of potassium hydroxide in 125 ml. of water and 95 ml. of 95% ethanol was added to the residue. The resulting solution was refluxed for 10 hr., and the ethanol was evaporated. The cooled mixture was washed with ether and combined with a 3 *M* sodium hydroxide extract of the ether washing. The aqueous layer was acidified with concentrated hydrochloric acid without cooling. After coming to room temperature, the resulting mixture was taken up in ether. The ether solution was extracted with several portions of saturated sodium bicarbonate solution and dried over sodium sulfate. Removal of the solvent left 5.6 g. of solid residue which was recrystallized from 40 ml. of hexane and a little ethanol. There was obtained 3.4 g. (27%) of spiro[cyclohexane-1,1'-phthalan]-3'-one (X), m.p. 78–81°. Recrystallization from hexane afforded an analytical sample, m.p. 81.5–82.5°.

Anal. Calcd. from $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.02; H, 6.79.

Acidification of the bicarbonate extracts above yielded 2.1 g. (28% based on starting N-methylbenzamide) of benzoic acid, m.p. 120.5–121.5°, undepressed on admixture with an authentic sample.

When the above condensation was effected by refluxing for 0.5 hr., there was obtained an 83% recovery of N-methylbenzamide (isolated by distillation). When the condensation was effected by stirring for 20 min. at 0°, and 45 min. at room temperature, there was obtained 18% of X and 33% of benzoic acid.

(C) With Cyclohexene Oxide.—The mixture containing II was heated at reflux while a solution of 7.84 g. (0.08 mole) of cyclohexene oxide in 80 ml. of ether was added during 12 min. The mixture was refluxed an additional 20 min. and then poured into 65 ml. of 2 *M* hydrochloric acid and 35 g. of ice. From this point the reaction mixture was worked up as described above under B for cyclohexanone. There was obtained 1.4 g. (23%) of benzoic acid and 2.3 g. of crude lactone which was recrystallized from hexane and a little ethanol to give 1.1 g. (11%) of 1,2,3,4,4a,10b-hexahydro-6H-dibenzo[*b*,*d*]pyran-6-one (XI), m.p. 93–94°. A second recrystallization from hexane gave an analytical sample, m.p. 94–94.5°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.92; H, 6.91.

Attempted Metalation of Benzamide.—A mixture of 0.05 mole of benzamide and 0.156 mole of *n*-butyllithium in 100 ml. each of tetrahydrofuran and hexane was refluxed for 15 min., and the resulting mixture was treated with 0.16 mole of benzophenone in 100 ml. of ether essentially as described above for the metalation of N-methylbenzamide and condensation with this ketone. On addition of water to the cooled reaction mixture, no precipitate formed. On working up the organic layer 65% of the benzamide was recovered. No *ortho* product was found. A similar result was obtained when monoglyme was used instead of tetrahydrofuran.

When the mixture of benzamide and butyllithium in tetrahydrofuran and hexane was refluxed for 17 hr. and water then added, a black oily material insoluble in the organic and water layers was produced.

Diazoniapentaphene Salts

C. K. BRADSHER AND J. C. PARHAM[1]

Department of Chemistry, Duke University, Durham, North Carolina

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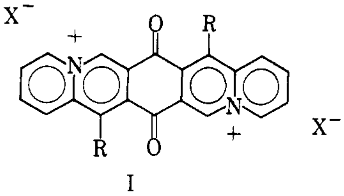
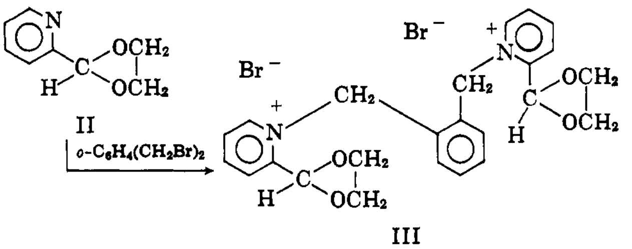
Through use of a recently developed technique, 12a,14a-, 4a,12a-, and 4a,8a-diazoniapentaphene salts have been prepared. These are believed to be the first completely aromatic condensed benzenoid compounds which contain two quaternary nitrogen atoms at bridgehead positions.

