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ACTION OF METAL SALTS ON α-BENZOINOXIME

E.A. EL-SAWI*, T.B. MOSTAFA, I.KH. EL-SAYED, and S.M. AHMED

University College For Women, Ain Shams University, Heliobolis, Cairo, EGYPT

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ABSTRACT

Cobalt (II) nickel (II) and copper (II) salts reacted with α-benzoinoxime in polar and non-polar solvents to give mono-, di-, and trimetallated porducts via replacement of hydroxy hydrogen followed by electrophilic substitution on organic moiety, bond cleavages and bond formation. The mechanism of the reactions were studied. The structures were confirmed by analytical data, IR, UV and mass spectra.

INTRODUCTION

It is well known that benzoinoxime behaves as a dibasic acid towards Cu^{+2} ions, where it forms, green amorphous precipitate of the copper (II) salt in neutral or ammoniacal solutions. This test is used as a spot test for Cu(II) (0.1 γ copper)[1] and copper benzoinoxime can be extracted in chloroform. It can be also used as 2 spot test for vanadium as metavanadate ion probably there is an anhydride formation between OH groups of the metallo acids and the OH or N-OH group of the benzoin-oxime molecule. The formation of the yellow acid insoluble vanadium benzoinoxime compound is specific for vanadium (1 γ copper)[2].

In continuation of our previous studies on metallation reactions,[3-8] and on the action of some metal salts on organic reagents,[9-17] this work is directed towards the study of the action of metal salts such as cobalt (II), nickel (II) and copper (II) acetates and chlorides on α-benzoinoxime in polar solvents such as methanol or acetic acid and a non-polar solvent such as toluene.

RESULTS AND DISCUSSION

Cobalt (II) acetate reacts with α-benzoinoxime in methanol under reflux to give mono-cobalated product, and the reaction is believed to

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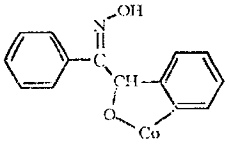
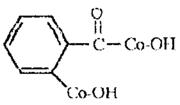
* To whom all correspondences should be addressed.

take place via replacement of the hydrogen of the hydroxyl group followed by electrophilic attack on phenyl moiety to give compound, **1**.



1

If the reaction is carried out in acetic acid it proceeds to give compounds, **2**, **3a**, and/or **3b**.



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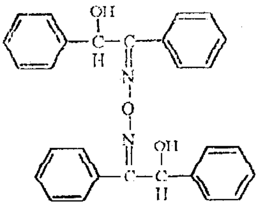
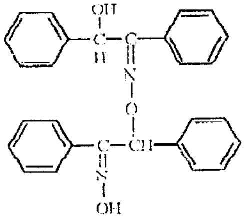


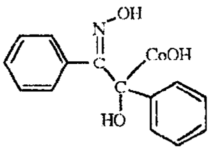
3a

or



3b

The reaction in refluxing toluene results in formulation of product, **4**.

