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Diazepines. II. Metal Complexes of 11*H*-Dibenzo[c,f]-[1,2]diazepine (1,2)

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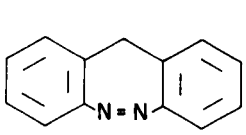
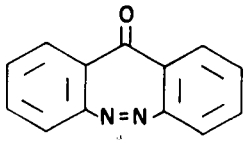
The participation of the azo group in metal chelate interaction has been reported by several groups (4) for aromatic azo compounds. More recently Porter and Murray have reported (4) on the complexes of 5,6-benzocinnoline, a cyclic aromatic azo compound. We now wish to report on our work on complexes of 11*H*-dibenzo[c,f]-[1,2]diazepine (I) and some related compounds.

Ethanolic solutions of the diazepine (I) were allowed to react with ethanolic solutions of the metal salts and dilute hydrochloric acid solutions of the diazepine (I) were allowed to react with dilute hydrochloric acid solutions of the metal salts. In most cases where a complex or salt formed precipitation occurred almost immediately but in all other cases the solutions were allowed to stand for several weeks at room temperature when in a few additional cases precipitates were obtained. Heating for short periods did not cause the formation of precipitates in any of the remaining cases. The results are summarized in Tables I and II.

It is of interest to note that both I and 5,6-benzocinnoline (4) gave immediate precipitates with either palladium chloride or silver nitrate while alcoholic solutions of azobenzene showed no noticeable interaction with either of these metal salts.



I



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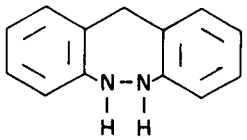

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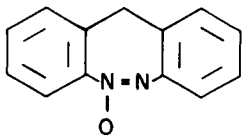

IV

TABLE I

Reactions of I with Metal Salts

Metal Salt Used	Solvent	Results
CuCl	EtOH	Ppt. after standing several weeks, see Table II
CuCl	dil HCl	No reaction apparent
H_2PtCl_6	EtOH	Ppt. after standing several weeks, see Table II
H_2PtCl_6	dil HCl	Immediate ppt., see Table II
$AgNO_3$	EtOH	Immediate ppt., see Table II
$AgNO_3$	dil HCl	No reaction apparent
$PdCl_2$	EtOH	Immediate ppt., see Table II
$PdCl_2$	dil HCl	No reaction apparent
$H_2OsCl_6 \cdot 2H_2O$	EtOH	No reaction apparent
$H_2OsCl_6 \cdot 2H_2O$	dil HCl	Immediate ppt., see Table II
$CoCl_3$	EtOH	No reaction apparent
$CoCl_3$	dil HCl	No reaction apparent
$OsCl_3$	EtOH	No reaction apparent
$OsCl_3$	dil HCl	No reaction apparent
$RuCl_3$	EtOH	No reaction apparent
$RuCl_3$	dil HCl	No reaction apparent
$UO_2(OAc)_2$	EtOH	No reaction apparent
$UO_2(OAc)_2$	dil HCl	No reaction apparent
$NiCl_2$	EtOH	No reaction apparent
$HAuCl_4 \cdot 3H_2O$	EtOH	Ppt. within 24 hours, see Table II
$Pd(NO_3)_2$	dil HCl	Immediate ppt., see Table II

TABLE II

Complexes Formed From I ($C_{13}H_{10}N_2$)