In earlier studies it was shown that diaryls could be synthesized with a quinolizinium nucleus in each moiety,[2] and that, as in 4a,11a-diazoniapentacene-6,13-quinone[3] (I), two quinolizinium nuclei may exist in a single fused ring system, separated by a quinone nucleus. The present communciation is concerned with the synthesis of the previously unknown class of compounds in which two quinolizinium nuclei are united through a fused benzenoid ring.

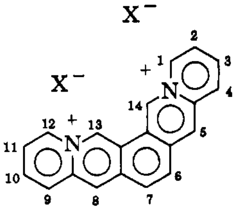


I

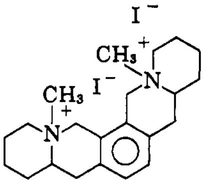
The problem involved in the synthesis of such a derivative is that a double cyclization must occur, the second step involving a cyclization into the greatly deactivated acridizinium nucleus. The recently demonstrated[4] ability of salts of 2-(1,3-dioxolan-2-yl)pyridine (II) to undergo cyclization, even in the presence of strongly deactivating groups, recommended the acetal (II) as a starting material.



III



IV



V

Reaction of the acetal (II) with α,α'-dibromo-*o*-xylene in dimethylformamide (DMF) or tetramethylene sulfone (TMS) produced the crystalline bisquaternary salt (III) in good yield. Cyclization of the salt in polyphosphoric acid at 145° followed by addition of perchloric acid to the diluted solution afforded what is presumably the perchlorate salt, but which detonated at 350° with such vigor that combustion analysis was out of the question. Anion-exchange resins, the usual recourse in such a situation, proved useless, in that the salt was attacked by the resin with the formation

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[1] This research was supported by a research grant (CA-05509) of the National Cancer Institute of the National Institutes of Health. A preliminary report of this work appeared as a Letter to the Editor, *Chem. Ind.* (London), 1247 (1963).

[2] C. K. Bradsher and N. L. Yarrington, *J. Org. Chem.*, **28**, 78 (1963).

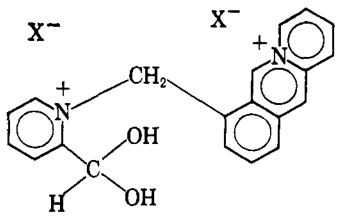
[3] C. K. Bradsher and M. W. Barker, *ibid.*, **29**, 61 (1964).

[4] C. K. Bradsher and J. C. Parham, *ibid.*, **28**, 83 (1963); J. C. Parham, Ph.D. dissertation, Duke University, 1963.

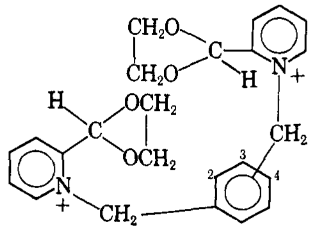
of a dark purple color. Like the diazoniapentacenequinone (I) salts,[3] the perchlorate of IV was attacked by polar solvents and could be recrystallized satisfactorily only from acidified solutions. As an alternative to the perchloric acid method, precipitation with potassium iodide was tried. The resulting "iodide," which may well have been the triodide, was too insoluble to purify for analysis, but when stirred with silver sulfate, it gave a low yield of the bisulfate (IV, X = HSO_4), the first pure diazoniapentaphene salt. The only successful method found for isolation of the diazoniapentaphene ion (IV) from phosphoric acid solution involved precipitation as the bistribromide (Br_3^-).[4] The extremely insoluble precipitate is easily converted to the bromide by heating in methanol–acetone, and provides a 47% over-all yield of the bromide (IV, X = Br) from the quaternary salt (III).

