Azonia Polycyclic Quinones, *o*-Diazo-Oxides and Related Products

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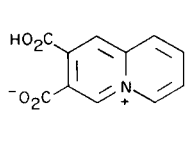
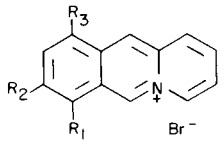
4*a*-Azoniaanthracene-5,6- and 5,8-dione salts have been prepared by nitric acid oxidation of their respective diols, and are shown to function as either an electrophilic dienophile or a diene component in Diels-Alder-type reactions. Several azonia *o*-quinones have been treated with tosylhydrazine in methanol saturated with hydrogen chloride to give unusually stable *o*-diazo-oxides. A four-step dehydroxylation procedure is detailed for the conversion of 5,6-dihydroxy-4*a*-azoniaanthracene salts to new 5-hydroxy-4*a*-azoniaanthracene salts.

Bradsher and Barker (1) obtained betaine I as the only isolable product following the nitric acid oxidation of dimethoxy-4*a*-azoniaanthracene salts IIa and IIb. We have described (2) the preparation of dihydroxy derivatives IIc, IId, and IIe. These and several other new diols have now



I



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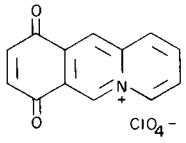
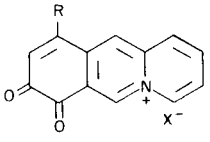


III

a: R_1, R_3 OMe, R_2 H
b: R_1, R_2 OMe, R_3 H
c: R_1, R_3 OH, R_2 H
d: R_1, R_2 OH, R_3 H
e: R_1, R_2 OH, R_3 C_6H_5



IV

a: R H
b: R C_6H_5

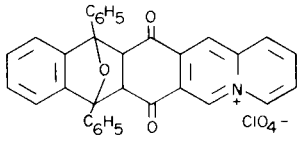
been converted to their respective azoniaanthraquinones, III and IV, under reaction conditions mild enough to negate similar ring degradation. The chemistry of azoniaanthraquinones has been examined with particular emphasis on their Diels-Alder reactivity and on the chemistry of the *o*-diazo-oxides derived from quinone IV.

Results and Discussion.

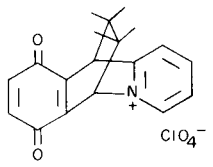
Oxidation of IIc, IId, and IIe to quinones III, IVa, and IVb, respectively, was accomplished without difficulty by using nitric acid at room temperature (3). Their structural assignments are supported by elemental analyses (Table I, Experimental Section), spectral evidence, and their chemical behavior, described in the succeeding sections.

Diels-Alder Reactions.

A notable chemical property of azoniaanthraquinones III and IV is their ability to function both as an electrophilic dienophile in conventional Diels-Alder-type reactions, and as an electrophilic diene in Diels-Alder reactions obeying the principle of "inverse" electron demand (4). This is to say that while III, for example, readily reacts with 1,3-diphenylisobenzofuran to give V, it will also undergo a 4 + 2 cycloaddition with nucleophilic dienophiles to yield VI-type adducts.



