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Abstract

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SYNTHESIS OF COMPLEXES OF ALDAZINES AND KETAZINES WITH CUPROUS HALIDE

As was found earlier, hydrazones of aldehydes and ketones readily react with mercuric acetate in water, methanol, and benzene media with liberation of nitrogen, basic mercury salts, and formation of organomercury compounds (1). In the course of studying the reactions of oxidation of hydrazones by salts of other heavy metals, we investigated the interaction of hydrazones with cupric acetate, and then with cupric chloride and bromide in water and methanol media. It turned out that previously undescribed complexes of aldazines and ketazines with cuprous halide of composition $(R = N—N = R) \cdot n$CuX are formed, where X is Cl, Br, or J, and $n = 2$ or 3.

The reactions proceed readily in the cold when a hydrazone is added to an aqueous or methanolic solution of a cupric halide; liberation of nitrogen and precipitation of a white precipitate of the complex are observed. When the reaction is carried out in methanol, an additional amount of complex is isolated by diluting the alcoholic filtrate with water. In the case of the reaction with cupric acetate, liberation of nitrogen and precipitation of a red precipitate of cuprous oxide are observed. The cuprous oxide is filtered off and the filtrate is treated with an aqueous solution of the corresponding potassium halide KX, where X is Cl, Br, or J.

Analogous complexes of azines are also formed upon interaction of azines with cupric halide salts in an aqueous medium, and in some cases upon interaction of aldehydes or ketones with copper salts and hydrazine hydrate*.

The preparation of azine complexes with cuprous halide by the three methods indicated above may be represented as follows:

I. **Interaction of hydrazones with cupric halide**

$$R_2C = N—NH_2 + CuX_2 \rightarrow (R_2C = N)_2 \cdot nCuX + N_2 + HX.$$

Apparently, the hydrazine formed as a result of disproportionation of the hydrazone (stage 1) reduces cupric halide to cuprous halide (stage 2); at the moment of formation the latter reacts with the azine, giving a complex (stage 3).

1) $R_2C=N—NH_2 \rightarrow (R_2C=N)_2 + NH_2NH_2$ **,
2) $NH_2NH_2 + CuX_2 \rightarrow CuX + N_2 + HX$,
3) $(R_2C=N)_2 + n\,CuX \rightarrow (R_2C=N)_2 \cdot n\,CuX$.

II. **Interaction of azines with cupric halide**

$$(R_2C=N)_2 + CuX_2 + H_2O \rightarrow (R_2C=N)_2 \cdot n\,CuX + N_2 + HX + R_2CO.$$

In this reaction, the hydrazine required for reduction of the salts

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* Direct interaction of azines with cuprous copper salts cannot serve as a convenient method for synthesizing the complexes, since the reaction proceeds with low yield, and the substances formed are highly contaminated and are difficult to purify.

** The formation of azine and hydrazine can also be represented in another way: $R_2C=N—NH_2 + H_2O \rightarrow R_2CO + NH_2NH_2$; $R_2C=N—NH_2 + R_2CO \rightarrow (R_2C=N)_2 + H_2O$, etc.

divalent copper, is formed upon hydrolysis of the azine:

1) $(R_2C=N)_2 + H_2O \rightarrow R_2CO + NH_2NH_2$,
2) $NH_2NH_2 + CuX_2 \rightarrow CuX + N_2 + HX$,
3) $(R_2C=N)_2 + nCuX \rightarrow (R_2C=N)_2 \cdot nCuX$.

III. Interaction of cupric halide with a mixture of a carbonyl compound and hydrazine hydrate:

$$R_2CO + NH_2NH_2 + CuX_2 \rightarrow (R_2C=N)_2 \cdot nCuX + N_2 + HX + H_2O.$$

1) $R_2CO + NH_2NH_2 \rightarrow (R_2C=N)_2 + H_2O$,
2) $NH_2NH_2 + CuX_2 \rightarrow CuX + N_2 + HX$,
3) $(R_2C=N)_2 + nCuX \rightarrow (R_2C=N)_2 \cdot nCuX$.

Reaction I was studied using hydrazones of acetaldehyde, acetone, methyl ethyl ketone, isovaleraldehyde, and cyclohexanone as examples, both in water and in methanol. It turned out that hydrazones of aliphatic aldehydes react with cupric bromide with formation of complexes of the type $(R=N-N=R)\cdot 2CuBr$, whereas hydrazones of aliphatic ketones form complexes of the type $(R=N-N=R)\cdot 3CuBr$.

All the reactions carried out with hydrazones are summarized in Table 1.

Table 1*

Starting hydrazone	Products of reaction with $CuBr_2$ in CH_3OH	Products of reaction with $CuBr_2$ in H_2O	Products of reaction with $CuCl_2 \cdot 2H_2O$ in CH_3OH	Products of reaction with $CuCl_2 \cdot 2H_2O$ in H_2O	Products of reaction with $Cu(OCOCH_3)_2 \cdot H_2O$ in CH_3OH	Products of reaction with $Cu(OCOCH_3)_2 \cdot H_2O$ in H_2O
Acetaldehyde hydrazone	A · 2CuBr	A · 2CuBr		A · 2CuCl		A · 2CuBrA · 3CuJ
Acetone hydrazone	A · 3CuBr	A · 3CuBr	A · 3CuCl	A · 2CuCl	A · 3CuBr	A · 3CuBr
Methyl ethyl ketone hydrazone	A · 3CuBr	A · 3CuBr	A · 3CuCl			A · 3CuBrA · 3CuJ
Isovaleraldehyde hydrazone	A · 2CuBr	Oil	A · 2CuCl	A · 2CuCl	Oil	
Cyclohexanone hydrazone	A · 2CuBr	A · 2CuBr	A · 3CuCl	A · 2CuCl	A · 3CuClA · 2CuBrA · 2CuJ	

* A —azine.

