Azonia Polycyclics from Hydroquinone and Catechols

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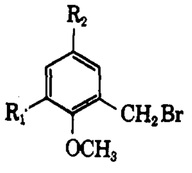
The syntheses of 5,6- and 5,8-dihydroxy-4a-azoniaanthracene bromides, 6,7-dihydroxy-4a,8a-diazoniapentaphene dibromide, and 7,8-dihydroxy-5a,9a-diazoniaheptaphene dibromide are described. The latter compound represents the first example of the diazoniaheptaphene ring system.

In the course of their studies on aromatic cyclodehydration reactions, Bradsher and co-workers have recently converted benzyl halides **1a** and **1b** into 5,8- and 5,6-dimethoxy-4a-azoniaanthracene bromides, **2a**[1] and **2b**,[2] respectively, by cyclizations of the intermediary pyridinium salts, **3a** and **3b**, in boiling 48% hydrobromic acid. The methoxyl groups withstood the hydrobromic acid treatment, and their one attempt to convert **2a** to **13** by ether cleavage was unsuccessful.



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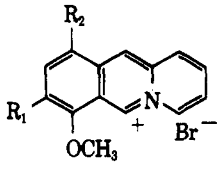

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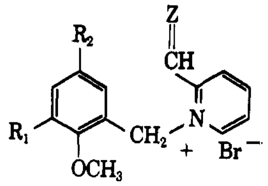

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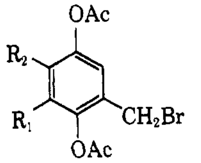
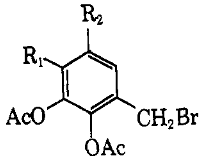
a, R_1 = H; R_2 = OCH_3
b, R_1 = OCH_3; R_2 = H; Z = O, NOH

We have recently described[3] a synthesis of acetylated bromomethylphenols which makes mono- and poly(bromomethyl)hydroquinone and catechol diacetates readily available. We report here the utilization of a number of these compounds (**4–9**) as precursors to dihydroxy azonia and dihydroxy- (or diketo-) diazonia polycyclics.

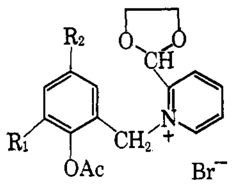


4, R_1, R_2 = H
5, R_1 = $BrCH_2$; R_2 = H
6, R_1 = H; R_2 = $BrCH_2$

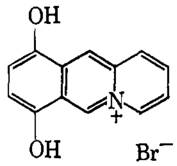


7, R_1, R_2 = H
8, R_1 = H; R_2 = C_6H_5
9, R_1 = $BrCH_2$; R_2 = H

Quaternization of 2-(1,3-dioxolan-2-yl)pyridine with bromides **4–9** was effected by refluxing a mixture of bromide and excess acetal in acetonitrile for 4–12 hr. The resulting pyridinium salt was then cyclized at reflux temperatures in either 48% hydrobromic acid or a 15–32% hydrogen bromide–acetic acid mixture, depending on the solubility of the final product. Thus, **10** and **11** derived from **4** and **7**, respectively, were cyclized in 15% hydrogen bromide–acetic acid to the corresponding dihydroxy-4a-azoniaanthracene bromides **13** and **14**. In both examples, crystallization commenced after the solution had refluxed for about 5 min., and afforded the product as nonfluorescent red needles in yields of 90–95% after a total reaction period of 30 min. 5,6-Dihydroxy-8-phenyl-4a-azoniaanthracene bromide (**15**), being less water-soluble, was obtained in 93% yield by employing 48% hydrobromic acid as the cyclization medium.