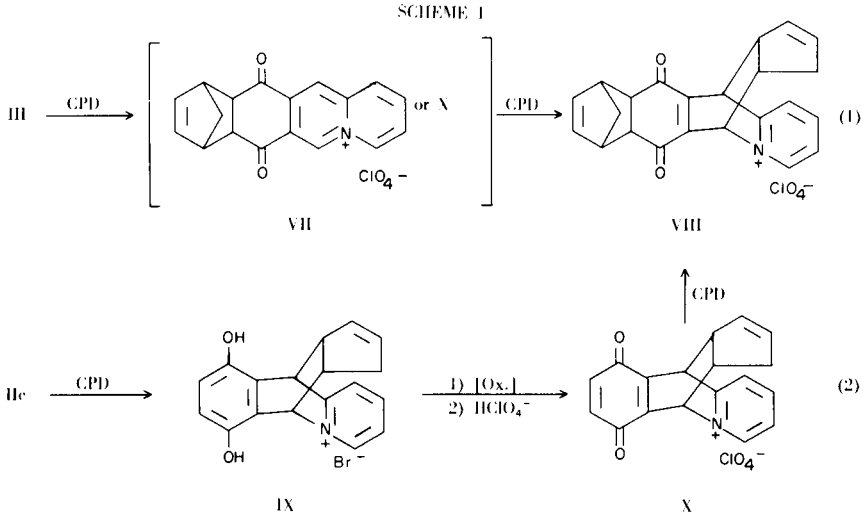
V



VI

An interesting illustration of this type of functional duality arises when III is treated with excess cyclopentadiene. The resulting product proved to be 2:1 adduct VIII, one to be expected since cyclopentadiene can itself serve very well as either nucleophilic diene or dienophile (5), and thus should further react with the initially formed 1:1 adduct, be it either VII or X, to produce VIII.

SCHEME I



The gross structure of VIII was established unequivocally by the independent synthesis shown in equation 2. In spite of the large number of isomer possibilities, authentic VIII thus prepared gave a superimposable x-ray powder diagram and identical ir, uv, and nmr spectra with those of VIII obtained by direct condensation depicted in equation 1. The question of which 1:1 adduct, VII or X, was the actual precursor to VIII was not answered. Our attempts to isolate such an intermediate 1:1 adduct by slow addition of the stoichiometric quantity of cyclopentadiene to III yielded only a mixture of III and VIII.

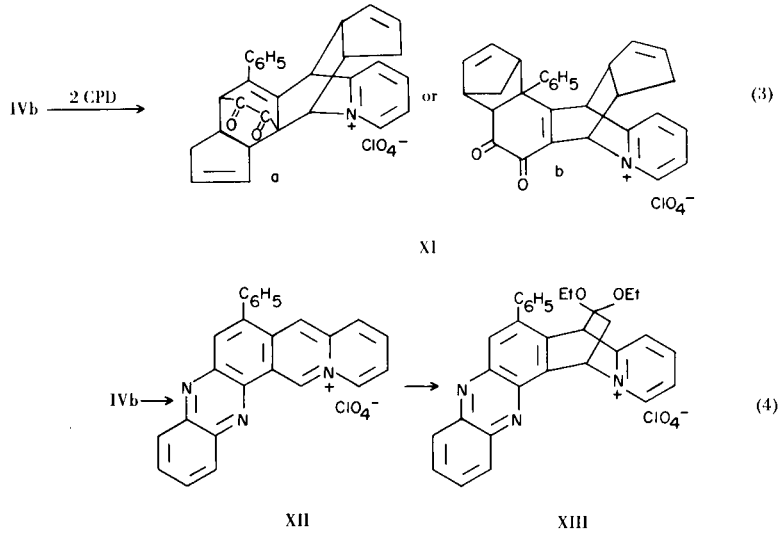
In an analogous study a 2:1 adduct was obtained in 91% yield by reaction of excess cyclopentadiene with *o*-quinone IVb ($X^- = ClO_4^-$). This adduct showed strong carbonyl absorption at 1749 cm^{-1} with a shoulder at 1735 cm^{-1} and no absorption in the 1660-1675 cm^{-1} region, which suggests XIa rather than XIb as a reasonable structure (6).

Carbonyl Reagents.

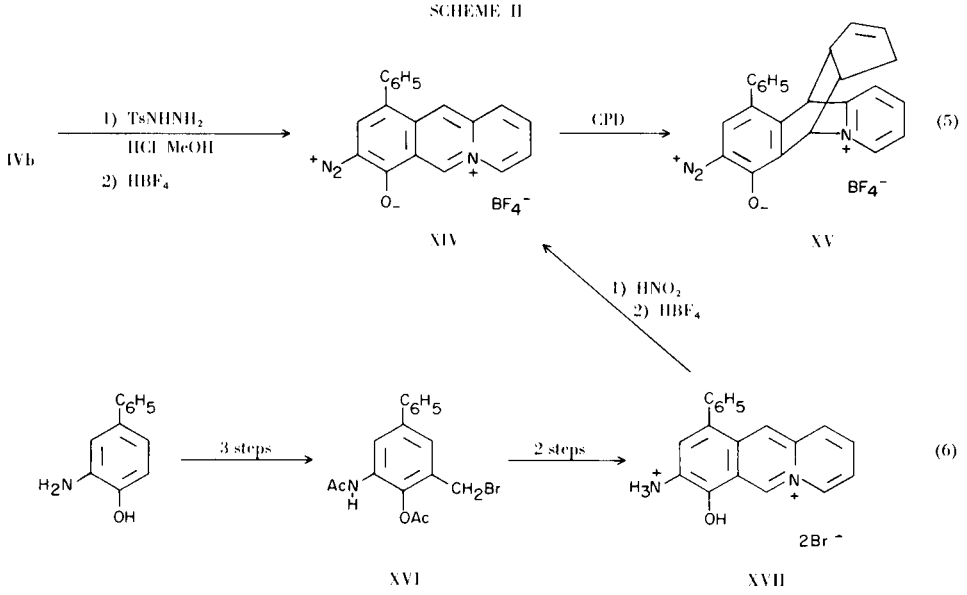
o-Quinones IVa and IVb have been treated with several conventional carbonyl reagents to provide new types of azonia polycyclic products, useful as starting materials in an associated study. A few illustrations of the types of products obtained are described in this section, using IVb as a representative starting material.

