

Diazepines. IX. 7,8-Dihydro-6*H*-dipyrido[1,2-*a*:2',1'-*c*][1,4] diazepinediium Dibromide; 6,7-Dihydro-5*H*-[1,4] diazepino[1,2,3,4-*lmn*][1,10]-phenanthrolinediium Dibromide; and Related Compounds (I)

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Diquat (1) and certain related diquaternary salts have attracted much attention as herbicides (2). Their mode of action is believed (3,4) to be connected with their ability to be rapidly reduced to stable radical cations. The hydrates of compounds 2 ($n = 2, 3,$ and 4) were prepared by treatment of 2,2'-dipyridyl with the appropriate dihalides (5). Apart from the studies of the reduction to the radical cation and some spectral studies (6) little has been reported on the chemistry of these compounds or on the generality of their preparation (7). In view of our interest in diazepines (1) it was decided to further investigate 7,8-dihydro-6*H*-dipyrido[1,2-*a*:2'-1'-*c*]-[1,4]diazepinediium dibromide (2 $n = 3$) and related compounds.

Compounds 2 ($n = 2, 3,$ and 4) have been obtained as the non-hydrated products after thorough drying. Use of 1,5-dibromopentane in an attempt to extend the synthesis to 2 ($n = 5$) did not lead to a cyclic product but gave 3. Use of 1,3-dibromo-2-propanol and 1,3-dibromobutane gave the diazepines 4 and 5, while use of 1,4-dibromo-2-butene and α,α' -dibromo-*o*-xylene gave the diazocines 6 and 7. Reaction of 1,10-phenanthroline with 1,3-dibromopropane gave the diazepine 8 (8). The spectral data for the new diazepines and diazocines is consistent with that previously reported for 2 (6).

Oxidation of the diazepines 2 ($n = 3$), 4, and 8 with alkaline potassium ferricyanide gave the bipyridones 9, 10, and 11 (9). The bipyridones had carbonyl absorption at 6.00-6.05 μ in the infrared (potassium bromide) while the absorption at 6.12-6.18 μ present in all of the dibromides was absent in the bipyridones.

Catalytic hydrogenation of the diazepines 2 ($n = 3$), 4, and 8 gave the reduction products 12, 13, and 14. The fact that one of the aromatic rings was not reduced in the reduction of 8 to 14 was confirmed by the presence of a two proton peak at 6.98 δ in the nmr of 14.

The principal peaks in the mass spectrum of 2 ($n = 3$), 2 ($n = 4$), and 3 resemble those found in the mass spectrum of 2,2'-dipyridyl, while those in 8 resemble those in the mass spectrum of 1,10-phenanthroline. The mass spectrum

of 11 is included in the Experimental and appears to involve cleavages of CH_2 , CO, and HCN. The mass spectrum of the reduced diazepines confirm the presence of one aromatic ring in 14 and the fact that hydrogenolysis of the hydroxy group had not taken place during the reduction of 4 to 13.