Although there existed only a single way in which dicyclization into the aromatic nucleus could occur, and both spectral and analytical data indicated dicyclization, it was felt that confirmatory chemical proof would be desirable. When the new ring system was hydrogenated, it absorbed the 8 moles of hydrogen necessary to saturate the two quinolizinium nuclei. The reduction product was converted to the methiodide (V) which had the expected composition but was probably a mixture of stereoisomers. Oxidation of the methiodide V yielded 1,2,3,4-benzenetetracarboxylic acid, confirming that dicyclization had occurred in the expected way.

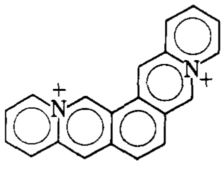
One other observation of note was that under mild cyclization conditions (90°) an acridizinium derivative (VI) could be isolated. The absence of infrared absorption in the carbonyl region and strong absorption in the hydroxyl region suggest that the compound forms a stable hydrate, a common phenomenon among 2-formylpyridinium salts.[5]



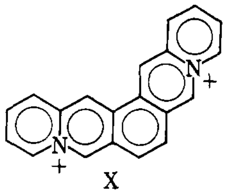
VI



Position 3 VII
Position 4 VIII

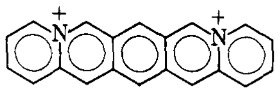


IX

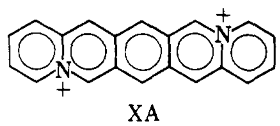


X

The diazoniapentaphene synthesis was repeated starting with the quaternary salts VII and VIII prepared from α,α'-dibromo-*m*-xylene and α,α'-dibromo-*p*-xylene and yielded 4a,12a-diazoniapentaphene (IX) and 4a,8a-diazoniapentaphene(X), respectively. Both were obtained from the dibromoxylene in over 50% over-all yield. The cyclization of the intermediate quaternary salts VII and VIII differs from that of the salt III (obtained from α,α'-dibromo-*o*-xylene) in that linear dicyclization products IXA and XA might be formed. These alternative formulas may be eliminated on the basis of ultraviolet spectral evidence (Table I). The spectra of IX and X show marked similarity to that of IV, about which no such uncertainty exists, and all three spectra resemble the spectrum of pentaphene much more closely than that of pentacene. Further evidence that IX and X are correctly formulated as diazoniapentaphenes instead of diazoniapentacenes (IXA and XA) lies in the yellow color of the products. Every analogy suggests that the compounds represented by IXA and XA should be blue since the linear hydrocarbon pentacene is deep violet blue.[6]



IXA



XA

Table

Ultraviolet Absorption Maxima (mμ) of Diazoniapentaphenes (Bromides)

12a,14a- (IV)		4a,12a- (IX)		4a,8a- (X)	
λ_{max}	Log ε	λ_{max}	Log ε	λ_{max}	Log ε
231	4.48	235	4.51	232[a]	4.32
242	4.47	258	4.59	255	4.44
263	4.63	286	4.39	274[a]	4.18
296	4.26	296	4.36	285.5	4.29
323[a]	4.20	347[a]	4.65	297.5	4.35
340	4.47	357	4.79	325[a]	4.30
348[a]	4.31	375	4.51	341	4.67
369	4.49	404	3.82	354.5	4.68
389	4.54	427	3.70	362	4.51
395[a]	4.45			384	4.59
415	3.60			422	3.73
				447	3.72

[a] Shoulder.

Experimental

Unless otherwise indicated, all analyses were by Dr. Ing. A. Schoeller, Kronach, Germany. Melting points were determined in capillaries on a Mel-Temp apparatus and are uncorrected. All ultraviolet absorption spectra were measured in 95% ethanol using 1-cm. quartz cells with the Cary Model 14 spectrophotometer.