Quinoxaline XII is produced by the condensation of IVb with *o*-phenylenediamine, and readily participates in a stereospecific cycloaddition with ketene diethyl acetal (4a) to give XIII.

Reaction of IVb with *p*-toluenesulfonylhydrazine in a saturated methanolic hydrogen chloride solution gives an unstable monotosylhydrazone (7), which, even in the strong acid environment, converts by internal oxidation-reduction to *o*-diazo-oxide XIV. Structural proof of XIV



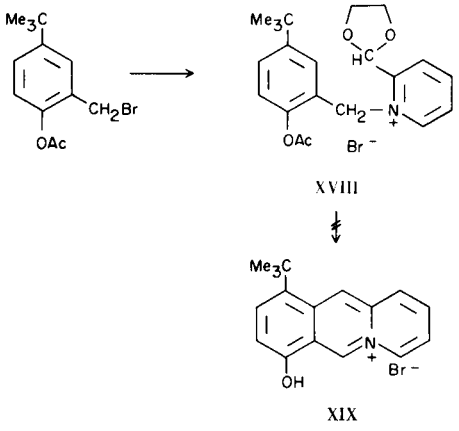
SCHEME II



as 6-diazo-5-oxo- rather than isomeric 5-diazo-6-oxo-8-phenyl-4*a*-azoniaanthracene ion was accomplished by independent synthesis outlined in equation 6, Scheme II (8).

While XIV shows the expected light sensitivity, it is unusually stable to thermal as well as strong acid treatment. For example, although XIV rather rapidly decomposes in boiling 48% hydrobromic acid to give 6-bromo-5-hydroxy-8-phenyl-4*a*-azoniaanthracene bromide, it has been partially recovered after being heated in the presence of concentrated hydrochloric acid for 15 minutes at reflux temperature. Interference with the resonance associated with the azoniaanthracene ring system reduces this stability, as substantiated by the fact that cyclopentadiene adduct XV is completely degraded within 3 minutes in refluxing ethanol or acetonitrile.

Of particular significance has been the application of some of this chemistry to the preparation of several new monohydroxy-substituted azoniapolycyclic salts, inaccessible by more conventional routes, and important to us in a different area of research. 8-*tert*-Butyl-5-hydroxy-4*a*-azoniaanthracene bromide (XIX) is one of these materials. Predictably, the Bradsher cyclodehydration procedure (9) failed when applied to pyridinium salt XVIII, the logical precursor to XIX, since acid-catalyzed cyclization of XVIII requires ring closure into a sterically hindered position, *meta* to the activating hydroxyl group generated during the reaction. The condensation occurred intermolecularly instead giving polymeric products. 8-*tert*-Butyl-5,6-dihydroxy-4*a*-azoniaanthracene bromide (XXII), on the other hand, was very easily obtained in good yield by cyclization of XXI. The 6-hydroxyl was then removed by the four-step sequence shown in Scheme III, to give XIX in 68% overall yield from XXII. The debromination of XXV



with triphenylphosphine (10) was unusually facile, being complete within 5 minutes in refluxing nitromethane.