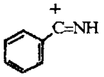


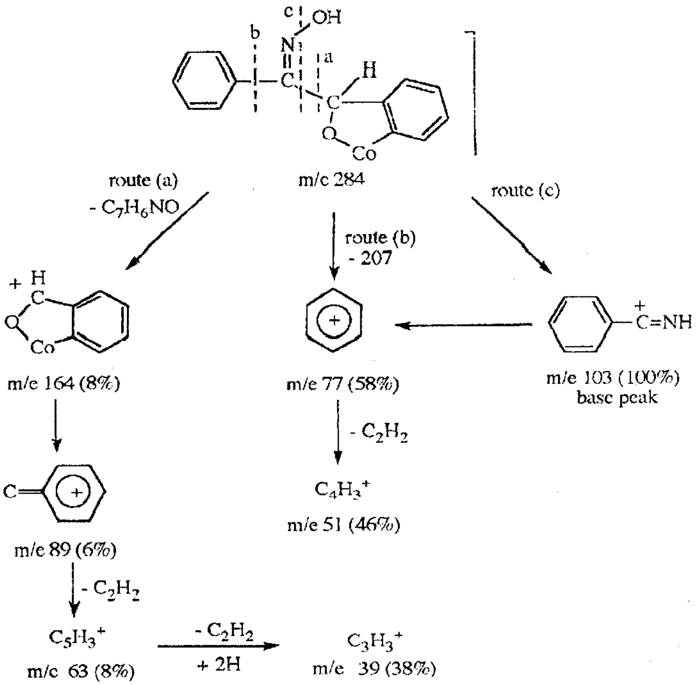
4

It is clear that the reaction in methanol proceeds via replacement of H of the hydroxyl group attached to carbon followed by electrophilic substitution, whereas the reaction in acetic acid proceeds via bond cleavage, metallation and oxidation, but in toluene metallation took place on carbon of the methine group.

The suggested structures are based on analytical data, IR, UV and MS spectra.

The IR spectrum for compound **1** shows new absorption bands at 535, 440 and 740 cm^{-1} due to $\upsilon_{C\text{-}Co}$, $\upsilon_{Co\text{-}C}$,[18] and $\upsilon_{C\text{-}H}$ out of plane deformation showing 1,2-disubstituted benzene, UV spectrum shows λ_{max} at 291.4 nm (ε = 0.1046 x 10^2) and a shoulder at 390.3 nm (ε = 0.0363 x 10^2), which can be attributed to π-π^* and n-π^* transitions. The MS spectrum shows the molecular ion peak at m/e 284. The base peak et m/e 103 is attributed to the ion shown below:

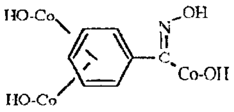




The IR spectrum for compound **2** shows $\upsilon_{O\text{-}H}$ at 3600-2800 cm^{-1}, $\upsilon_{C=O}$ at 1660 cm^{-1}, $\upsilon_{C\text{-}Co}$ 535 cm^{-1} and $\upsilon_{C\text{-}H}$ out of plan deformation showing 1,2-disubstituted benzene at 770-735 cm^{-1}. The UV spectrum shows λ_{max}, at 308.5 nm (ε = 0.1395 x 10^2). The suggested structures for compounds **3a** & **3b** are in good agreement with the data obtained.

The IR spectrum for compound **4** shows new absorption bands at 520 and 420 cm^{-1} due to $\upsilon_{Co\text{-}C}$ and $\upsilon_{Co\text{-}O}$ respectively. The UV spectrum shows λ_{max} at 292 nm (ε = 0.809 x 10^2) and at 388.6 nm (shoulder) (ε = 0.220 x 10^2).

α-Benzoinoxime reacts with cobalt chloride either in methanol or in toluene to give crystalline product **5**.



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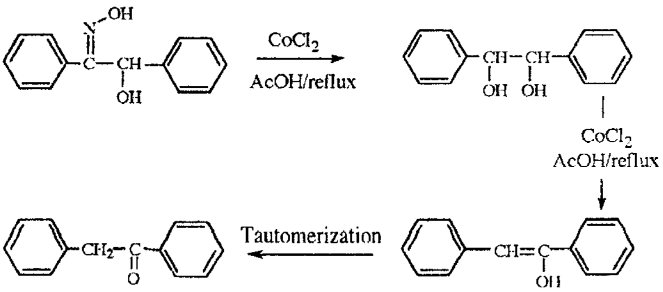
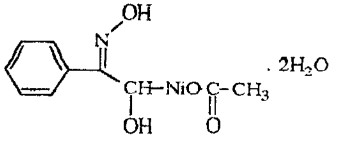
The IR spectrum shows new bands for Co-O and Co-C at 430 cm^{-1} and 520 cm^{-1}. The UV spectrum shows λ_{max} at 287.6 nm (ε = 0.129 x 10^2) and λ_{max} at 382.6 nm (ε = 0.391 x 10^2).