10, R_1 = H; R_2 = OAc
11, R_1 = OAc; R_2 = H
12, R_1 = OAc; R_2 = C_6H_5



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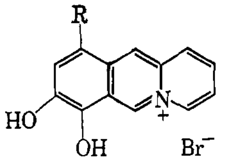
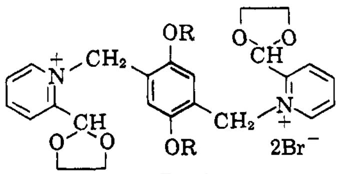


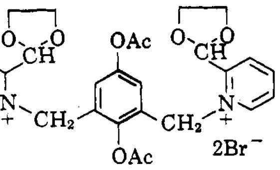
14, R = H
15, R = C_6H_5

The structures of these salts were confirmed by elemental analysis, by their infrared and ultraviolet absorption spectra, and by conversion to the corresponding yellow, fluorescent diacetates.

The double cyclodehydration of bispyridinium salts **16** and **18**, derived from **5** and **6**, respectively, gave the corresponding isomeric diazoniapentacenediones **19** and **20** in 68 and 50% yields rather than the precursor diols. The sensitivity of the unisolated diols to air oxidation is in agreement with the findings of Bradsher and Barker,[1] who obtained quinone **19** after cyclization of **17**, and is



16, R = Ac
17, R = CH_3



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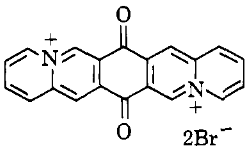

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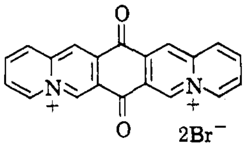

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[1] C. K. Bradsher and M. W. Barker, *J. Org. Chem.*, **29**, 61 (1964).

[2] C. K. Bradsher and J. H. Jones, *J. Am. Chem. Soc.*, **79**, 6033 (1957).

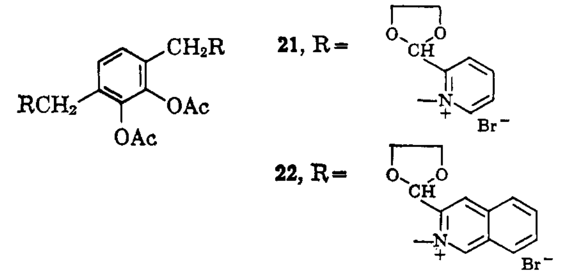
[3] D. L. Fields, J. B. Miller, and D. D. Reynolds, *J. Org. Chem.*, **29**, 2640 (1964).

not unexpected considering the probable relative resonance stability of a pentacene-6,13-dione compared with that of the corresponding diol.[4]

Attempted reductive acetylation, as well as mild catalytic hydrogenation of **19**, to give the diacetoxy- or dihydroxydiazoniapentacene dibromides, was unsuccessful, owing, at least in part, to overreduction of the quinolizinium nuclei.

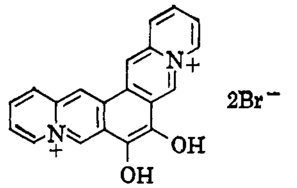
Interestingly enough, 6,7-dihydroxy-4a,8a-diazoniapentaphene dibromide (**23**) was readily isolated as nonfluorescent purple needles in 84% yield after a solution of **21** in 15% hydrogen bromide–acetic acid had been refluxed for 45 min. Unlike the diazoniapentacene system, diol **23** is relatively stable to oxidation and there was no indication of contamination by quinone in the crude cyclized product.

The mild conditions applicable to this bis cyclization represent a clear demonstration of the effectiveness of the two hydroxyl groups in activating the sites where ring closure must occur, and may be contrasted to the 17-hr., 145° polyphosphoric acid treatment recently employed by Bradsher and Parham[5] to produce the first diazoniapentaphene salts, starting with *o*-, *m*-, and *p*-xylylene bromides.