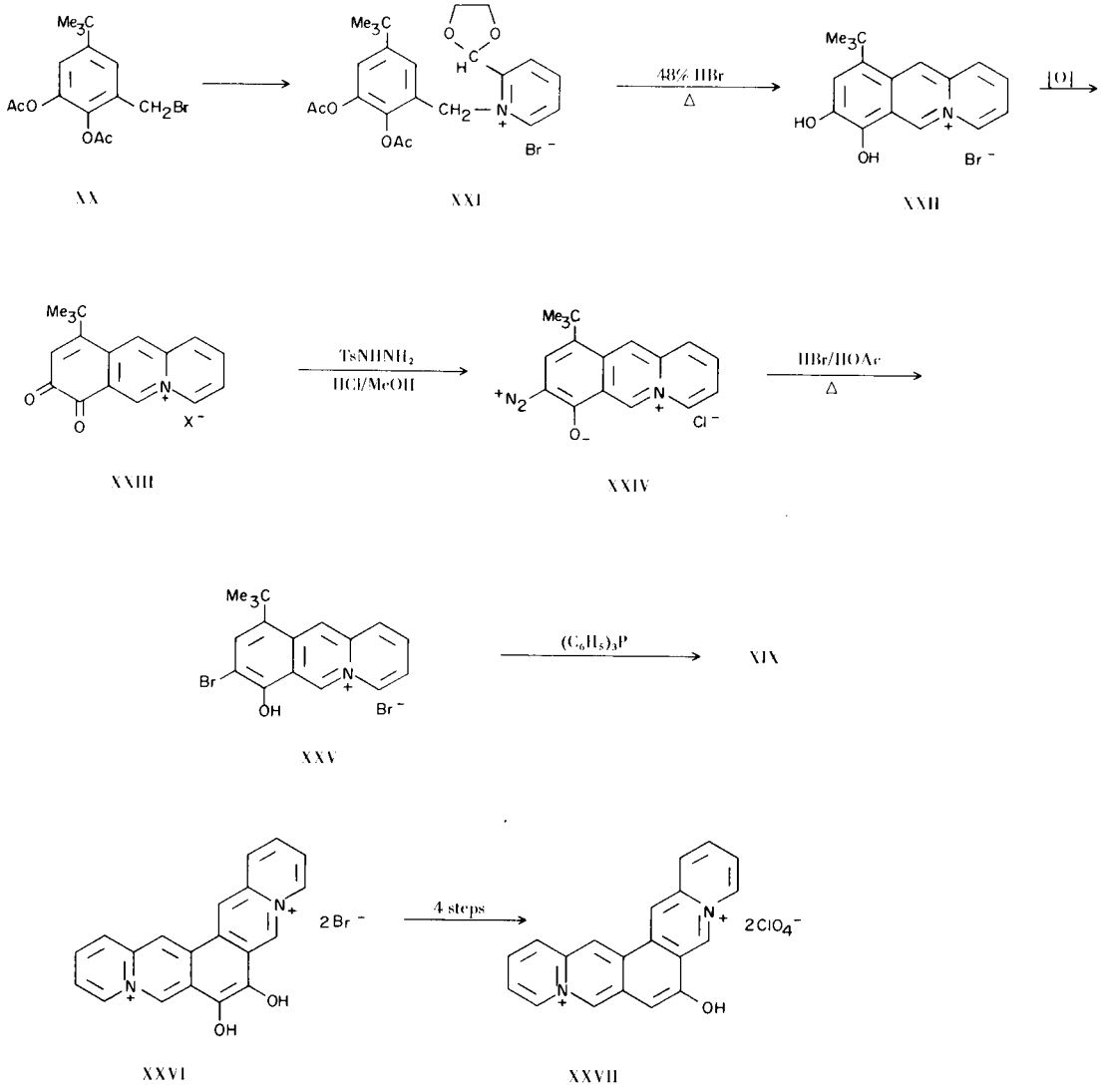
This dehydroxylation procedure has been successfully applied to several other *ortho*-substituted dihydroxy-azoniapolycyclics, including the conversion of XXVI → XXVII.

EXPERIMENTAL (11)

Azoniaanthraquinones (Table I).

As a representative example, 5,6-dihydroxy-8-phenyl-4*a*-azoniaanthracene bromide hemihydrate (IIe) (2) was oxidized by dropwise addition of concentrated nitric acid to the dry starting material until the red diol was completely converted to yellow quinone. The mixture was diluted with 50 ml. of ethanol and then 200 ml. of ether. The resulting crystals (IVb, $X^- = NO_3^-$) were collected, dissolved in 200 ml. of warm water, and treated with a saturated sodium perchlorate solution. Perchlorate salt, IVb, $X^- = ClO_4^-$, crystallized, was collected, dried and recrystallized as yellow needles (4.3 g., 84%) from acetonitrile-ether.

