**Tetrahedron Letters No.20, pp. 1465-1469, 1965. Pergamon Press Ltd.
Printed in Great Britain.**

THE 8a,10a-DIAZONIAPHENANTHRENE CATION

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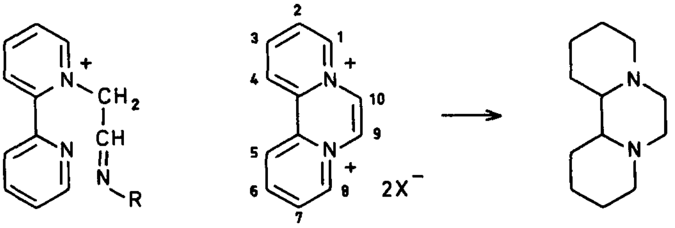
(Received 29 March 1965)

CORR and Glover reported recently that 8a,10a-diazoniaphenanthrene dibromide dihydrate (I;X=Br;2H$_2$O), m.p. 272-273° (decomp.) was formed by treatment of the quaternary salt (II; R= HO-) with hydrobromic acid.[1] These authors also prepared the dipicrate monohydrate (I;X=C$_6$H$_2$N$_3$O$_7$;H$_2$O), m.p. 185-186°, of the product of this cyclisation and reported that catalytic hydrogenation of this ring system gave dodecahydro[1,2-a:2',1'-c] dipyridopyrazine (III), identical with the perhydro base obtained similarly from (IV).[cf.2]



II I III

While these data are consistent with the structure (I) for the product of the acid-catalysed cyclisation of (II;R= HO-), the ultra-violet spectrum of the compound described by Corr and Glover is incompatible with the spectrum to be expected from an 8a,10a-dizoniaphenanthrene salt[3] and in fact it resembles closely the ultra-violet spectrum of (IV).[4]

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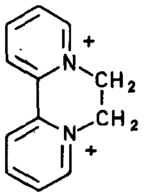
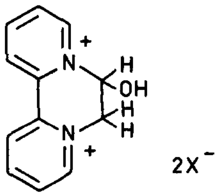

IV


V

We now describe a synthesis of the 8a,10a-diazoniaphenanthrene cation (I), the key step of which is based on the use of thionyl chloride for the dehydration of 9-hydroxy-9,10-dihydro-8a,10a-dizoniaphenanthrene dibromide monohydrate (V).[cf.3] This salt was prepared in 71% overall yield in two steps from 2,2'-bipyridyl Bromoacetaldehyde-2,4-dinitrophenylhydrazone[5] reacted with 2,2'-bipyridyl in boiling acetonitrile to give the quaternary salt (II; R= 2,4-$(NO_2)_2C_6H_3$-NH-)(83%), which crystallised with one molecule of methanol as orange prisms[6], m.p. 146-149° (decomp.), from methanol. This salt was cyclised by warming it with an excess of 48% hydrobromic acid; the resulting mixture was treated with boiling acetone and the precipitate was dissolved in water and freed of coloured matter by extraction with chloroform. Evaporation gave 9-hydroxy-9,10-dihydro-8a,10a-diazoniaphenanthrene dibromide monohydrate (V;X=Br;H_2O)(86%), which crystallised from methanol-acetone as pale yellow needles[6] m.p. 272-273° (decomp.). The dipicrate (V;X=$C_6H_2N_3O_7$) separated from water as yellow plates[6], m.p. 184-185°. The ultraviolet spectrum of the dibromide was recorded in 10% sulphuric acid and showed λ_{max} (ϵ) at 311.5 mμ(19,900), a shoulder at 317 mμ(18,900), and λ_{min} (ϵ) at 271 mμ(1,400). This spectrum is similar to that of (IV).[4] The p.m.r. spectrum of the dibromide was measured at 60 mc/sec. in 15% CF_3CO_2D/D_2O relative to external dioxan. It showed a doublet at τ4.18 (2 protons; CH_2), a triplet at 2.76 (one proton; CH), two multiplets centered at 1.14 and 0.63 (2 and 4 protons, respectively;

aromatic protons), and two doublets with further couplings at 0.33 and 0.17 (one proton each; aromatic protons adjacent to nitrogen).

