CHEMISTRY LETTERS, pp. 1391-1392, 1981. © The Chemical Society of Japan 1981

DIRECT ALKYLAMINATION OF 1,4-DIHYDROXYANTHRAQUINONE IN THE PRESENCE OF SODIUM DITHIONITE

Masashi KIKUCHI, Takamichi YAMAGISHI, and Mitsuhiko HIDA*
Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158

In the presence of sodium dithionite, 1,4-dihydroxyanthraquinone reacted with n-butylamine to give 2-butylamino-1,4-dihydroxyanthraquinone in high yield under air. Under a nitrogen atmosphere, this reaction gave 1,4-bis(butylamino)anthraquinone nearly quantitatively.

1,4-Diaminoanthraquinone and its N-alkyl or N-aryl derivatives have been synthesized by the reaction of 1,4-dihydroxyanthraquinone(**1**) with ammonia or amines in the presence of sodium dithionite. It has been believed that **1** is reduced to its leuco-compound(**1′**), and 1-amino-4-hydroxyanthraquinones and 1,4-diaminoanthraquinones are produced by the reaction between **1′** and amines, followed by oxidation. In the course of our study of the reaction mechanism of amination of leucoquinizarin we have found that the reaction of **1** with n-butylamine gave 2-butylamino-1,4-dihydroxyanthraquinone(**2**) in the presence of both sodium dithionite and oxygen, but neither 1-butylamino-4-hydroxyanthraquinone(**3**) nor 1,4-bis(butylamino)anthraquinone(**4**). 2-Amino-1,4-dihydroxyanthraquinones have been prepared by amination of 2-bromo-1,4-dihydroxyanthraquinone.1) E.P.Fokin2) and M.Matsuoka3) have recently reported the direct aminations of **1** at its 2-position in the presence of oxidizing agent.

In this paper we report a new and convenient synthesis of 2-alkylamino-1,4-dihydroxyanthraquinones by the direct amination of **1** in the presence of sodium dithionite and oxygen. In a typical experiment, a mixture of **1**, sodium dithionite and n-butylamine in water(5 ml) in a 100 ml flask equipped with a reflux condenser was heated at 90°c in aerated solvent in a closed flask. The products were separated by column chromatography and preparative TLC on silica gel using benzene as eluent and identified by comparison with authentic samples. The results of amination of **1** are summarized in Table 1. Currently 1,4-diaminoanthraquinones have been produced from **1** in the presence of sodium dithionite and a small amount of leucoquinizarin or leucodiaminoanthraquinones The yield of **4** under a nitrogen atmosphere, however, was little affected by addition of leucoquinizarin(Runs 1 to 3). Even in the absence of both leucoquinizarin and sodium dithionite **4** was obtained in a fairly good yield(Runs 2 and 3). The presence of sodium dithionite was effective to produce **4** selectively(Run 1). On the other hand, **2** was formed predominantly under air in the presence of sodium dithionite and / or leucoquinizarin(Runs 5,8,9,11). It is noted that the addition of reducing agent made the formation of **2** predominant. With an increase of amine concentration the yield of **2** decreased and that of the unidentified brown products increased, though **1** was completely consumed(Runs 6 and 7). Decreasing the amine concentration suppressed the conversion of 1, but only 2 was isolated in a lower yield(Run 8). The prolonged reaction decreased the yield of 2. This is because 2 suffers further reaction with n-butylamine to give the unidentified brown products(Runs 5 and 9). The presence of a small amount of leucoquinizarin did not affect on the yield of 2 so much, but this direct amination requires sodium dithionite(Runs 9 and 10). By use of large amount of sodium dithionite 2 was obtained almost selectively in a good yield(Run 11). It is concluded that sodium dithionite and molecular oxygen play an important role to cause the selective amination at its 2-position of 1. These results suggest that 1 is reduced to an unstable leucocompound by sodium dithionite, which is susceptible to air to give 1,4-diketo form of 1 immediately, giving 2 via Michael type addition of n-butylamine in water. This may be supported by the fact that the reaction of 1,4-dimethoxyanthraquinone and n-butylamine both in the presence and absence of sodium dithionite does not afford 2-butylamino-1,4-dimethoxyanthraquinone under air.

Table 1. Amination of 1,4-dihydroxyanthraquinone in the presence of sodium dithionite

Run a)	(1) (mmol)	LQ b) (mmol)	$Na_2S_2O_4$ c) (mg)	$BuNH_2$ (mmol)	Time (h)	atmosphere	(2)%	(3)%	(4)%	(1)% d)
1	0.42	0.027	52.1	9.48	2	N_2	0	0	90.8	0
2	0.42	0.031	0	8.47	2	N_2	0	3.7	90.4	0
3	0.45	0	0	7.88	2	N_2	0	4.3	84.6	0
4	0.42	0	0	7.59	5	air	14.4	13.5	trace	5.3
5	0.42	0.028	51.8	8.62	4	air	62.7	6.2	0	0
6	0.42	0.027	51.8	21.28	5	air	37.1	4.4	0	0
7	0.42	0.028	51.7	40.89	5	air	29.8	3.9	0	0
8	0.42	0.027	51.9	2.26	5	air	28.5	0	0	46.3
9	0.42	0.028	51.9	8.49	2	air	71.3	trace	0	trace
10	0.42	0.030	0	8.41	2	air	21.3	5.3	trace	10.8
11	0.42	0	200.1	9.04	2	air	89.3	0	0	0

a) Runs(4-11) were carried out in aerated solvent in a closed flask.
b) Leucoquinizarin. c) Commercial origin(the purity is more than 85%).
d) The yield of the products isolated by column chromatography and preparative TLC.

References

1) G.S.Johnson, J.H.Shown, Can.1,016,941(Cl 260-236.25) GAF Corp.(1977): C.A. 88, 8496d(1978).
2) E.P.Fokin,V.V.Russkikh,S.A.Russkikh and V.G.Mazur, Zhur.Prikl.Khim., 44,2271(1971).
3) M.Matsuoka, Y.Makino, K.Yoshida and T.Kitao, Chem. Lett.,1979,219; ibid.,1979,1347; Dyes and Pigments, 1, 27(1980).

(Received July 16, 1981)