–123° (monohydrate) after one recrystallization from water. Its ir and nmr spectra were consistent with the assigned structure.

*Anal.* Calcd for $C_{15}H_{15}NO_2 \cdot H_2O$: C, 74.7; H, 6.2; N, 5.8. Found: C, 74.4; H, 6.5; N, 5.9.

**9,12-Dihydro-12,12-dimethoxy-11,11-dimethyl-4a-azonia-9,10-ethanoanthracene Perchlorate** (**10**).—A mixture of 4a-azoniaanthracene perchlorate[4] (**1a**, $X^- = ClO_4^-$, 5.34 g, 0.019 mol) and 1,1-dimethoxy-2-methylpropene[5] (20.0 g, 0.185 mol) in 50 ml of acetonitrile slowly reacted while shaking for 18 hr on a wrist-action shaker. The product (6.45 g, 85%) was precipitated by the addition of ether–ligroin (1:1, v/v) and recrystallized as white needles from water: mp 229–232°; nmr $\delta$ 0.90 (s, 6, C-11 methyls), 3.25 (s, 3, C-12 methoxyl), 3.30 (s, 3, C-12 methoxyl), 5.64 (s, 1, C-9 bridgehead proton), 6.17 (s, 1, C-10 bridgehead proton), and 7.37–9.41 (m, 8, aromatic H).

*Anal.* Calcd for $C_{19}H_{22}ClNO_6$: C, 57.7; H, 5.6; Cl, 9.0; N, 3.5. Found: C, 57.9; H, 5.3; Cl, 9.0; N, 3.5.

**9,10-Dihydro-11,11-dimethyl-12-oxo-4a-azonia-9,10-ethanoanthracene perchlorate** (**11**), mp 268–269° dec, was isolated as white needles in 87% yield after heating under reflux a mixture of **9** (3.50 g, 0.089 mol) in 50 ml of 6 *N* hydrochloric acid for 4 hr, followed by refrigeration of the mixture for 1 hr at 5°: ir 1740 $cm^{-1}$ (C=O); nmr $\delta$ 0.90 (s, 3, C-11 methyl), 0.97 (s, 3, C-11 methyl), 5.97 (s, 1, C-9 bridgehead proton), 6.75 (s, 1, C-10 bridgehead proton), 7.50–8.97 (m, 7, aromatic H), and 9.47 (d, 1, pyridyl proton $\alpha$ to $N^+$).

*Anal.* Calcd for $C_{17}H_{16}ClNO_5$: C, 58.4; H, 4.6; Cl, 10.2; N, 4.1. Found: C, 58.2; H, 4.7; Cl, 10.1; N, 3.9.

**9,10-Dihydro-9,11-dimethyl-12,12-diethoxy-4a-azonia-9,10-ethanoanthracene perchlorate** (**13**), mp 165–171°, was prepared in 94% yield by the Diels–Alder addition of 1,1-diethoxypropene[5] with 9-methyl-4a-azoniaanthracene perchlorate[6] following a previously described procedure.[1]

*Anal.* Calcd for $C_{21}H_{26}ClNO_6$: C, 59.5; H, 6.1; Cl, 8.2; N, 3.3. Found: C, 59.9; H, 6.1; Cl, 8.4; N, 3.1.

**Acid Cleavage of 13 to 14 and 15.**—A solution of adduct **13** (4.00 g, 0.0095 mol) in 30 ml of 6 *N* hydrochloric acid was heated under reflux for 1 hr and then concentrated under reduced pressure to a crystalline solid. This residue was dissolved in a mixture of 200 ml of 5% aqueous sodium bicarbonate solution and 100 ml of ether. The aqueous layer was separated, acidified with concentrated hydrochloric acid, and treated with sodium perchlorate to give 3.08 g (89%) of crystalline **15**. Recrystallization from water gave white needles: mp 186–189°; ir 1710 $cm^{-1}$ (C=O); nmr $\delta$ 1.08 (d, 3, C-9 $CH_3$), 1.92 [broadened d, 3, $-HC(CH_3)CO_2H$], 2.81–3.53 (m, 1, $>CHCO_2H$), 4.57–5.10 (m, 1, C-9), 6.30 (broadened d, 1, C-10), and 7.34–9.50 (m, 8, aromatic H).