SCHEME III



7,12-Epoxy-6a,7,12,12a-tetrahydro-6,13-dioxo-7,12-diphenyl-4*a*-azoniapentacene Perchlorate (V).

To a solution of 1.6 g. (0.005 mole) of III in 50 ml. of acetonitrile was added 1.4 g. (0.005 mole) of 1,3-diphenylisobenzofuran, with stirring. The furan slowly dissolved. After 75 minutes, the mixture was diluted to 500 ml. with ether; the product separated as pale yellow needles. One recrystallization from acetonitrile-ether gave an analytical sample, m.p. 156-160° dec.; uv max (acetonitrile) 248 mμ (log ε 4.67), 310 (3.96), 327 (3.96), 388 (4.35), 412 (4.32).

Anal. Calcd. for $C_{33}H_{22}ClNO_7$: C, 68.3; H, 3.8; Cl, 6.1; N, 2.4. Found: C, 68.4; H, 3.6; Cl, 5.8; N, 2.1.

Adduct VIII from III and Cyclopentadiene.

To 3.1 g. (0.01 mole) of III suspended in 25 ml. of acetonitrile was added 1.4 g. (0.02 mole) of cyclopentadiene in 10 ml. of acetonitrile. Complete solution was obtained after the mixture had been stirred for 15 minutes. The resulting 2:1 adduct, VIII (3.6 g., 82%), was precipitated as tan needles by diluting the solution with ether. After recrystallization from water acidified with perchloric acid, VIII had m.p. 186-195° dec.; uv max (acetonitrile) 243 mμ (log ε 3.97), 272 (3.76); ir 1664 and 1685 cm^{-1} (C=O); nmr δ 1.20-2.00 (m, 3), 3.00-3.60 (m, 6, allylic), 5.30 (d, 1, α-picolinium bridgehead proton), 5.38-5.83 (m, 4, olefinic), 6.55 (d, 1, bridgehead proton α to N^+), 7.60-8.83 (m, 3, aromatic), 9.21-9.41 (doublet of multiplets, 1, pyridyl H α to N^+).

Anal. Calcd. for $C_{23}H_{20}ClNO_6$: C, 62.4; H, 4.5; Cl, 8.0; N, 3.2. Found: C, 62.6; H, 4.4; Cl, 8.2; N, 3.5.

Adduct VIII *via* IX and X.

Following a previously described procedure (4a), diol IX was obtained in 93% yield by shaking for 3 hours on a wrist-action shaker a mixture of IIc and three-fold molar excess of cyclopentadiene in acetonitrile. It was recrystallized from water as long white needles, m.p. >300°.

Anal. Calcd. for $C_{18}H_{16}BrNO_2$: C, 60.3; H, 4.5; N, 3.9. Found: C, 60.2; H, 4.3; N, 3.9.

TABLE I

Azoniaanthraquinone Salts

Quinone	Yield, %	M.p., °C	Ultraviolet CH_3CN λ max	(log ε)	Analyses, % Calcd. C	H	N	Found C	H	N
III (a)	70	192 (dec)	240 mμ	(4.34)	47.7	3.1	4.3	47.5	2.6	4.3
			358	(3.90)						
IVa (b)	65	180 (dec)	254	(4.31)	50.4	2.6	4.5	50.8	3.0	4.6
			302	(3.90)						
			314	(3.92)						
			397	(4.10)						
IVb (b)	84	305 (dec)	245 sh	(4.33)	59.1	3.1	3.6	59.4	2.9	3.8
			356	(4.12)						
			372	(4.16)						
			405	(3.85)						
XXIII (c)	86	292 (dec)	262	(4.45)	57.8	4.6	4.0	57.7	4.7	3.9
			303	(3.87)						
			316	(3.89)						
			400	(4.00)						

(a) H_2O. (b) $X^- = ClO_4^-$. (c) $X^- = BF_4^-$.

