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The Direct Chlorination of Anthraquinone Oxime. The Regioselective Chlorination of Anthraquinone

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Synopsis. The reaction of anthraquinone oxime with chlorine in the presence or absence of a catalyst was investigated. In concentrated sulfuric acid, the direct chlorination of anthraquinone oxime takes place easily at 100 °C. The chlorination occurs selectively in the β-position in the absence of a catalyst and in the α-position in the presence of palladium acetate.

Selective aromatic substitution is an important subject in organic synthetic chemistry. In the case of anthraquinone, there have been much investigations of selective sulfonation, whereas few investigations have been made of direct chlorination. It has been generally impossible to carry out the direct chlorination of anthraquinone selectively.[1,2]

In the present paper, we will report that the chlorination of anthraquinone proceeds selectively when anthraquinone is used as a form of its oxime, and that the chlorination occurs selectively in the α-position in the presence of palladium acetate and in the β-position in the absence of a catalyst.

Results and Discussion

The reaction of anthraquinone oxime with chlorine in sulfuric acid, followed by the hydrolysis of the product, led to the formation of chloroanthraquinones without any accompanying Beckmann-type rearrangement. Table 1 shows the results obtained from reactions in the presence of various kinds of catalysts. In experiments using palladium salt catalysts at 100 °C, with palladium acetate chlorination occurred predominantly in the α-position of anthraquinone, whereas with palladium sulfate in the β-position, and with palladium chloride the chlorination proceeded with a low selectivity. The activity of palladium sulfate and chloride was, probably because of their lower solubility in sulfuric acid, always lower than that of palladium acetate. In the reaction without a catalyst it is noteworthy that β-substitution was predominant. From this fact, it may be assumed that most of the β-substitution observed in the experiments with palladium sulfate and chloride occurred independently of the catalysts. Ferric chloride, which is known to be a useful catalyst for chlorination, was not effective in the present reactions. Iodine showed a catalytic activity, but the chlorination proceeded with a low selectivity.

Table 1. Direct chlorination of anthraquinone oxime
(Anthraquinone oxime, 4.48 mmol; Chlorine, 10 ml/min; H_2SO_4, 10 ml; Reaction temp, 100 °C; Reaction time, 2 h)

AQ-oxime	Catalyst		Yield[a] of AQs	Composition of the product[b] %			
		g	g	AQ[e]	1-Cl[f]	2-Cl[g]	Others
mono[c]	$Pd(OAc)_2$	0.20	0.85	84	15	1	0
mono	$PdSO_4$[h]	0.20	0.92	85	1	11	3
mono	$PdCl_2$	0.20	0.85	91	3	6	0
mono	$FeCl_3$	0.20	0.89	96	1	3	0
mono	I_2	0.10	0.94	72	17	7	4
di[d]	I_2	0.10	0.86	97	2	1	0
mono	none	—	0.90	92	1	6	1

a) Yield of free anthraquinone and chlorinated anthraquinones obtained by the hydrolysis of the product of the chlorination of anthraquinone oxime. b) Product obtained by the hydrolysis of the product of the chlorination of anthraquinone oxime. c) Monoxime. d) Dioxime. e) Anthraquinone. f) 1-Chloroanthraquinone. g) 2-Chloroanthraquinone. h) Reaction time, 6 h.

Table 2. Chlorination of anthraquinone oxime in the presence of palladium acetate
(Anthraquinone oxime, 4.48 mmol; Chlorine, 10 ml/min; $Pd(OAc)_2$, 0.20 g)

Run No.	AQ-oxime	Reaction temp °C	Reaction time h	H_2SO_4 ml	Yield[a] of AQs g	Composition of product[b] %								
						AQ[e]	1-[f]	2-	1,4-	1,5-	1,8-	1,6-	1,7-	1,2-
1	mono[c]	100	2	5	0.81	73.0	24.3	0.8	1.2	0.7	+			
2[g]	mono	100	4	5	0.95	52.4	40.3	0.6	2.2	2.2	1.0	+	+	+
3	mono	120	2	5	0.83	60.3	33.5	1.8	1.5	0.5	0.6	+	+	
4	mono	150	2	5	0.87	24.6	36.3	3.3	3.9	3.9	6.3	1.9	4.8	1.0
5[g]	mono	100	12	5	0.95	29.2	35.5	2.2	5.3	4.6	4.5	1.5	3.4	1.7
6	mono	100	4	10	0.85	69.1	28.4	1.5	+	+				
7	di[d]	100	4	10	0.61	83.2	15.9	0.7	+	+				
8	AQ[e]	100	4	10	1.10	58.2	23.8	4.4	2.7	2.7	2.3	0.9	2.0	0.7
9	mono	100	4	10[h]	0.83	93.8	6.2	+						

a)—e) The symbols are the same as in Table 1. f) 1-Chloroanthraquinone. The other chloroanthraquinones are shown similarly. The numerical symbol indicates the position of the chlorosubstituent. g) As the catalyst 0.40 g of $Pd(OAc)_2$ was used. h) Tetrachloroethylene was used instead of sulfuric acid.