---

(4) C. K. Bradsher and L. E. Beavers, *J. Amer. Chem. Soc.*, **77**, 4812 (1955).

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

(6) C. K. Bradsher and T. W. G. Solomons, *ibid.*, **81**, 2550 (1959).

*Anal.* Calcd for $C_{17}H_{18}ClNO_6$: C, 55.5; H, 4.9; N, 3.8. Found: C, 54.9; H, 4.8; N, 3.6.

The ether extract was concentrated to a syrup, which subsequently crystallized. Recrystallization from methanol–water afforded 0.10 g (4%) of **14** as long, white needles: mp 99.5–100.5°; ir 1630 $cm^{-1}$ (C=O); nmr $\delta$ 1.85 (s, 3 H), 2.01 (s, 3 H), 6.67–7.50 (m, 8, aromatic and olefinic protons), and 9.32 (doublet of multiplets, 1, pyridyl H $\alpha$ to N).

*Anal.* Calcd for $C_{17}H_{15}NO$: C, 82.0; H, 6.4; N, 5.6. Found: C, 81.7; H, 5.9; N, 5.7.

**Base Cleavages of Bicyclic Ketones. A. Cleavage of 11.**—The addition of sodium methoxide (0.40 g, 0.074 mol) to a suspension of **11** (0.70 g, 0.02 mol) in 10 ml of methanol gave immediately a red, crystalline precipitate. The mixture was diluted with 50 ml of water and filtered, and the product was recrystallized from acetone–water, giving 0.35 g (63%) of **16** as long, red needles: mp 104–106°; ir 1735 $cm^{-1}$ (C=O); nmr ($CDCl_3$) $\delta$ 1.12 and 1.22 (two s, 3 H each, *gem*-dimethyls), 3.65 (s, 3, ester methyl), 5.13 and 5.17 (two s, 1 H each, $H_a$ and $H_b$), 5.30–5.61 (m, 1, $H_e$), 6.18–6.33 (m, 2, $H_c$ and $H_d$), 6.50 (doublet of multiplets, 1, $H_f$), and 6.80–7.30 (m, 4, aromatic H).

*Anal.* Calcd for $C_{18}H_{19}NO_2 \cdot {}^1/_4H_2O$: C, 75.6; H, 6.7; N, 4.9. Found: C, 75.6; H, 6.8; N, 5.3.

The nmr spectrum of a sample of **16** in DMSO-$d_6$ and 3 drops of concentrated hydrochloric acid was completely consistent with structure **17**: $\delta$ 1.18 (s, 6, *gem*-dimethyl), 3.63 (s, 3, ester methyl), 4.70 (broadened s, 2, C-9 methylene), 6.55 (s, 1, C-10 H), 7.38–8.97 (m, 7, aromatic H), and 9.25 (d, 1, aromatic H $\alpha$ to $N^+$).

**B. Cleavage of 4c.**—Sodium methoxide (1.00 g, 0.0185 mol) added to a suspension of **4c** (2.00 g, 0.005 mol) in 10 ml of methanol immediately produced a red precipitate. The mixture was diluted with 15 ml of methanol–water (1:1, v/v) and filtered, and the residue (**18**) was air-dried and then recrystallized from ligroin (bp 60–90°) as red needles (1.02 g, 62%): mp 148–149°; uv max ($CH_3CN$) 238 m$\mu$ (log $\epsilon$ 4.37), 337 (sh, 3.28), 354 (3.60), 430 (4.16), 492 (3.76), and 522 (3.45); ir 1710 $cm^{-1}$ (C=O); nmr ($CDCl_3$) $\delta$ 3.41 (s, 3, ester methyl), 4.25 (d, 1, $J$ = 10 Hz, $H_a$), 4.73–5.00 (m, 1, $H_f$), 5.20 (broadened d, 1, $J$ = 10 Hz, $H_b$), 5.35 (s, 1, $H_c$), 5.69–6.25 (m, 3, $H_d$, $H_e$, $H_g$), and 6.87–7.57 (m, 4, aromatic H).