Nitric acid oxidation of IX gave X, which was isolated as its perchlorate salt and recrystallized as light yellow needles from water, m.p. 210° dec.; ir 1668 cm^{-1} with shoulder at 1678 cm^{-1} (C=O).

Anal. Calcd. for $C_{18}H_{14}ClNO_6 \cdot 0.25H_2O$: C, 56.8; H, 3.8; N, 3.7. Found: C, 56.9; H, 4.2; N, 3.8.

The product (VIII) obtained after treating IX in acetonitrile with cyclopentadiene was identical in every respect with that obtained from the reaction of III with cyclopentadiene, as described above.

Adduct XI from IVb and Cyclopentadiene.

A mixture of IVb ($X^- = ClO_4^-$, 4.20 g., 0.0011 mole), cyclopentadiene (4.0 g., 0.06 mole), and 150 ml. of nitromethane was allowed to stand at room temperature for 30 minutes and then was slowly diluted with 400 ml. of ether. The resulting crystals were collected and recrystallized from nitromethane-ether (5.14 g., 91%), m.p. 215° dec.; uv max (acetonitrile) 270 mμ (log ε 4.07); ir 1749 cm^{-1} with shoulder at 1735 cm^{-1} (C=O).

Anal. Calcd. for $C_{29}H_{24}ClNO_6 \cdot 0.5H_2O$: C, 66.1; H, 4.8; N, 2.7. Found: C, 66.3; H, 4.5; N, 2.5.

5,14-Diaza-7-phenyl-12*a*-azoniapentaphene Perchlorate (XII).

A mixture of quinone IVb ($X^- = ClO_4^-$, 8.0 g., 0.02 mole), *o*-phenylenediamine (3.0 g., 0.03 mole), and a few crystals of *p*-toluenesulfonic acid in 300 ml. of nitromethane was heated to reflux, cooled, and ether added to the point of incipient opalescence. The product crystallized as a hemihydrate and was recrystallized from nitromethane-ethyl acetate as fine yellow fluorescent needles (8.1 g., 89%), m.p. 330° dec.; uv max (acetonitrile) 248 mμ (log ε 4.62), 265 sh (4.53), 301 sh (4.45), 314 (4.46), 324 (4.46), 390 (4.12), 420 (4.39), 437 (4.47).

Anal. Calcd. for $C_{25}H_{16}ClN_3O_4 \cdot 0.5H_2O$: C, 64.4; H, 3.6; N, 9.0. Found: C, 64.4; H, 3.9; N, 9.2.

Adduct XIII.

This adduct was isolated in quantitative yield after treatment of an acetonitrile solution of XII with excess ketene diethyl acetal for 1 hour at room temperature, m.p. 188-189° with dec.; partial nmr δ 5.80 (s, 1, 8-bridgehead hydrogen).

Anal. Calcd. for $C_{31}H_{28}ClN_3O_6$: C, 64.9; H, 4.9; Cl, 6.2; N, 7.3. Found: C, 64.7; H, 4.7; Cl, 6.2; N, 6.9.

6-Diazo-5-oxo-8-phenyl-4*a*-azoniaanthracene Fluoroborate (XIV) (12).

A mixture of IVb ($X^- = NO_3^-$, 34.8 g., 0.1 mole) and *p*-toluenesulfonhydrazide (25 g., 0.13 mole) was dissolved in 100 ml. of methanol which had been saturated with hydrogen chloride. After standing at autogeneous temperature for 15 minutes, the red solution was diluted with 200 ml. of water and 50 ml. of 50% fluoroboric acid. A yellow crystalline product (26.1 g., 68%) immediately separated and was collected after refrigerating the reaction mixture for 2 hours at -20°. An analytical sample was recrystallized from acetonitrile-ether, m.p. 180-190° dec.; ir *ca.* 2160, 2180 cm^{-1} (diazo).

Anal. Calcd. for $C_{19}H_{12}BF_4N_3O$: C, 59.3; H, 3.1; N, 10.9. Found: C, 59.6; H, 3.5; N, 10.8.

Adduct XV.

A solution of XIV (11.6 g., 0.03 mole), cyclopentadiene (6.6 g., 0.1 mole), 100 ml. of nitromethane, and 100 ml. of acetonitrile was mechanically stirred for 0.5 hour and then slowly diluted to 300 ml. with ether. Adduct XV crystallized during this process as golden plates and was recrystallized as a trihydrate from nitromethane-ether which had been acidified with 50% fluoroboric acid, m.p. 159-185° dec.