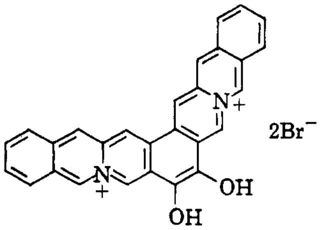


21, R=

22, R=



23



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The success of the preparation of diazoniapentaphene **23** suggested a logical extension to the synthesis of the new 5a,9a-diazoniaheptaphene ring system, *i.e.*, 7,8-dihydroxy-5a,9a-diazoniaheptaphene dibromide (**24**). Thus, the bisisoquinolinium salt **22** and 48% hydrobromic acid were refluxed for 30 min. A highly insoluble bronze microcrystalline product separated from solution during this period and was isolated in 56% over-all yield based on the starting halide. Although no suitable solvent was found to recrystallize this product, its elemental analysis and ultraviolet spectra were in good agreement with the proposed diazoniaheptaphene structure.

Experimental[6]

5,8-Dihydroxy-4a-azoniaanthracene Bromide (13).—A mixture of 2-bromomethylhydroquinone diacetate (**4**)[3] (196 g., 0.683 mole) and 2-(1,3-dioxolan-2-yl)pyridine[7] (140 g., 0.928 mole) in 400 ml. of acetonitrile was refluxed for 12 hr. and then concentrated to a viscous sirup. Crystallization was effected by trituration in ether. A total of 260 g. (87% yield) of **10** as white needles was obtained after one recrystallization from ethanol–ether, m.p. 155–157°.

Anal. Calcd. for $C_{19}H_{20}BrNO_6$: C, 52.0; H, 4.6; N, 3.2. Found: C, 51.9; H, 4.8; N, 3.2.

A mixture of pyridinium salt **10** (136.4 g., 0.311 mole) and 600 ml. of 32% hydrogen bromide in acetic acid was refluxed. When solids separated, 250 ml. of acetic acid was added. The mixture was refluxed for a total of 30 min. After addition of 600 ml. of acetic anhydride, the solution was stripped to yield a bright red paste. Washing the paste with two 100-ml. portions of acetic acid and then with ether gave a yield of 82 g. (90%) crude product. Recrystallization from 48% hydrobromic acid gave an analytical sample of **13** as red needles: m.p. 326° dec.; $\lambda_{\max}^{\text{MeOH}}$ 248 mμ (log ϵ 4.41), 375 mμ (log ϵ 3.73).

Anal. Calcd. for $C_{13}H_{10}BrNO_2$: C, 53.4; H, 3.4; Br, 27.4; N, 4.8. Found: C, 53.7; H, 3.5; Br, 27.7; N, 4.6.

A sample of 5,8-dihydroxy-4a-azoniaanthracene bromide (**13**) was acetylated with acetic anhydride–sulfuric acid. An aqueous solution of the crude material thus obtained was treated with a sodium perchlorate solution to yield a crude sample of product. Recrystallizations from acetic acid and acetonitrile–ether gave pure material: $\lambda_{\max}^{\text{CH}_3\text{CN}}$ 250 mμ (log ϵ 4.78), 364 mμ (log ϵ 4.04).

Anal. Calcd. for $C_{17}H_{14}ClNO_8$: C, 51.5; H, 3.5; Cl, 9.0; N, 3.5. Found: C, 51.1; H, 3.7; Cl, 9.2; N, 3.6.

5,6-Dihydroxy-4a-azoniaanthracene Bromide (14).—The pyridinium bromide intermediate **11**, m.p. 150–152°, was isolated in 92% yield following the general procedure just described for the preparation of **10**.

Anal. Calcd. for $C_{19}H_{20}BrNO_6$: C, 52.0; H, 4.6; N, 3.2. Found: C, 52.3; H, 4.3; N, 3.2.

A solution of 260 g. (0.593 mole) of **11** in 1 l. of a 15% hydrogen bromide–acetic acid mixture was refluxed for 30 min. The mixture was cooled to room temperature and slowly diluted with 500 ml. of ether. The product was collected and recrystallized as red needles (160 g., 92.5% yield) from 20% hydrobromic acid: $\lambda_{\max}^{\text{MeOH}}$ 245 mμ (log ϵ 4.07), 347 (4.05), 363 (4.08).

Anal. Calcd. for $C_{13}H_{10}BrNO_2$: C, 53.4; H, 3.4; Br, 27.4. Found: C, 53.6; H, 3.8; Br, 27.4.