Reaction II was studied using azines of acetone, methyl ethyl ketone, and cyclohexanone as examples. For the reaction to proceed, the presence of water is necessary (partial hydrolysis of the azine with liberation of hydrazine). The same complexes as from hydrazones are formed as reaction products. The reactions are given in Table 2.

Table 2*

Starting azine	Products of reaction with $CuBr_2$	Products of reaction with $CuCl_2 \cdot 2H_2O$	Products of reaction with $Cu(OCOCH_3)_2 \cdot H_2O$
Acetone azine	A · 3CuBr	A · 2CuCl	
Methyl ethyl ketone azine	A · 3CuBr	A · 3CuCl	

Starting azine	Products of reaction with $CuBr_2$	Products of reaction with $CuCl_2 \cdot 2H_2O$	Products of reaction with $Cu(OCOCH_3)_2 \cdot H_2O$
Cyclohexanone azine	A · 2CuBr		A · 2CuBrA · 2CuCl

* A –azine; medium –water.

Reaction III was studied with acetaldehyde, acetone, methyl ethyl ketone, and cyclohexanone as examples. In all cases, with cuprous bromide in methanol medium, complexes of the type $(R = N - N = R) \cdot 2CuBr$ are formed.

Complexes $(R = N - N = R) \cdot nCuX$ could be obtained from the azines of acetone ($n = 3$) and cyclohexanone ($n = 2$) and cuprous bromide by heating the initial components in methanol (see the footnote on p. 1098). For the azines of acetaldehyde, methyl ethyl ketone, and isovaleraldehyde, it proved impossible to carry out this reaction at all. Apparently, the complexes formed on boiling in methanol decompose back, with liberation of the initial azine and cuprous halide.

The complexes obtained are white crystalline substances, soluble with decomposition in ammonia and dilute hydrochloric acid. For analysis they can be purified by recrystallization from a mixture of methanol and an aqueous solution of the corresponding potassium or sodium halide. The substances are stable in air in the dry state and are rapidly oxidized in the moist state.

Table 3

R	X	n	Methods of preparation	M.p., °C	Calc. C, %	Calc. H, %	Calc. X, %	Calc. N, %	Found C, %	Found H, %	Found X, %	Found N, %
CH_3CH	Cl	2	I, II, III	Decomp.	17.03	2.84	25.14		16.60	2.87	25.51	
CH_3CH	Br	2	I, II, III	187 – 188	12.95	2.15	43.09		12.82	2.23	43.26	
CH_3CH	I	3	I	Decomp.	7.32	1.22			6.58	1.32		
$(CH_3)_2C$	Cl	2	I, II	Decomp.	23.23	3.87		9.03	23.29	4.01		8.98
$(CH_3)_2C$	Cl	3	I, II	Decomp.	17.65	2.93			16.75	2.90		
$(CH_3)_2C$	Br	2	III	Decomp.	18.06	2.99			17.33	2.96		

R	X	n	Methods of preparation	M.p., °C	Calc. C, %	Calc. H, %	Calc. X, %	Calc. N, %	Found C, %	Found H, %	Found X, %	Found N, %
$(CH_3)_2C$	Br	3	I, II, III	233 – 235	13.27	2.21		5.17	13.27	2.15		5.09
C_2H_5 CH_3 C	Cl	3	I, II	Decomp.	21.98	3.66	24.34	6.41	22.15	3.78	24.62	6.45
C_2H_5 CH_3 C	Br	3	I, II	Decomp.	16.84	2.80	42.03	4.90	16.63	2.82	42.85	4.81
C_2H_5 CH_3 C	I	3	I, II	Decomp.	13.50	2.24			12.28	2.23		
iso-C_4H_9CH	Cl	2	I	Decomp.	33.05	5.46	19.37		32.49	5.43	20.12	
iso-C_4H_9CH	Br	2	I, II	Decomp.	26.59	4.39	35.91		26.35	4.33	35.65	
cyclohexylidene	Cl	2	I, II	179 – 180	36.94	5.12	18.00		36.53	5.48	17.10	
cyclohexylidene	Br	2	I, II	225 – 226	30.06	4.17	33.37	5.83	30.11	4.13	33.26	5.97
cyclohexylidene	I	2	I	218 – 220	25.15	3.49			24.42	3.46		

The complexes with cuprous bromide are usually more stable than those with cuprous chloride. The structure of the complexes was established on the basis of analytical data and by decomposition on heating with 10% alkali to cuprous oxide and the corresponding azine.

Table 3 summarizes all the complexes of azines with cuprous halide obtained by us, $(R = N - N = R) \cdot nCuX$.

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Note: Figure translations are in progress. See original paper for figures.

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