The melting points of the dibromide hydrate and of the dipicrate of (V), as well as the ultra-violet spectrum of this cation agree with the constants published by Corr and Glover for the product of the acid-catalysed cyclisation of (II;R= HO-),[1] and we suggest that the product described by these authors is in fact the 9-hydroxy-9,10-dihydro-8a,10a-diazoniaphenanthrene dibromide monohydrate (V;X=Br;H_2O) described now. The conversion of (V;X=Br;H_2O) into (III) as reported by Corr and Glover does not contradict our proposal, since the hydrogenolysis of the hydroxyl groups of derivatives of 9-hydroxy-9,10-dihydro-8a,10a-diazoniaphenanthrene salts appears to occur invariably during the catalytic hydrogenation of these salts.[7]

The dibromide monohydrate of (V) was aromatised by stirring it with boiling thionyl chloride. The residue left after removal of volatile matter was dissolved in glacial acetic acid and converted to the bromide by way of the perbromide. *8a,10a-Diazoniaphenanthrene dibromide monohydrate* (I;X=Br;H_2O)(77%) crystallised from methanol-acetone in colourless prisms[6], m.p. 271-272°(decomp.). The aromatic nature of this cation is shown by its ultra-violet spectrum which was measured in water and showed λ_{max} (ϵ) at 224,(21,300), 239 (23,200), 264 (40,300), 272 (53,400), and at 323 mμ(19,300); shoulders occurred at 310 (15,800) and at 340 mμ(3,500) and λ_{min} (ϵ) at 220 (20,100), 228 (20,000), 247 (20,600), 266 (38,600), and at 285 mμ(7,000). In its p.m.r. spectrum (Table 1) the signal due to the 9- and 10-protons appears as a singlet. The resonances of the 4- (5-) protons occur downfield as in phenanthrene[8] together with signals of the 1-(8-) protons, which are deshielded by the quaternary nitrogen atoms. The splitting pattern of the 1-(8-),2-(7-),3-(6-) and 4-(5-)

protons forms an ABXY system.

Chemical evidence for the structure of (I) was obtained by catalytic hydrogenation of the dibromide monohydrate at room temperature and pressure in the presence of platinum, which resulted in the uptake of 7 moles of hydrogen to give dodecahydrodipyrido [1,2-a:2',1'-c] pyrazine (III), isolated as the dipicrate, m.p. 248-252° (lit.[2], m.p. 248-252°), identified by direct comparison with an authentic specimen prepared from (IV)[2].

Like its 9-methyl derivative the 8a,10a-diazoniaphenanthrene cation is decomposed by bases. Aqueous solutions of (I) appear to be stable in diffuse day light but on exposure to ultra-violet light hydration of the 9,10-bond occurs to give (V) (29% after 24 hours; isolated as the dipicrate). A full account of this work will be published elsewhere.

Acknowledgements. - We thank C.S.I.R.O. for award of a Senior Postgraduate Studentship (to I.C.C.), and Dr. T. McL. Spotswood for measuring the p.m.r. spectra.

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TABLE 1

The PMR Spectrum of 8a,10a-Diazoniaphenanthrene Dibromide Monohydrate*

Shift in cps from internal dioxan	Signal		Number of Protons	Assignment
-291.34 -292.89	d		2	2-(7-)
-297.64 -298.88 -300.30	t			
-304.93 -306.55	d			
-318.48 -319.85	d		4	3-(6-) 9-(10-)
-326.77** -328.45	**			
-334.39 -335.85	d			
-352.74 -353.68 -354.63 -355.28 -356.10 -356.73 -357.39	m		4	1-(8-) 4-(5-)
-358.78 -359.48	d	d		1-(8-)
-360.18 -361.00	d			
-363.60 -364.28	d	d		4-(5-)
-365.17 -365.77	d			

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* Measured at 60 mc/sec ; slow scan.

** The 9- and 10-proton appear as singlet in this signal.