The reaction with cobalt chloride in refluxing acetic acid, gives rise to product **6** which is believed to be formed by a series of reactions i.e. C-C bond cleavage followed by dimerization, dehydration and tautomerisation under the reaction conditions. In this reaction cobalt chloride acts as a catalyst.



The IR spectrum shows $\upsilon_{C=O}$ at 1670 cm^{-1}, υ_{C-H} bending at 1450 cm^{-1} and υ_{C-H} stretching at 2990-2820 cm^{-1}. The UV spectrum shows λ_{max} at 289.3 nm (ε = 0.06518 x 10^2).

The reactions of nickel (II) acetate in methanol; acetic acid and toluene give rise to mononickelated product **7** where C-C bond cleavage took place; dinickelated product **8** and **9** respectively. Product **9** was identilfied to be dl-syn form of α-benzoinoxime. Analytical data, IR and UV spectra confirm the proposed structures.



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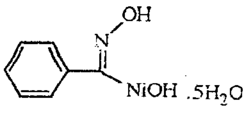
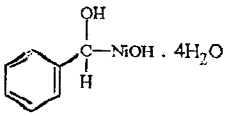


8

α-Benzoinoxime reacts with nickel (II) chloride either in methanol or in toluene under reflux to give crystalline products **10** and **11**, where compound **11** is obtained on evaporating the filtrate. They took place via C-C bond cleavage followed by metallation.



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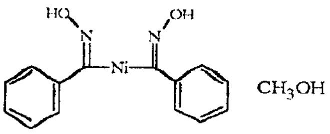

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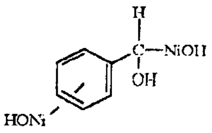
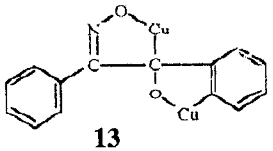
When the reaction is carried out in acetic acid it gives rise to dinickelated product, **12**.



12

The IR spectra for compounds **7**, **8**, **10** and **12** show new absorption bands for $\upsilon_{C\text{-}Ni}$; at 490 cm^{-1} and $\upsilon_{O\text{-}Ni}$ at 420 cm^{-1}. The IR for compound **11** show $\upsilon_{C\text{-}Ni}$ at 490 cm^{-1} and $\upsilon_{C=N}$ at 1640 cm^{-1}.

Copper (II) acetate reacts with α-benzoinoxime under reflux in polar solvents such as methanol and acetic acid to give product **13** and products **14** and **15** respectively.



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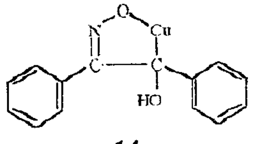

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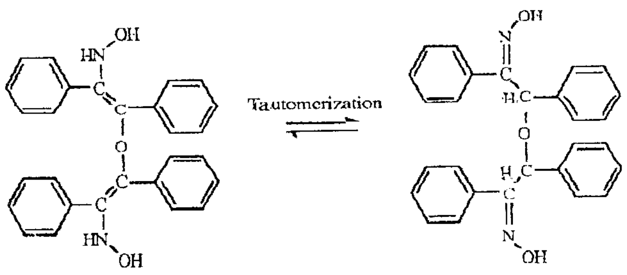
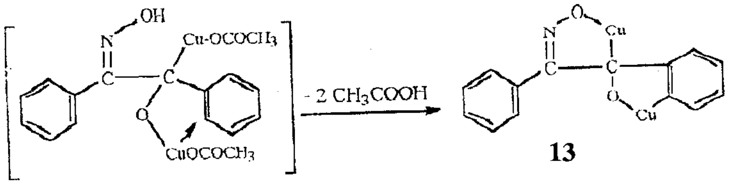


enhydroxylamine **15a** oxime **15b**

The IR spectrum for compound **13** shows $\upsilon_{C=N}$, $\upsilon_{Cu\text{-}C}$ and $\upsilon_{Cu\text{-}O}$ at 1640 cm^{-1}, 510 cm^{-1} and 460 cm^{-1} and shows difference in the region of $\upsilon(Ar)_{C\text{-}H}$ out of plane bending frequency with reference to the parent compound, which may be attributed to electrophilic substitution on one ring as shown.