Acetylation of 5,6-dihydroxy-4a-azoniaanthracene bromide (**14**) as described above gave, after recrystallization from acetone–ether, an analytical sample of the diacetate perchlorate: m.p. 251° dec.; $\lambda_{\max}^{\text{CH}_3\text{CN}}$ 248 mμ (log ϵ 4.79), 283 (sh) (4.09), 357 (4.01), 382 (3.97), 402 (3.95).

Anal. Calcd. for $C_{17}H_{14}ClNO_8$: C, 51.6; H, 3.5; Cl, 9.0; N, 3.5. Found: C, 52.2; H, 3.6; Cl, 8.7; N, 4.2.

5,6-Dihydroxy-8-phenyl-4a-azoniaanthracene Bromide (15).—3-Bromomethyl-5-phenylcatechol diacetate (**6**)[3] (363 g., 1.0 mole) and 2-(1,3-dioxolan-2-yl)pyridine (196 g., 1.3 moles) in 750 ml. of acetonitrile were refluxed for 12 hr. The resulting quaternary salt was isolated as a white, hygroscopic powder by precipitation into 4 l. of ether. Without further purification, this product was dissolved in 400 ml. of 48% hydrobromic acid which, in turn, was refluxed for 30 min. The deep red solution was refrigerated at 5° for 18 hr. and the product was collected (347 g., 92% yield) as red needles. An analytical sample of the hemihydrate was obtained by recrystallization from water–ethanol: $\lambda_{\max}^{\text{MeOH}}$, 340 m$\mu$ (sh) (log ϵ 3.93), 356 (4.08), 372 (4.10), 400 (3.79).

Anal. Calcd. for $C_{19}H_{14}BrNO_2 \cdot 0.5H_2O$: C, 60.5; H, 4.0; N, 3.7. Found: C, 60.2; H, 4.0; N, 3.7.

Acetylation of 5,6-dihydroxy-8-phenyl-4a-azoniaanthracene bromide (**15**) as just described gave, after recrystallization from acetonitrile–ether, an analytical sample of the diacetate per-

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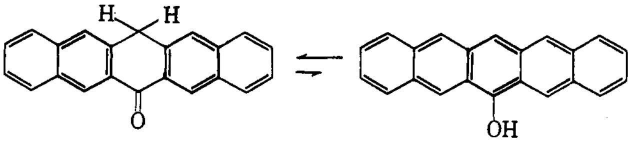
(4) For example, the phenol of 6-keto-13-dihydropentacene is unknown.



See E. Clar, "Aromatische Kohlenwasserstoffe," 2nd Ed., J. Springer-Verlag, Berlin, 1952, p. 64.

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

(6) Melting points were taken on a Mel-Temp apparatus. Ultraviolet spectra were taken on a Cary Model 15 recording spectrophotometer using acidified solutions, except for those samples run in acetonitrile.

(7) C. K. Bradsher and J. C. Parham, *J. Org. Chem.*, **28**, 83 (1963).

chlorate: m.p. 206–208°; $\lambda_{max}^{CH_3CN}$, 240 mμ (log ε 4.64), 250 (4.56), 366 (4.12), 390 (3.92), 410 (3.88).

Anal. Calcd. for $C_{23}H_{18}ClNO_8$: C, 58.6; H, 3.8; Cl, 7.5; N, 3.0. Found: C, 58.3; H, 3.7; Cl, 7.5; N, 2.6.

4a,7a-Diazoniapentacene-6,13-dione Dibromide (**20**).—A mixture of 2,6-bis(bromomethyl)hydroquinone diacetate (**5**)[3] (169 g., 0.444 mole) and 2-(1,3-dioxolan-2-yl)pyridine (200 g., 1.32 moles) in 1 l. of acetonitrile was refluxed for 8 hr. and cooled to room temperature; the resulting salt **18** (251 g., 83%) was collected by filtration. Without further purification, 61.1 g. (0.09 mole) of it in 150 ml. of 48% hydrobromic acid was refluxed for 12 hr. and then refrigerated at 5° for 4 hr. The resulting crystals were filtered and recrystallized as yellow plates (21.0 g., 50%) from boiling water acidified with hydrobromic acid: $\lambda_{max}^{H_2O}$ 253 mμ (log ε 4.78), 383 mμ (log ε 4.36). The infrared spectrum exhibited a strong absorption at 5.95 μ.