1,2-Bis(1-methylene-2-[1,3-dioxolan-2-yl]pyridinium bromide)-benzene (III).—A solution containing 13.40 g. of α,α'-dibromo-*o*-xylene and 15.1 g. of 2-(1,3-dioxolan-2-yl)pyridine[4] (II) in 12 ml. of dimethylformamide was allowed to stand for 2 days in a stoppered flask. The solid mass of salt was broken up and washed thoroughly with ethyl acetate, then crystallized from methanol–ethyl acetate; yield 24.28 g. (81%), m.p. 177–180°.

An analytical sample was obtained from the same solvents as large white prisms, m.p. 185–186° dec.

Anal. Calcd. for $C_{24}H_{26}Br_2N_2O_4$: C, 50.88, H, 4.59; N, 4.94. Found: C, 51.06; H, 4.59; N, 5.18.

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(5) G. M. Steinberg, E. J. Poziomek, and B. E. Hackley, *J. Org. Chem.*, **26**, 368 (1961).

(6) E. Clar and Fr. John, *Ber.*, **62**, 3021 (1929); **63**, 2967 (1930).

The **perchlorate** crystallized from methanol as small colorless prisms, m.p. 220–221°.

Anal. Calcd. for $C_{24}H_{26}Cl_2N_2O_{12}$: C, 47.61; H, 4.33; N, 4.63. Found: C, 47.45; H, 4.13; N, 4.97.

12a,14a-Diazoniapentaphene Bromide (IV, X = Br).—A solution containing 5.66 g. of the quaternary salt (III, X = Br) in 82 g. of polyphosphoric acid was stirred on the steam bath for 2 hr. to assure homogeneity. It was then maintained at 150–160° for 17 hr. with vigorous stirring. After cooling the solution, 100 g. of ice was added with stirring. The diluted reaction mixture was stirred on the steam bath for 2 hr. to assure complete hydrolysis of the polyphosphoric acid and prevent precipitation of polyphosphate salts. The cooled solution was stirred rapidly while the "tribromide reagent" (three volumes of hydrobromic acid to one volume of bromine) was added dropwise until precipitation was complete. The orange-yellow tribromide (IV, X = Br_3) was collected and washed well with cold water.

The tribromide was suspended in a mixture containing 250 ml. of acetone and 250 ml. of methanol and heated on the steam bath with stirring until the salt dissolved. The solution was treated with charcoal, concentrated, and ethyl acetate added. From the *chilled solution, 2.13 g. (48%) of the bromide was obtained as* yellow needles. Recrystallization from acidified (HBr) methanol–ethyl acetate gave 2.07 g., (47%), m.p. >400°. The analytical sample consisted of tiny bright yellow needles, m.p. >400°, with darkening above 300°.

Anal. Calcd. for $C_{20}H_{14}Br_2N_2$: C, 54.32; H, 3.19; N, 6.33. Found: C, 54.35; H, 3.11; N, 6.25.

The **2-anthraquinone sulfonate** was prepared by addition of a saturated aqueous solution of sodium 2-anthraquinone sulfonate to an aqueous solution of the bromide. The analytical sample was recrystallized from acidified (HCl) methanol–ethyl acetate as small yellow prisms, m.p. 318° dec. and gas evolution.

Anal. Calcd. for $C_{48}H_{28}N_2O_{10}S_2 \cdot H_2O$: C, 65.89; H, 3.46; N, 3.20. Found: C, 66.05; H, 3.46; N, 3.35.

The **bisulfate** (IV, X = HSO_4) was obtained from the crude "iodide" by stirring a suspension of the salt and silver sulfate (10 molar excess) in very dilute sulfuric acid. The insoluble salts were removed by repeated filtration of the solution through a sintered glass funnel. The salts were washed with methanol and the washing combined with the filtrate. Vacuum evaporation of the solvents and crystallization of the residue repeatedly from methanol–ethyl acetate (acidified with sulfuric acid) afforded the product as blunt brownish yellow needles, m.p. >400°, with gradual charring above 270°.

Anal. Calcd. for $C_{20}H_{16}N_2O_8S_2$: C, 50.41; H, 3.38; N, 5.88. Found: C, 50.09; H, 3.38; N, 6.01.