*Anal.* Calcd for $C_{22}H_{19}NO_2$: C, 80.2; H, 5.8; N, 4.3. Found: C, 79.9; H, 5.3; N, 4.3.

Acidification of a sample of **18** with dilute perchloric acid gave **19**, mp 202–206°, as white needles. Its nmr and elemental analyses were consistent with the assigned structure.

The aqueous filtrate from the initial cleavage reaction was acidified with 5% hydrochloric acid and then treated with 5% sodium bicarbonate to give an amorphous precipitate. Upon trituration in methanol this residue was converted into an off-white, crystalline product (0.15 g, 10%), which was identical in all respects with authentic 3-phenyl-1-(2-pyridyl)-2-naphthol (**5c**).

**C. Cleavages of 4a (See Scheme II).**—Heating under reflux a solution of **4a** ($X^-$ = $ClO_4^-$, $\cdot CH_3CN$) (1.00 g, 0.0275 mol) in 50 ml of 0.5 *N* sodium hydroxide for 5 min transformed the initial deep red solution to a light pink one. Its neutralization to pH 6.7 gave **8** in 58% yield.

A mixture of 1.00 g of **4a**, 0.30 g of sodium acetate, and 10 ml of water was heated under reflux for 3 min, acidified with 5% hydrochloric acid, and treated with sodium perchlorate to give 0.88 g (97%) of **6a**.

Similarly, a mixture of 1.00 g of **4a**, 0.30 g of sodium acetate, and 10 ml of acetonitrile was heated under reflux for 3 min and then diluted with 50 ml of water to give **5a** in 75% yield.

**D. Cleavage of 20.**—A solution consisting of **20**[7] (2.00 g, 0.09 mol), potassium *t*-butoxide (3.00 g), 35 ml of dry methyl sulfoxide, and 0.35 ml of water was placed under nitrogen and allowed to stand at room temperature for 30 min. The red solution was acidified with 5% hydrochloric acid, producing a yellow, crystalline precipitate. This product was collected by filtration, dissolved in 5% sodium bicarbonate, and filtered, and the filtrate was again acidified with 5% hydrochloric acid, giving 1.91 g (88%) of off-white, crystalline **21**. An analytical sample, mp 159–168°, was obtained after one recrystallization from methylcyclohexane: nmr ($CDCl_3$) $\delta$ 2.61 (d, 2, $J$ = 7 Hz, $-CH_2CO_2H$), 3.97 (d, 2, $Ar_2CH_2$), 4.50 (t, 1, $J$ = 7 Hz, $>CHCH_2CO_2H$), and 11.57 (s, 1, $-CO_2H$).

*Anal.* Calcd for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9. Found: C, 80.8; H, 5.9.

**Registry No.**—**4a**, 23825-07-2; **4c**, 23825-08-3; **5a**, 23825-09-4; **5a** O-acetyl derivative, 23825-10-7; **5b**, 23825-11-8; **5c**, 23825-12-9; **6a**, 23825-13-0; **6b**, 23825-14-1; **7**, 23825-15-2; **8**, 23825-16-3; **9**, 23825-17-4; **10**, 23796-76-1; **11**, 23825-18-5; **14**, 23796-77-2; **15**, 23825-19-6; **16**, 23825-20-9; **17**, 23825-21-0; **18**, 23825-22-1; **19**, 23825-23-2; **21**, 23825-24-3.

**Acknowledgments.**—The authors wish to thank Dr. J. B. Miller for helpful discussions, Mrs. Jean C. Dignan for technical assistance, and Mr. D. P. Maier for mass spectral interpretations.

(7) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).