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THE 9-METHYL-8a,10a-DIAZONIAPHENANTHRENE CATION, AN AROMATIC RING SYSTEM WITH TWO QUATERNARY NITROGEN BRIDGEHEAD ATOMS IN ONE RING

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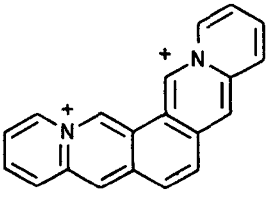
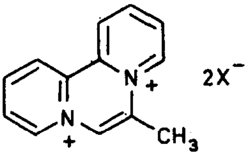
THE first aromatic ring systems with quaternary nitrogen atoms at two bridgehead positions were recently prepared by Bradsher and Parham (1). These authors describe several isomeric diazoniapentaphene salts, e.g., (I), in which the two quaternary nitrogen atoms are located in different rings. Among factors of interest determining the chemistry of ions of this type are the mutual repulsion between the two positive charges and the extent to which these charges are delocalised. These considerations have prompted us to study the chemistry of tricyclic aromatic compounds in which two quaternary nitrogen atoms are situated at bridgehead positions in one ring. We now report the first synthesis of one of these ions, the 9-methyl-8a,10a-diazoniaphenanthrene cation (II).



(I)



(II)

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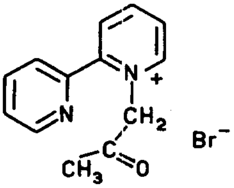
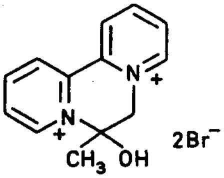
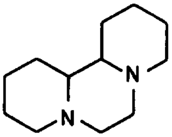
1-Acetonyl-2-(2-pyridyl)pyridinium bromide (III), which crystallised from ethanol-acetone in colourless plates, m.p. 163–164°, (2) was prepared from 2,2'-bipyridyl and bromoacetone in 73% yield. When treated at room temperature with 48% hydrobromic acid this salt was converted to 9-hydroxy-9-methyl-9,10-dihydro-8a,10a-diazoniaphenanthrene dibromide (IV) (85%), which crystallised from water-acetone as pale green needles, m.p. 220–225° (decomp.)(2) $\lambda^{\text{water}}_{\text{max}}$ at 224 (sh) (ϵ 9,300), and 286 mμ (ϵ 11,200), ν (nujol) at 3360 and 3425 cm^{-1}. The structure proposed is consistent with the p.m.r. spectrum (3), which showed two singlets at 1.78 p.p.m. (3 methyl protons) and at -1.66 p.p.m. (2 methylene protons). Two doublets at -5.50 and -5.82 p.p.m. (one proton each) are assigned to the two aromatic protons next to the quaternary nitrogen atoms. Two multiplets centered at -4.75 p.p.m. (2 protons) and at -5.20 p.p.m. (4 protons) account for the remaining aromatic protons. Chemical evidence for the structure of (III) was obtained by catalytic hydrogenation (60°; 1500 lbs/sq.in.) in the presence of platinum. This yielded 6-methyldecahydrodipyrido [1,2-a:2',1'-c]pyrazine (V) (62%), b.p. 80–82°/0.2 mm (2). This base was transparent in the infrared between 1480 and 2000 cm^{-1} and between 3000 and 4000 cm^{-1}. It was characterised by the preparation of its dipicrate, which separated from acetone-water as yellow prisms, m.p. 263–264°(2); the dibromide sesquihydrate of (V), colourless prisms from ethanol, m.p. 293–295°(2) was also obtained.



(III)



(IV)



(V)

On treatment with boiling thionyl chloride 9-methyl-9-hydroxy-9,10-dihydro-8a,10a-diazoniaphenanthrene dibromide (IV) was converted in ca. 60% to a mixture of the 9-methyl-8a,10a-diazoniaphenanthrene dichloride (II; X = Cl) and dibromide (II; X = Br). The cation (II) was characterised as the dipicrate, which crystallised from acetone-water as yellow plates,m.p.243-245° (decomp.)(2), and as the dibromide hydrate, which separated from methanol as pale green needles, m.p. 300-305°(decomp.)(2). The structure of the new cation follows from its spectroscopic properties. Thus, its ultraviolet spectrum [$\lambda^{\text{water}}_{\text{max}}$ at 237.5; 244; 267; 276; 311.5; 325; and 351 $m\mu$ (Σ 16,300; 38,200; 52,100; 11,400; 13,650; 3,200) and a shoulder at 301 $m\mu$ (Σ 8,100)] resembles that of 9-methylphenanthrene, the main differences being a loss of fine structure and a bathchromic shift of the β- and p- band systems (4). In the p.m.r. spectrum of the cation (II) the resonance of the methyl group appears as a doublet (J=1.0 c.p.s.) at 0.60 and 0.615 p.p.m. (3). This splitting is reminiscent of the p.m.r. spectrum of 9-methylphenanthrene (5). The splitting of the methyl signal in (II) was shown by spin-decoupling to be caused by coupling to the 10-proton whose signal at -5.41 p.p.m. is part of a multiplet centered at -5.36 p.p.m. (2 protons). Two other multiplets at -4.97 and at -5.98 p.p.m. account for two and four aromatic protons respectively.

The structure of the 9-methyl-8a,10a-diazoniaphenanthrene cation is confirmed by the following observations. Oxidation with aqueous potassium permanganate at room temperature produced 2,2'-bipyridyl (53%). Thermal decomposition of the dibromide hydrate of (II;X=Br) above its melting point also gave 2,2'-bipyridyl (53%). Catalytic hydrogenation in the presence of platinum yielded 6-methyldecahydrodipyrido[1,2-a:2',1'-c]pyrazine (V) (71%). Aqueous solutions of the salts of (II) are stable when exposed to diffuse day light and air for several weeks, but decomposition occurs within hours on exposure to ultraviolet light. The action of bases gives deeply coloured products which have not been examined. The study of the chemistry of the cation (II) and of related compounds is being continued.

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References

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

2. Satisfactory analytical data have been obtained for this compound.

3. P.m.r. spectra were measured at 60 mc/sec. in D_2O; shifts are given in p.p.m. relative to dioxan as internal standard.

4. R.A. Friedel and M. Orchin, Ultraviolet Spectra of Aromatic Compounds, spectrum no.342. John Wiley and Sons, New York (1951).

5. H. Rottendorf and S. Sternhell, Work in the press.