Di(1,4,6,7,8,9-hexahydro-9a*H*-quinolizino)[2,3-*a*:3,2-*b*]benzene Dimethiodide (V).—Hydrogenation at room temperature and atmospheric pressure of a methanolic solution (100 ml.) containing 1.06 g. of 12a,14a-diazoniapentaphene chloride (obtained by stirring the "iodide" with silver chloride) resulted in an uptake of 95% of the calculated 8 moles of hydrogen. The solution was filtered and concentrated, and ethyl acetate was added. The fluffy white salt which precipitated, presumably the dihydrochloride, m.p. 339–340° (1.03 g.), was converted to the free base and methylated with methyl iodide affording the dimethiodide (V). This was crystallized from methanol–ethyl acetate affording crystals which decomposed gradually above 225°; yield 1.31 g. (81%). The analytical sample consisted of colorless prisms, m.p. 230–240°, and may have been a mixture of stereoisomers.

Anal. Calcd. for $C_{22}H_{34}I_2N_2$: C, 45.53; H, 5.90; N, 4.83. Found: C, 45.19; H, 5.93; N, 5.03.

Oxidation of the Dimethiodide (V).—To a solution containing 0.58 g. of the methiodide (V) in 20 ml. of water at 100°, 6.3 g. of potassium permanganate dissolved in 100 ml. of water was added, along with 10 ml. of 10% sodium hydroxide solution. After the addition period (2 hr.), heating was continued overnight. Excess permanganate was destroyed by addition of isopropyl alcohol, and the manganese dioxide was removed by filtration. The clear filtrate was acidified with concentrated hydrochloric acid and heated on the steam bath for 2 hr. Inorganic salts were removed by percolating the solution through a Dowex 50-X cation-exchange resin column loaded with hydrogen ion, The eluate and washings were evaporated to dryness *in vacuo* (aspirator) and the residue sublimed *in vacuo*. The sublimate (probably 1,2,3,4-benzenetetracarboxylic acid anhydride) was heated in 5 ml. of water and concentrated to dryness *in vacuo;* yield 45 mg. (17%) of crude 1,2,3,4-benzenetetracarboxylic acid, m.p. 228–231° (lit.[7,8] m.p. 236–238°). Methylation with diazomethane gave the tetramethyl ester of 1,2,3,4-benzenetetracarboxylic acid as colorless needles from ether–ligroin, m.p. 128–129° (lit.[8] m.p. 131.1–131.8 cor.).

Anal. Calcd. for $C_{14}H_{14}O_8$: C, 54.19; H, 4.54. Found: C, 54.32; H, 4.50.

7-(1-Methylene-2-dihydroxymethylpyridinium perchlorate)-acridizinium Perchlorate (VI).—A solution containing 8.5 g. of the quaternary salt (III) in 104 g. of polyphosphoric acid was stirred for 8 hr. on the steam bath. The mixture was diluted, heated, and finally treated with the "tribromide reagent." The red gummy precipitate first formed turned to an orange solid after standing for 2 hr. in ice. When this solid was suspended in 200 ml. of acetone, a yellow solid identified as 12a,14a-diazoniapentaphene separated.

The oily residue obtained by concentration of the filtrate was dissolved in water and converted to the perchlorate by addition of 35% perchloric acid. The pale yellow perchlorate (VI) was recrystallized from methanol–ethyl acetate; yield 1.77 g. (23%), m.p. 237–238° dec. The analytical sample consisted of short yellow-tan needles, m.p. 253–254°; λ_{max} (log ϵ), 211[9] (4.12), 245[9] (4.53), 250 (4.54), 363 (3.87), 381 (4.03), and 400.5 mμ (3.99).

Anal. Calcd. for $C_{20}H_{18}Cl_2N_2O_{10}$: C, 46.44; H, 3.51; N, 5.42. Found: C, 46.97; H, 3.66; N, 5.43.