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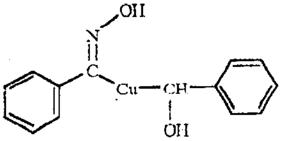
IR spectrum for compound **14** shows $\upsilon_{Cu\text{-}O}$, $\upsilon_{Cu\text{-}C}$ and $\upsilon_{C\text{-}OH}$ at 510, 460 and 1150 cm^{-1}. Compound **15a** is obtained beside compound **14** from the same reaction. It shows new bands for $\upsilon_{C=C}$ (or) $\upsilon_{C=N}$, $\upsilon_{C\text{-}O\text{-}C}$, $\upsilon_{C\text{-}H}$, υ_{NH} and υ_{OH} at 1655, 1170, 2980, 2850, 3180 and 3340 cm^{-1} respectively.

Its UV spectrum shows λ_{max} at 304 nm ($\varepsilon = 0.158 \times 10^2$) when carried out in methanol at the moment of preparing the solution. After 2 days the UV spectrum shows λ_{max} at 287.8 nm for the same solution, this can be attributed to tautomeric form **15b**.

The reaction of copper (II) acetate with α-benzoinoxime in boiling toluene yields product **16**. The reaction proceeds via C-C bond cleavage and formation of C-Cu-C bond.



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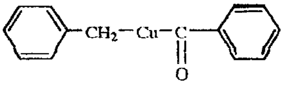
Copper (II) chloride reacts with α-benzoinoxime (1:1 molar ratio) in refluxing methanol, acetic acid as polar solvents or in toluene as non-polar solvent to give products **17**, **18** and **19** respectively.



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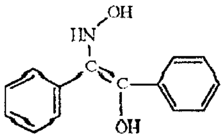

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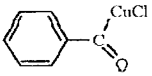
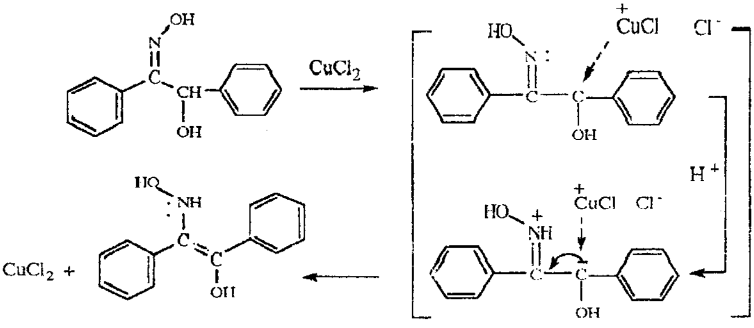


19

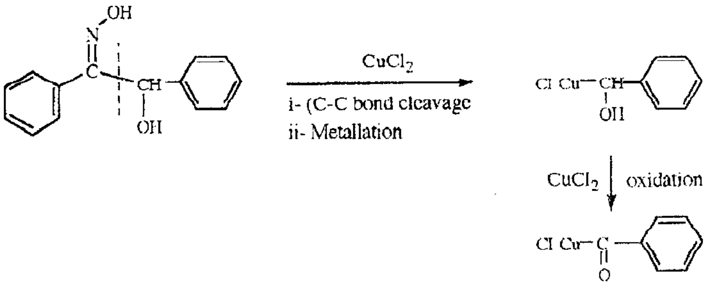
Compound **18** is formed according to the proposed mechanism as follows:



18

All the suggested structures are confirmed by analytical data, IR & UV.

Compound **19** was thought to be formed via C-C bond cleavage, metallation and finally oxidation.



