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2-AMINATION OF 1,4-DIHYDROXYANTHRAQUINONE PROMOTED BY COPPER IONS

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2-Amination of 1,4-dihydroxyanthraquinone(DHAQ) was initiated by the formation of copper complex, which was oxidized to quinizarinquinone followed by the Michael addition of amines. Quantitative 2-amination of quinizarinquinone and reduction of copper ions to metal copper supported the mechanism.

In our previous paper1), the quantitative 2-butylamination of DHAQ 1 in the presence of copper salts at ambient temperature was reported. Metal complex formed between quinone carbonyl group and α-hydroxy group played a great role on this amination. It had been reported that the reaction of DHAQ-dimetaborate with amine gave 2-amino-DHAQ in a quantitative yield under atmospheric oxygen2). Some of the oxidizing agents, such as metal ions or oxygen, were necessary on this amination.

In this paper, we intend to clear the mechanism of this 2-amination of 1. In the reaction of 1 with butylamine in the presence of copper salts, reduction of copper ions to metal copper was observed (Table 1).

Table 1. The effect of copper salt on the 2-amination of 1a)

Run	Copper salt	Mole ratio Cu-salt/DHAQ	Temp. (°C)	Time (hr)	1b)	Yield(%) 2c)	3d)	4e)	Cu
1	none	-	30	24	0	7.3	21.4	48.1	0
2	$CuCl_2 \cdot 2H_2O$	2	34	24	0	0	0	100	0
3	"	1	30	24	0	0.6	0	76.3	3.8
4	"	1/2	30	48	1.8	6.9	0	61.5	22.8
5	CuCl	2	34	24	0	0	0	100	30.8

a) Reactant 1 (5 mmol) was stirred in pyridine(8 ml) with butylamine(228 mmol) and copper salt in presence of air. b)Recovered of 1. c) 1-Hydroxy-4-butylaminoanthraquinone. d) 1,4-Bisbutylaminoanthraquinone. e) 1,4-Dihydroxy-2-butylaminoanthraquinone.

None of the reduction of copper salts was observed when copper salts in pyridine were treated with amines without DHAQ. Therefore, the oxydation of 1 by copper salts was proposed. The amount of copper deposited was increased with a decrease in the mole ratio of Cu-salt/DHAQ, and the yield of 4 was decreased with the increase of 2. If there were enough amount of copper ion, none of metal copper was isolated(Run 2). In the case of Cu(I)Cl, 4 was obtained in a quantitative yield and 30.8% of metal copper was isolated (Run 5). Comparison of the results of Run 2 and Run 5 suggest one electron reduction of copper ion for each of chelate ring. If stoichiometrically enough copper ion did not present (Run 3 and 4), the reduction of Cu(II) ion to metal copper might proceed, but the details were not obvious. Without copper salt, 4 was obtained together with 2 and 3. From these results, it was found that the competitive α- and β-amination of 1 proceeded during the reaction but the metal complex was predominantly aminated at β-position. The effects of atmospheric oxygen as an oxidizing agent[3)] were obvious but undesirable by-products (2 and 3) were obtained under the atmospheric oxygen without metal ions (Run 1). The yields of 5 were decreased drastically under N_2 atmosphere or without oxygen (Run 7 and 8). While if enough amount of cupric chloride was present, 4 was obtained quantitatively even under the N_2 atmosphere (Run 9).

Table 2. The effect of atmosphere on the 2-amination of 1[a)]

Run	Metal salt	Amine	Atmosphere	Temp.(°C)	Time(hr)	Yield(%) 1[b)]	Yield(%) 5[c)]
6	none	Piperidine	open	30	48	0.5	89.3
7[d)]	"	"	N_2	30	24	4.1	28.0
8[e)]	"	"	f)	30	24	3.1	28.3
9	$CuCl_2 \cdot 2H_2O$[g)]	Butylamine	N_2	23	24	0	100[h)]

a) The mole ratio of reagents are the same as that of Table 1. b) Recovered of 1. c) 1,4-Dihydroxy-2-piperidinoanthraquinone. d) 2,2'-Bis-DHAQ was obtained in a yield of 27.8%. e) α-Amination also proceeded as same the case of Run 1. f) Deoxygenation was carried out three times as follows; The reaction mixture was frozen with liquid N_2 and deoxygenated under reduced pressure. The reaction was carried out under reduced pressure. g) Cu-salt/DHAQ (mole ratio)=2 h) The yield of 4.

On the other hand, butylamination of quinizarinquinone 6, which was prepared previously by the oxidation of 1 with lead tetraacetate[4)], gave 4 quantitatively at ambient temperature. These Michael addition of amines to p-quinone were well known[5)].

The possible mechanism of 2-amination of 1 may be proposed as follows.

$$1 + 2\,RNH_2 \longrightarrow \text{Dianion} + 2\,RNH_3^+ \quad \text{----- (1) Dianion formation}$$

$$\text{Dianion} + 2\,CuCl \longrightarrow \text{Cu(I)-Complex} \quad \text{----------- (2) Complex formation}^{6)}$$

$$\text{Cu(I)-Complex} \longrightarrow \text{Quinizarinquinone } 6 + 2\,Cu \quad \text{--- (3) Oxidation of 1}$$

$$6 + RNH_2 \longrightarrow 4 \quad \text{-------------- (4) Michael addition}$$

References and Notes

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