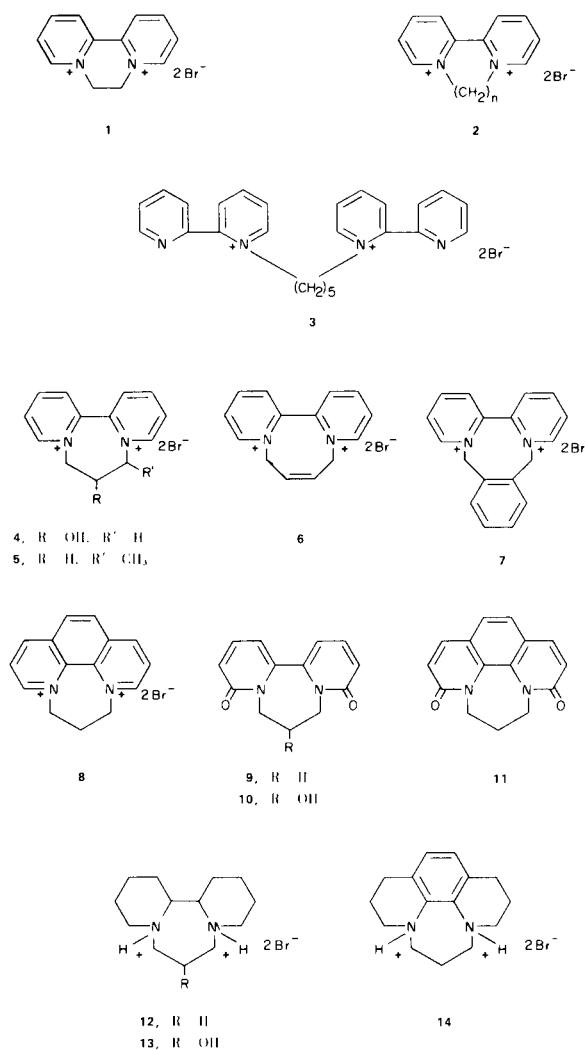


TABLE I
Condensation of Dihalides with 2,2'-Dipyridyl and 1,10-Phenanthroline

Compd. No.	Heating Period hours	Yield %	M.p.	Formula	Anal. (a)			Calcd. Found
					C	H	N	Br
2 (n = 2)	18.5	30	>365 (b)	C ₁₂ H ₁₂ Br ₂ N ₂	41.89	3.52		
					41.78	3.57		
2 (n = 3)(e)	18.5	44	320-321 (d)	C ₁₃ H ₁₄ Br ₂ N ₂	43.60	3.94	7.82	44.63
					43.56	3.88	7.79	44.42
2 (n = 4)	18.5	42	259-250 (e)	C ₁₄ H ₁₆ Br ₂ N ₂ (h)	42.13	4.12	7.02	
					42.03	4.18	6.91	
3	18.5	80	230-231	C ₂₅ H ₂₆ Br ₂ N ₄	55.36	4.83	10.33	29.48
					55.09	5.00	10.22	29.40 (f), 29.42 (g)
4	18.5	21	>360	C ₁₃ H ₁₄ Br ₂ N ₂ O	41.74	3.77	7.49	42.73
					41.84	3.84	7.38	42.60 (g)
5	18.5	30	271-272	C ₁₄ H ₁₆ Br ₂ N ₂	45.18	4.33	7.53	42.95
					45.13	4.34	7.58	42.91
6	1.0	84	225-229	C ₁₄ H ₁₄ Br ₂ N ₂				43.19
								43.13 (f), 42.96 (g)
7	0.75	90	269-271	C ₁₈ H ₁₆ Br ₂ N ₂	51.45	3.84	6.67	38.04
					41.32	3.77	6.64	37.89 (g)
8	3.5	87	279-281 (i)	C ₁₅ H ₁₄ Br ₂ N ₂	47.15	3.69	7.33	41.83
					47.34	3.78	7.47	41.66

(a) After drying at 110° *in vacuo*. (b) Reported (5) for hydrate, m.p. 340°. (c) Dipicrate, m.p. 213-214° (ethanol), Calcd. for C₂₅H₁₈N₈O₁₄: C, 45.88; H, 2.77; N, 17.12. Found: C, 45.85; H, 2.81; N, 17.33. (d) Reported (5) for hydrate, m.p. >300°. (e) Reported (5) for ·H₂O·1/3HBr, m.p. 265°. (f) Total Br. (g) Ionic Br. (h) Analysis includes 1/3HBr, see also footnote c. (i) Reported (7) m.p. 286°.

EXPERIMENTAL (10)

Typical Condensation.

A mixture of equimolar quantities of the dihaloalkane and the diazaheterocyclic compound were heated on a steam bath. After it had stood at room temperature, the mixture was filtered and washed with hexane or benzene to give after re-crystallization from methanol the compounds shown in Table I.

Oxidation of **2** (n = 3).

To 1.08 g. (0.003 mole) of **2** (n = 3) in 25 ml. of water was added with stirring 8.8 g. (0.027 mole) of potassium ferricyanide in 25 ml. of water. After stirring for 15 minutes 40 ml. of benzene was added and then 4.0 g. (0.1 mole) of sodium hydroxide in 40 ml. of water was added with stirring over 15 minutes. The mixture was stirred for 30 minutes and the benzene separated. Fresh benzene was added and the mixture was stirred for an additional 2 hours. The combined benzene phases were evaporated and the residue was recrystallized from ethanol to give 0.13 g. (20%) of **9**, m.p. 305-307°.

Anal. Calcd. for C₁₃H₁₂N₂O₂: C, 68.41; H, 5.30; N, 12.28. Found: C, 68.47; H, 5.51; N, 12.08.

Oxidation of **4**.

Reaction of **4** with alkaline potassium ferricyanide as described above gave a 33% yield of **10**, m.p. 194-196°.

Anal. Calcd. for C₁₃H₁₂N₂O₃: C, 63.92; H, 4.95; N, 11.47. Found: C, 63.78; H, 5.14; N, 11.33.

Oxidation of **8**.

Reaction of **8** with alkaline potassium ferricyanide as described above gave a 45% yield of **11**, m.p. 333-334°; mass spectrum: 253 (18%), 252 (100%), 251 (17%), 238 (13%), 237 (83%), 224 (6%), 223 (20%), 209 (6%), 208 (8%), 197 (19%), 196 (6%), 195 (6%), 179 (7%), 168 (7%), 126 (7%).

Anal. Calcd. for C₁₅H₁₂N₂O₂: C, 71.41; H, 4.80; N, 11.11. Found: C, 71.46; H, 4.78; N, 11.02.

Reduction of **2** (n = 3).