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EXPERIMENTAL

General procedure

A mixture of metal salt (0.01 mole) and α-benzoinoxime (0.01 mole) in 20 ml solvent was boiled under reflux for three hours. The reaction mixture was left to cool. The separated crystalline product was filtered dried and recrystallized.

The suitable solvent for crystallisation, melting points, % yields and elemental analysis are given in Table (1).

Table 1

Compd. No	Molecular Formula	M.P.°C (Solvent of cryst.)	% yield	% Analysis, (f/Calcd.) C	H	N	M
1	$C_{14}H_{11}O_2NCo$	208-9	98.67	59.00	4.1	5.0	20.41
		(*)		59.17	3.87	4.93	20.74
2	$C_7H_6O_3Co_2.6H_2O$	224-5	41.20	23.7	5.20	–	31.98
		(**)		23.09	4.94	–	32.38
3	$C_{28}H_{24}O_3N_2$	85-86	45.80	77.09	5.43	6.8	–
		(*)		77.06	5.50	6.40	–
4	$C_{14}H_{13}O_3NCo.3H_2O$	220	98.30	47.40	5.0	3.9	6.46
		(**)		47.20	5.33	3.93	6.54
5	$C_7H_7O_4NCo_3.8H_2O$	225	91.89	17.20	5.10	2.50	35.89
		(**)		17.15	4.69	2.86	36.08
6	$C_{14}H_{12}O$	59.60	94.45	79.43	6.29	–	–
		(***)		79.34	6.39	–	–
7	$C_{10}H_{11}O_4NNi.2H_2O$	220 (d.)	18.78	39.40	5.20	4.60	18.95
		(*)		39.50	4.90	4.60	18.32
8	$C_7H_7O_3NNi.5H_2O$	115-16	97.11	23.58	4.50	3.30	32.33
		(***)		23.30	4.71	3.80	32.57
9	$C_{14}H_{13}O_2N$	99	88.10	73.85	5.35	6.40	–
		(***)		74.00	5.72	6.17	–

* Pet. Ether (40-60) ** Methanol/Ether *** Ether

Analytical data *continue*

Compd.	Molecular	M.P.°C	% yield	% Analysis, (f/Calcd.)			
No	Formula	(Solvent of cryst.)		C	H	N	M
10	$C_{14}H_{12}O_2N_2Ni.$	220 (d)	30.23	54.67	5.03	8.40	17.54
	CH_3OH	(**)		54.42	4.83	8.40	17.75
11	$C_7H_8O_2Ni.4H_2O$	235 (d)	62-81	32.45	6.21	–	23.00
				32.97	6.28	–	23.04
12	$C_{11}H_{13}O_5Ni_2.8H_2O$	230 (d)	92.25	27.78	5.78	–	23.95
		(***)		27.13	5.96	–	24.13
13	$C_{14}H_9O_2NCu_2.$	250	93.33	42.20	4.50	3.50	27.97
	$2CH_3OH.2H_2O$	(*)		42.60	4.60	3.10	28.22
14	$C_{14}H_{11}O_2NCu.H_2O$	265	32.62	55.30	4.20	4.40	20.55
		(**)		54.80	4.20	4.30	20.71
15	$C_{28}H_{24}O_3N_2$	85	57.33	77.10	3.50	6.70	–
		(*)		77.06	3.50	6.40	–
16	$C_{14}H_{13}O_2NCu.$	125	89.41	49.40	5.20	4.00	18.68
	$2.5H_2O$	(**)		50.07	5.30	4.17	18.92
17	$C_{14}H_{12}OCu.5CH_3OH$	80-81	95.35	53.90	7.67	–	15.05
		(**)		54.35	7.62	–	15.13
18	$C_{14}H_{13}O_2N$	80	88.10	73.70	5.64	5.89	–
		(**)		74.00	5.72	6.17	–
19	$C_7H_5OCu.Cl.2H_2O.$	136	90.42	30.63	3.43	–	22.57
	HCl	(**)		30.37	3.60	–	22.96

* Pet. Ether (40-60) ** Methanol/Ether *** Ether

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