Anal. Calcd. for $C_{24}H_{18}BF_4N_3O \cdot 3H_2O$: C, 57.1; H, 4.8; N, 8.3. Found: C, 57.3; H, 4.4; N, 8.4.

2-Acetamido-6-bromomethyl-4-phenylphenyl Acetate (XVI).

Following a previously described general procedure (13), a solution of 552 g. (3.0 moles) of 2-amino-4-phenylphenol and 536 g. (3.1 moles) of isobutoxymethylmorpholine in 3 liters of ethanol was refluxed for 2 hours. One-half of the solvent was stripped and the resulting solid was separated by filtration.

The solid was then refluxed with 3 liters of acetic anhydride for 1 hour, let stand at room temperature over the weekend, and was then refluxed for an additional hour. Stripping of the solvent left a residue of heavy oil.

The oil was dissolved in 500 ml. of methylene chloride and 2 liters of 40% hydrogen bromide in acetic acid was added. After the solution had stood overnight, two liters of acetic anhydride was added and the mixture was stripped of solvents until it turned solid. The solid was slurried in acetic acid, removed by filtration and washed with ether followed by ethanol. After drying, 604 g. (55% overall yield) of XVI was obtained, m.p. 203-207°.

Anal. Calcd. for $C_{17}H_{16}BrNO_3$: C, 56.4; H, 4.4; Br, 22.1. Found: C, 56.4; H, 4.5; Br, 21.9.

6-Ammonium-5-hydroxy-8-phenyl-4*a*-azoniaanthracene Dibromide (XVII).

The compound was prepared in 62% yield by the Bradsher cyclodehydration procedure involving refluxing for 20 minutes a mixture of the pyridinium salt, obtained from XVI and 2-(1,3-dioxolan-2-yl)pyridine (14), and 40% hydrobromic acid. An analytical sample was recrystallized from dilute hydrobromic acid, m.p. 168° dec.

Anal. Calcd. for $C_{19}H_{16}Br_2N_2O$: C, 50.8; H, 3.6; Br, 35.7; N, 6.2. Found: C, 50.8; H, 4.0; Br, 35.3; N, 6.0.

A solution of 5 g. of the above azonia compound in 100 ml. of 50% acetic acid was cooled below 5°. A half-saturated solution of sodium nitrite was added dropwise until starch-iodide paper indicated an excess. The addition of 100 ml. of water followed by 20 ml. of 40% fluoroboric acid gave 3.1 g. (74%) of 5-oxo-6-diazo-8-phenyl-4*a*-azoniaanthracene fluoroborate identical with that prepared from IVb and *p*-toluenesulfonhydrazide.

3-Bromomethyl-5-*tert*-butylcatechol Diacetate (XX).

Benzyl bromide XX was prepared following a previously described general procedure (12) in 70% overall yield starting with 4-*tert*-butylcatechol. The new products include:

5-*tert*-Butyl-3-morpholinomethylcatechol, m.p. 148-150° (from ethyl acetate).

Anal. Calcd. for $C_{15}H_{23}NO_3$: C, 68.0; H, 8.7; N, 5.3. Found: C, 67.7; H, 8.3; N, 5.2.

3-Acetoxymethyl-5-*tert*-butylcatechol diacetate, m.p. 91-93° (ethanol).

Anal. Calcd. for $C_{17}H_{22}O_6$: C, 63.4; H, 6.9. Found: C, 63.2; H, 6.8.

3-Bromomethyl-5-*tert*-butylcatechol diacetate (XX), m.p. 111-113° (cyclohexane).

Anal. Calcd. for $C_{15}H_{19}BrO_4$: C, 52.5; H, 5.5; Br, 23.2. Found: C, 52.9; H, 5.8; Br, 23.5.

8-*tert*-Butyl-5,6-dihydroxy-4*a*-azoniaanthracene Bromide (XXII).

The cyclization of pyridinium salt XXI, m.p. 154-155°, prepared in the usual manner, to red, crystalline XXII (81%) was complete within 0.5 hour in a refluxing 30% hydrogen bromide-acetic acid mixture, m.p. 300-305° (from methanol-ether).

