

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-dimethanolate 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 1^{a)}

Run	Copper salt	Mole ratio Cu-salt/DHAQ	Temp. (°C)	Time (hr)	Yield(%)				Cu
					<u>1</u> ^{b)}	<u>2</u> ^{c)}	<u>3</u> ^{d)}	<u>4</u> ^{e)}	
1	none	-	30	24	0	7.3	21.4	48.1	0
2	CuCl ₂ ·2H ₂ O	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 agent³⁾ 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 N₂ atmosphere or without oxygen (Run 7 and 8). While if enough amount of cupric chloride was present, 4 was obtained quantitatively even under the N₂ atmosphere (Run 9).

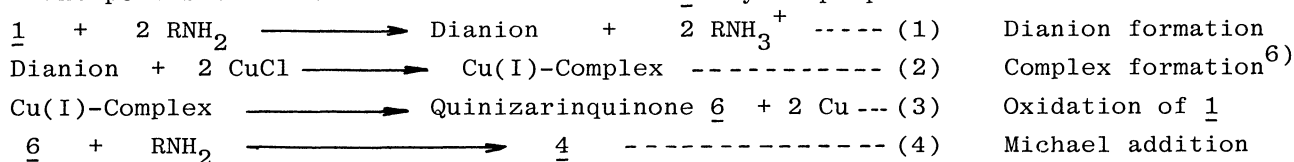
Table 2. The effect of atmosphere on the 2-amination of 1^{a)}

Run	Metal salt	Amine	Atmosphere	Temp.(°C)	Time(hr)	Yield(%)	
						<u>1</u> ^{b)}	<u>5</u> ^{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 ·2H ₂ O ^{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 N₂ 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 tetraacetate⁴⁾, gave 4 quantitatively at ambient temperature. These Michael addition of amines to p-quinone were well known⁵⁾

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



References and Notes

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