1,3-Bis(1-methylene-2-[1,3-dioxolan-2-yl]pyridinium bromide)-benzene (VII).—The quaternization reaction with 13.40 g. of α,α'-dibromo-*m*-xylene was carried out as in the case of the *ortho* isomer yielding 26.83 g. (95%) of the bisquaternary salt (VII).

The analytical sample was obtained from methanol–ethyl acetate as colorless rhombohedral prisms, m.p. 95.5–97°.

Anal. Calcd. for $C_{24}H_{26}Br_2N_2O_4$; C, 50.88; H, 4.59; N, 4.94. Found: C, 50.84; H, 4.70; N, 5.14.

The **perchlorate** formed colorless platelets from methanol–ethyl acetate, m.p. 155.5–156.5°.

Anal. Calcd. for $C_{24}H_{26}Cl_2N_2O_{12}$: C, 47.61; H, 4.33; N, 4.63. Found: C, 47.98; H, 4.29; N, 4.98.

4a,12a-Diazoniapentaphene (IX) Bromide.—The cyclization of the bisquaternary salt (VII) was carried out essentially as in the case of the *ortho* isomer, except that at no time was all of the tribromide completely dissolved in the acetone–methanol mixture; yield 54%.

The analytical sample was obtained from acidified (hydrobromic acid) methanol–ethyl acetate, m.p. >400° (charring above 380°).

Anal. Calcd. for $C_{20}H_{14}Br_2N_2$: C, 54.32; H, 3.19; N, 6.33. Found: C, 54.32; H, 3.13; N, 6.38.

1,4-Bis(1-methylene-2-[1,3-dioxolane-2-yl]pyridinium bromide)-benzene (VIII).—A solution of 10.5 g. of α,α'-dibromo-*p*-xylene in 20 ml. of dimethylformamide was allowed to react with 12.1 g. of 2-(1,3-dioxolan-2-yl)pyridine (II) as in the formation of the isomeric salts (III and VII); yield 13.87 g. (61%), m.p. 195–199°. The analytical sample crystallized from methanol–ethyl acetate as small white needles, m.p. 201–202° dec., and previous shrinkage.

Anal. Calcd. for $C_{24}H_{26}Br_2N_2O_4$: C, 50.88; H, 4.59; N, 4.94. Found: C, 50.82; H, 4.34; N, 4.94.

The **perchlorate** formed colorless irregular prisms from methanol, m.p. 244–244 5°.

Anal. Calcd. for $C_{24}H_{26}Cl_2N_2O_{12}$: C, 47.61; H, 4.33; N, 4.63. Found: C, 47.93; H, 4.56; N, 4.74.

4a,8a-Diazoniapentaphene (X) Bromide.—The cyclization of 11.32 g. of the quaternary salt (VIII) was carried out as in the case of the isomers, except that 1 l. of acetone–methanol was used for conversion of the tribromide salt (X, X = Br_3) to the bromide (X, X = Br). The total recrystallized yield was equivalent to 5.75 g. (65%), m.p. >400°. The analytical sample was obtained from acidified methanol as a yellow microcrystalline powder, m.p. >400°, with charring above 390°.

Anal. Calcd. for $C_{20}H_{14}Br_2N_2$: C, 54.32; H, 3.19; N, 6.33. Found: C, 54.00; H, 3.31; N, 6.35.

The **2-anthraquinone sulfonate** salt was crystallized from acidified (hydrochloric acid) methanol–ethyl acetate as a yellow microcrystalline powder, m.p. 282° dec., and previous shrinkage.

Anal. Calcd. for $C_{48}H_{28}N_2O_{10}S_2 \cdot {}^1/_2H_2O$: C, 66.58; H, 3.38; N, 3.57. Found: C, 66.21; H, 2.95; N, 3.24.

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(7) L. I. Smith and E. J. Carlson, *J. Am. Chem. Soc.*, **61**, 291 (1939).

(8) F. Gonzalez-Sanchez, *Tetrahedron*, **1**, 231 (1957).

(9) Shoulder.