Anal. Calcd. for $C_{20}H_{12}Br_2N_2O_2$: C, 50.9; H, 2.5; Br, 34.0. Found: C, 50.6; H, 2.3; Br, 33.8.

In a similar manner, **4a,11a-diazoniapentacene-6,13-dione** (**19**)[1] was obtained in 68% yield, starting with 2,5-bis(bromomethyl)hydroquinone diacetate.[3] It was recrystallized as lustrous yellow plates from boiling water containing a trace of hydrobromic acid. After drying at 140° over P_2O_5, the product existed as a monohydrate: λ_{max}^{MeOH} 224 mμ (log ε 4.66), 251 (4.70), 377 (4.41). The infrared spectrum exhibited a strong absorption at 5.95 μ.

Anal. Calcd. for $C_{20}H_{12}Br_2N_2O_2 \cdot H_2O$: C, 49.0; H, 2.9. Found: C, 49.0; H, 2.9.

6,7-Dihydroxy-4a,8a-diazoniapentaphene Dibromide (**23**).—A mixture of 3,6-bis(bromomethyl)catechol diacetate[3] (399 g., 1.05 moles) and 2-(1,3-dioxolan-2-yl)pyridine (400 g., 2.65 moles), in 750 ml. of acetonitrile was refluxed for 4 hr. The intermediary bis quaternary salt began to separate slowly as white needles as the viscous reaction mixture cooled to room temperature. Dilution with 2 l. of ether precipitated the remainder of the product as a semicrystalline mass. Recrystallization was effected by dissolving the product, with vigorous stirring, in 400 ml. of warm ethanol, which, in turn, was diluted with 1 l. of acetone and then ethyl acetate to incipient opalescence. The product **21** (522 g., 76%) slowly crystallized over a 12-hr. period at 5° and had m.p. 145–146°.

Anal. Calcd. for $C_{28}H_{30}Br_2N_2O_8 \cdot H_2O$: C, 48.1; H, 4.3. Found: C, 48.5; H, 4.5.

A mixture of a portion of the above product (36.4 g., 0.053 mole) and 200 ml. of 30% hydrogen bromide in acetic acid was refluxed for 45 min. Deep red crystals separated from solution during this period. After cooling, the mixture was diluted with 400 ml. of ether and the product was collected by filtration. Diazoniapentaphene (**23**) (21.2 g., 84%) was obtained as dark purple needles (hemihydrate) after recrystallization from boiling water containing 2 ml. of 48% hydrobromic acid, m.p. >450°. This material is not fluorescent and had λ_{max}^{MeOH} 229 mμ (log ε 4.51), 262 (4.42), 363 (4.61), 380 (4.60).

Anal. Calcd. for $C_2H_{14}Br_2N_2O_2 \cdot 0.5H_2O$: C, 49.6; H, 3.1. Found: C, 49.6; H, 3.0.

6,7-Diacetoxy-4a,8a-diazoniapentaphene bisperchlorate, m.p. 283° dec., was obtained as yellow needles by acetylation of **23** with acetic anhydride–sulfuric acid and then converting the product to the perchlorate salt. It is highly fluorescent in solutions of methanol, ethanol, or acetonitrile and had λ_{max}^{MeOH} 218 mμ (log ε 4.63), 253 (4.47), 300 (4.06), 345 (4.32), 360 (4.31), 367 (4.31), 386 (4.41).

Anal. Calcd. for $C_{24}H_{18}Cl_2N_2O_{12} \cdot 0.5H_2O$: C, 47.5; H, 3.1; Cl, 11.7. Found: C, 47.5; H, 3.2; Cl, 11.8.