Table 3. Chlorination of anthraquinone oxime without a catalyst
(Anthraquinone oxime, 4.48 mmol; H_2SO_4, 10 ml; Chlorine, 10 ml/min)

Run No.	AQ-oxime	Reaction temp °C	Reaction time h	Yield[a] of AQs g	Composition of product[b] %								
					AQ[e]	1-Cl[f]	2-Cl	1,6-	1,7-	1,2-	2,6-	2,7-	2,3-
10	mono[c]	100	2	0.90	92.1	0.6	6.2						
11	mono	100	6	0.92	71.5	1.5	19.1				0.9	0.8	0.3
12	mono	100	12	0.94	53.2	3.5	30.2	0.5	0.5	0.6	2.1	2.5	1.1
13	mono	150	2	0.89	46.5	7.2	27.2	1.8	1.9	1.3	1.9	2.5	1.1
14	di[d]	100	6	0.88	72.0	+	19.1				2.3	3.7	0.9
15	di	150	2	0.71	50.8	0.9	32.4		+		4.8	6.2	2.1
16[g]	mono	100		0.94	41.3	23.4	14.2	2.3	4.6	1.6	0.9	0.9	+
17	AQ[e]	100	4	0.92	97.5	2.0	0.5						

a)—e) The symbols are the same as in Table 1. f) The same as in Table 2. g) The reaction was carried out without a catalyst for 6 hours, and then 0.20 g of palladium acetate was added to the reaction mixture and the reaction was continued for a further 4 h.

More detailed research was done in order to elucidate the difference between reactions in the presence of palladium acetate and in the absence of a catalyst. Table 2 shows the results of the chlorination using palladium acetate as the catalyst. As is clear from the comparison of the results of Run No. 6 with those o No. 8, the α-selectivity of the chlorination of anthraquinone oxime is much higher than that of the chlorination of free anthraquinone. The chlorination of the oxime, as may be seen from the results of No. 2, tends to stop at the stage of monochlorination to give 1-chloroanthraquinone with a high selectivity, and this greatly differs from the chlorination of free anthraquinone.[3] As to the effect of the temperature, the selectivity for α-substitution decreases with the rise in the reaction temperature. Anthraquinone dioxime (No. 7) shows a similar selectivity for α-substitution, although the reactivity of the dioxime is lower than that of the monoxime.

It is well known that palladium coordinates with nitrogen more strongly than with oxygen.[4] In the reaction with palladium acetate, it seems reasonable, therefore, to think that palladium interacts with the nitrogen of the oxime and, because of this interaction, chlorination occurs selectively in the α-position neighboring the C=N–OH group.

The results of the chlorination in the absence of a catalyst are shown in Table 3. In the reaction of anthraquinone monoxime and chlorine without a catalyst at 100 °C chlorination occurred predominantly in the β-position; this is in contrast to the reaction with palladium acetate and the reaction of free anthraquinone without a catalyst (No. 17). As for the dioxime, chlorination occurred exclusively in the β-position at 100 °C, and a similar result was obtained even at 150 °C. In the reaction of the monoxime at 150 °C, however, an increase in α-chlorinated products was observed. The α-chlorination in this case, in view of the results described above, seems to have occurred at the opposite side of the C=N–OH group.

In the experiment of Run No. 16, β-chlorination was at first carried out in the absence of a catalyst, and then α-chlorination was carried out in the presence of palladium acetate. As a result, the formation of a comparatively great amount of 1,7-dichloroanthraquinone was observed. This result seems to suggest that the β-chlorination in the absence of a catalyst tends to occur on the same side of the C=N–OH group. Although the mechanism in which the chlorination of anthraquinone oxime in the absence of a catalyst occurs selectively in the β-position is not clear at present, the contribution of the *meta*-orientation of $=N^+-$ formed in the C=N–OH group in sulfuric acid seems to be possible.

Experimental

Anthraquinone mono and dioxime were prepared according to the methods described in the literature.[5,6] Reagent-grade concd sulfuric acid (95%) was used without further treatment. The products were analyzed by means of high-speed liquid chromatography in a manner similar to that described in a preceding paper:[2] column, Zorbax-Sil 25 cm; eluent, pentane (containing 0.02% MeOH); flow rate, 100 ml/h, (90 kg/cm²); temperature, 20 °C; detector, UV-254 nm.

Chlorination of Anthraquinone Oxime. Anthraquinone monoxime (1 g, 4.48 mmol) was dissolved in 5 ml of concd sulfuric acid, and then 0.20 g of palladium acetate was added, the mixture was thereafter heated for two hours at 100 °C with stirring under a flow of chlorine (10 ml/min). The reaction mixture was then poured into ice water and filtered. The precipitate was treated with a mixture of 7 ml of concd hydrochloric acid and 10 ml of formalin for 5 h on a water bath in order to hydrolyze the oxime. The mixture was filtered, and the residue was washed repeatedly with water and dried at 100 °C. The product was passed through a short active alumina column, using dichloromethane as the eluent, in order to separate the undecomposed oxime and by-products. A part of the product was analyzed by HLC.

References

1) There are several patents relating to the preparation of tetrachloroanthraquinone, *e.g.*, U. S. Patent, 2378745 (1945).

2) T. Ito, Y. Kindaichi, and Y. Takami, *Nippon Kagaku Kaishi*, **1977**, 82.

3) In our previous study, we observed that the reactivity of 1-chloroanthraquinone toward chlorine is greater than that of anthraquinone; consequently, the chlorination of free anthraquinone does not stop at the stage of monosubstitution.[2]

4) F. Basolo and R. G. Peason, "Mechanisms of Inorganic Reactions," John Wiley & Sons (1965), pp. 23, 60.

5) M. A. Haq, J. N. Ray, and M. T. Malkana, *J. Chem. Soc.*, **1934**, 1326.

6) J. Meisenheimer and E. Mahler, *Ann.*, **508**, 185 (1935).