A mixture of 3.6 g. (0.01 mole) of **2** (n = 3) and 0.2 g. of platinum oxide in 140 ml. of ethanol was hydrogenated at room temperature and 50 psi. After 1 hour the uptake of hydrogen had stopped and the mixture was filtered. Evaporation of the ethanol gave 3.48 g. (94%) of a gum which was crystallized from ethanol to give **12**, m.p. 270-272°; mass spectrum: 209 (6%), 208 (30%), 193 (3%), 179 (3%), 166 (3%), 152 (3%), 151 (3%), 136 (3%), 126 (3%), 125 (13%), 124 (46%), 123 (14%), 122 (11%), 111 (10%), 110 (100%), 109 (9%), 98 (62%), 97 (86%), 96 (29%), 83 (36%), 82 (59%), 81 (20%), 80 (59%), 79 (20%), 69 (18%), 55 (15%), 42 (14%), 41 (22%).

Anal. Calcd. for C₁₃H₂₆Br₂N₂: C, 42.18; H, 7.08; N, 7.57. Found: C, 42.06; H, 6.99; N, 7.48.

Treatment with picric acid gave a picrate, m.p. 237-239°.

Anal. Calcd. for C₂₅H₃₀N₈O₁₄: C, 45.05; H, 4.54; N, 16.81. Found: C, 45.15; H, 4.69; N, 16.80.

Treatment with methyl iodide gave a methiodide, m.p. 247-248°.

Anal. Calcd. for $C_{15}H_{30}I_2N_2 \cdot 2H_2O$: C, 34.10; H, 6.49; N, 5.30. Found: C, 33.83; H, 6.18; N, 5.45.

Reduction of **4**.

In a similar manner reduction of **4** gave a 95% yield of a gum which was crystallized from ethanol to give **13**, m.p. 283-285°.

Anal. Calcd. for $C_{13}H_{26}Br_2N_2O$: C, 40.43; H, 6.79; N, 7.26. Found: C, 40.86; H, 7.04; N, 6.96.

Treatment with picric acid gave a dipicrate, m.p. 232-234°.

Anal. Calcd. for $C_{25}H_{30}N_8O_{15}$: C, 43.99; H, 4.43. Found: C, 43.79; H, 4.43.

Treatment with methyl iodide gave a dimethiodide, m.p. 221-223°; mass spectrum of the dimethiodide: 224 (3%), 207 (3%), 206 (5%), 156 (6%), 142 (59%), 141 (6%), 140 (5%), 128 (100%), 127 (66%), 126 (40%), 124 (6%), 98 (26%), 97 (30%), 96 (8%), 84 (7%), 45 (11%), 31 (27%).

Reduction of **8**.

In a similar manner reduction of **8** gave a 97% yield of **14**, m.p. 226-229° (from ethanol); mass spectrum: 229 (18%), 228 (100%), 227 (18%), 213 (5%), 212 (5%), 200 (10%), 199 (39%), 198 (5%), 187 (5%), 185 (7%), 172 (5%), 171 (10%), 170 (6%), 156 (5%), 114 (5%), 100 (10%), 82 (26%), 81 (10%), 80 (27%), 79 (10%).

Anal. Calcd. for $C_{15}H_{22}Br_2N_2$: C, 46.17; H, 5.68; N, 7.23. Found: C, 46.30; H, 5.68; N, 7.23.

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REFERENCES

- (1) For Part VIII see: A. C. Casey and F. D. Popp, *Org. Prepn. Proc.*, **2**, 29 (1970).
- (2) W. R. Boon, *Chem. Ind. (London)*, 782 (1965).
- (3) R. F. Homer, G. C. Mees, and T. E. Tomlinson, *J. Sci. Food Agric.*, **11**, 309 (1960).
- (4) G. C. Mees, *Ann. App. Biol.*, **48**, 601 (1960).
- (5) R. F. Homer and T. E. Tomlinson, *J. Chem. Soc.*, 2498 (1960).
- (6) I. C. Calder, T. McL. Spotswood, and C. I. Tanzer, *Aust. J. Chem.*, **20**, 1195 (1967).
- (7) Attempts to prepare the compound **2** ($n = 1$) have resulted in the formation of other structures: I. C. Calder, W. H. F. Sasse, and T. McL. Spotswood, *Aust. J. Chem.*, **16**, 289 (1963); and I. C. Calder and W. H. F. Sasse, *ibid.*, **18**, 1819 (1965).
- (8) After this portion of our work was completed, this compound was reported by L. A. Summers, *Tetrahedron*, **24**, 5433 (1968).
- (9) While this manuscript was in preparation the mono and dipyrindones of **2** ($n = 2$) were reported: A. Calderbank, D. F. Charlton, J. A. Ferrington, and R. James, *J. Chem. Soc. Perkin I*, 138 (1972).
- (10) Melting points were taken in capillaries and are corrected. Analyses by Spang Microanalytical Laboratory, Ann Arbor, Mich.