Metal Salt Used	M.p., °C	Formula	Calcd. C	Calcd. H	Calcd. N	Calcd. Cl	Calcd. Metal	Found C	Found H	Found N	Found Cl	Found Metal
CuCl (b)	>360	$(C_{13}H_{10}N_2)CuCl$ (c)	53.25	3.44	9.55	12.09	21.67	53.16	3.37	9.60	12.21	21.48
H_2PtCl_6 (d)	>360	$(C_{13}H_{10}N_2)_2H_2PtCl_6$ (c)	39.11	2.78	7.02	26.64	24.45	38.85	2.84	6.83	26.78	24.42
H_2PtCl_6 (b)	>360	$(C_{13}H_{10}N_2)PtCl_2$ (e)	33.91	2.19	6.09	15.40	42.41	34.49	1.92	6.13	14.90	41.37
$AgNO_3$ (b)	245-7	$(C_{13}H_{10}N_2)AgNO_3$ (c)	42.88	2.77	11.54		29.63	42.68	2.88	11.45		29.80
$PdCl_2$ (b)	274-6	$(C_{13}H_{10}N_2)_2PdCl_2$ (e)	55.16	3.56	9.89	12.52	18.84	54.98	3.70	9.72	12.60	18.95
$H_2OsCl_6 \cdot 2H_2O$ (d)	>360	(f)						32.15	2.99	6.20	17.65	33.60
$HAuCl_4 \cdot 3H_2O$ (b)	>360	$(C_{13}H_{10}N_2)AuCl_3$ (e,g)	31.36	2.03	5.63	21.37	39.62	30.38	1.86	5.59	20.67	40.80
$Pd(NO_3)_2$ (d)	>360	(f)						53.98	3.59	9.20	14.30	14.07

(a) Analysis by Spang, Gailbraith, and Schwarzkopf Laboratories. (b) In ethanol. (c) Molecular weight determination agrees with this structure. (d) In dilute hydrochloric acid. (e) Too insoluble for molecular weight determination, formula may be a multiple of this. (f) Analysis does not indicate any reasonable, simple structure. (g) Gave analytical results that were difficult to reproduce.

The copper complex of I hydrolyzed to the starting diazepine upon standing overnight in water, the palladium and silver complexes of I, however, were stable under these conditions and in fact the silver complex of I was stable when refluxed with dilute hydrochloric acid.

The infrared spectra of the three complexes formed in dilute hydrochloric acid were essentially identical while the infrared spectra of the five complexes formed in ethanol were very similar to each other but considerably more complex than the spectra of the complexes formed in dilute hydrochloric acid. Both sets of spectra differed from that of the diazepine (I) but the spectra of the complexes formed in ethanol were more closely related to the spectrum of I.

Reaction of ethanolic silver nitrate with the related compounds II and IV and reaction of chloroplatinic acid in dilute hydrochloric acid with II and III under the conditions used with compound I did not lead to the formation of any complex. Reaction of ethanolic silver nitrate with III led to the isolation of a small amount of black powder believed to be metallic silver and the silver complex of I (identical to that formed from I and ethanolic silver nitrate) through an oxidation-reduction reaction.

Oxidation of the silver complex of I (under conditions used for the oxidation of compounds of the type I to ketones of the type II (1)) gave rise to the ketone II.

EXPERIMENTAL

Formation of Complexes.

A solution of 0.05 g. of diazepine (I) (or compounds II, III, or IV) in ethanol or 5% hydrochloric acid was treated with an excess of the metal salt in ethanol or 5% hydrochloric acid and allowed to stand at room temperature as indicated in Table I. Any precipitate obtained was filtered and washed (in a few cases the complexes could be recrystallized but generally they were too insoluble in common solvents). The complexes obtained are included in Table II. In cases where a precipitate was not obtained on standing the solutions were heated on a steam bath without any effect.

Oxidation of $[C_{13}H_{10}N_2]AgNO_3$.

A solution of 0.1 g. of the silver complex in 20 ml. of refluxing glacial acetic acid was treated with 0.06 g. of chromic oxide (1) to give dibenzo[c,f]-[1,2]diazepin-11-one (II).

REFERENCES

(1) Part I. A. Catala and F. D. Popp, *J. Heterocyclic Chem.*, 1, 178 (1964).

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(3) N.S.F. Undergraduate Research Participant.

(4) For leading references see J. J. Porter and J. L. Murray, *J. Am. Chem. Soc.*, 87, 1628 (1965).

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