Anal. Calcd. for $C_{17}H_{18}BrNO_2$: C, 58.8; H, 5.2; N, 4.0. Found: C, 58.7; H, 5.0; N, 3.9.

8-*tert*-Butyl-5-hydroxy-4*a*-azoniaanthracene Bromide (XIX).

Nitric acid oxidation of XXII to quinone XXIII ($X^- = NO_3^-$), m.p. 250° dec., and its conversion to diazo-oxide, XXIV, m.p. 127-131° dec., were effected by the procedures described in the above sections.

Anal. Calcd. for $C_{17}H_{16}ClN_3O$: C, 65.1; H, 5.1; Cl, 11.3; N, 13.4. Found: C, 64.7; H, 5.2; Cl, 11.2; N, 13.3.

Diazo-oxide XXIV (50 g., 0.16 mole) was added in portions, over a 10-minute period, to a boiling 30% hydrogen bromide-acetic acid mixture, producing an immediate evolution of nitrogen. When the gas evolution stopped, the mixture was cooled, and product XXV precipitated as yellow needles (54.0 g., 82%) on addition of ether.

For use in another study, a portion of XXV was acetylated with acetic anhydride-sulfuric acid and isolated as its perchlorate salt, m.p. 245°.

Anal. Calcd. for $C_{19}H_{19}BrClNO_6$: C, 48.3; H, 4.0; N, 3.0. Found: C, 48.7; H, 3.6; N, 2.8.

A mixture of 10 g. (0.024 mole) of XXV and 10 g. of triphenylphosphine in 200 ml. of nitromethane was held at reflux temperature for 5 minutes, cooled, and then slowly diluted with 1 liter of ether giving 7.90 g. (98%) of XIX as pale yellow needles.

Acetylation of XIX and ion exchange gave 5-acetoxy-8-*tert*-butyl-4*a*-azoniaanthracene perchlorate as golden yellow plates (acetonitrile-ether), m.p. 238-241°; uv max (acetonitrile) 253 mμ (log ε 4.81), 367 (4.10), 389 (3.98), 410 (3.89).

Anal. Calcd. for $C_{19}H_{20}ClNO_6$: C, 57.9; H, 5.1; Cl, 8.9; N, 3.6. Found: C, 57.8; H, 5.0; Cl, 8.8; N, 3.7.

6-Hydroxy-4*a*,8*a*-diazoniapentaphene Diperchlorate (XXVII).

In a similar manner, purple diol XXVI was oxidized with nitric acid to its yellow quinone dinitrate. A sample was converted to the diperchlorate salt for characterization purposes; uv max (acetonitrile) 276 mμ (log ε 4.61), 296 sh (3.97), 328 sh (3.76), 344 (4.05), 359 (3.22), 397 sh (4.25), 414 (4.33); ir 1720 cm^{-1} (C=O).

Anal. Calcd. for $C_{20}H_{12}Cl_2N_2O_{10}$: C, 47.0; H, 2.3; N, 5.5. Found: C, 46.8; H, 2.0; N, 5.4.

Quinoxaline derivative, uv max (acetonitrile) 247 mμ (log ε 4.62), 263 sh (4.53), 300 (4.44), 313 (4.46), 322 (4.46), 388 (4.11), 411 (4.39), 435 (4.46).

Anal. Calcd. for $C_{19}H_{12}ClN_3O_4$: C, 59.7; H, 3.1; N, 11.0. Found: C, 59.4; H, 3.5; N, 10.8.

The quinone dinitrate was then converted without difficulty to XXVII *via* diazo-oxide and bromo-hydroxy diazoniapentaphene intermediates. The product was isolated as its diperchlorate salt and crystallized from water acidified with perchloric acid as orange plates, m.p. > 300°; uv max (acetonitrile) 220 mμ (log ε 4.66), 256 (4.56), 292 (4.37), 358 (4.77), 380 (4.55), 467 (3.52).

Anal. Calcd. for $C_{20}H_{14}Cl_2N_2O_9$: C, 48.3; H, 2.8; Cl, 14.3; N, 5.6. Found: C, 48.3; H, 2.6; Cl, 14.4; N, 5.6.

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(11) 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 or Beckman IR-12 Spectrophotometer. 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 ppm to lower field from TMS (δ = 0).

(12) Caution: the perchlorate salts of azonia diazo-oxides usually are shock-sensitive.

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