7,8-Dihydroxy-5a-8a-diazoniaheptaphene Dibromide (**24**).—3-(1,3-Dioxolan-2-yl)isoquinoline, b.p. 127° (0.05 mm.), $n^{25}D$ 1.6055, was prepared from isoquinoline-3-carboxaldehyde[8] following the procedure used by Bradsher and Parham[7] for the synthesis of 2-(1,3-dioxolan-2-yl)pyridine.

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.6; H, 5.5; N, 7.0. Found: C, 71.5; H, 5.7; N, 7.1.

A mixture of 3,6-bis(bromomethyl)catechol diacetate[3] (22.8 g., 0.06 mole) and 3-(1,3-dioxolan-2-yl)isoquinoline (30 g., 0.15 mole) in 150 ml. of nitromethane was refluxed for 12 hr. The resulting quaternary salt was precipitated as a white powder by pouring the cooled solution into 500 ml. of ether. The product was collected and then a solution of it in 200 ml. of 48% hydrobromic acid was boiled for 30 min. A fine, bronze-colored crystalline material separated from solution during this period and was isolated by filtration. It was washed with ethanol and then ether, giving 19.0 g. (56%) of product, m.p. >450°. It was virtually insoluble in all of the common organic solvents and had $\lambda_{max}^{H_2O}$ 248 mμ (log ε 4.52), 269 (4.54), 300 (sh) (4.34), 419 (4.35), 440 (4.43).

Anal. Calcd. for $C_{28}H_{18}Br_2N_2O_2$: C, 58.6; H, 3.1; Br, 27.9; N, 4.9. Found: C, 58.5; H, 3.3; Br, 27.9; N, 4.9.

Acknowledgment.—The authors wish to thank Miss Jane O. Fournier for her assistance in some of the experimental work and Mr. D. G. Borden for providing the ultraviolet spectra.

(8) C. E. Teague and A. Roe, *J. Org Chem.*, **73**, 689 (1951).

Conformational Preferences in Malondialdehyde and Acetylacetaldehyde Enols Investigated by Nuclear Magnetic Resonance

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The spin–spin coupling constants obtained for the enol forms of malondialdehyde and acetylacetaldehyde indicate that the former is predominantly *sym-trans*, whereas the latter (and also the enol form of acetylacetone) is predominantly *sym-cis*. The conformational preferences of acrolein derivatives, therefore, depend on the existence and nature of substituents, and not solely on the possibilities for intramolecular hydrogen bonding. The n.m.r. parameters for *trans-β*-ethoxyacrolein are also presented.

Considerable space has been devoted in the literature to determinations of the conformation about the central C–C single bond in 1,3-butadiene and acrolein derivatives. In most cases, in the absence of constraints such as a bridging ring system, it has been shown that the stable form is planar *sym-trans*. There is considerable doubt as to whether the metastable form is planar *sym-cis* or nonplanar. In a few instances[2] it has been shown that either the *sym-cis* or the nonplanar conformation is actually more stable than the *sym-trans* form. One of the best known instances is the enol form of acetylacetone (I). In this case it is presumed that the planar *sym-cis* form is stabilized by the presence of an intramolecular hydrogen bond,[3] as in Ia. The n.m.r. spectrum obtained from such a compound, however, is the average of the spectra expected for Ia and b, since

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[1] Author to whom inquiries should be addressed.

[2] E. S. Waight and R. L. Erskine in "Steric Effects in Conjugated Systems," G. W. Gray, Ed., Butterworth and Co. (Publishers) Ltd., London, 1959; R. L. Erskine and E. S. Waight, *J. Chem. Soc.* 3425 (1960); G. J. Szasz and N. Sheppard, *Trans. Faraday Soc.*, **49**, 358 (1953); H. Wynberg, A. de Groot, and D. W. Davies, *Tetrahedron Letters*, 1083 (1963).

[3] S. Bratoz, D. Hadzi, and G. Rossmy, *Trans. Faraday Soc.*, **52**, 464 (1956), and references therein.