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Synthesis of 5-nitro- and 5-aminobenzimidazolone-2

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Abstract

The pure mononitro derivative of benzimidazolone-2 can be obtained only when the nitration reaction is carried out in mild conditions, otherwise di-, tri- and tetranitro derivatives are also formed. The results of our studies derived optimum conditions for the nitration process necessary to obtain pure 5-nitrobenzimidazolone-2. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Benzimidazolone-2 and its derivatives have invoked considerable interest, connected mostly with their ability to form strong hydrogen bonds, and they have a molecular structure for use in organic pigments [1] as well as some direct [2,3] and disperse dyes [4]. The significance of benzimidazolone compounds arose after A.-G. Hoechst produced highly resistant monoazo pigments, the so called benzimidazolone pigments [5], synthesized from amides of 3-hydroxy-2-naphthoic acid and acetylacetic acid, which were derivatives of 5-aminobenzimidazolone-2, which was in turn, obtained by reduction of 5-nitrobenzimidazolone-2.

The results of our investigations show that 5-nitrobenzimidazolone-2, as well as other intermediate products, should be of a high degree of purity, since impurities present in the substrates can accumulate in the products, causing a substantial deterioration of the properties of the pigments.

According to the literature data, 5-nitrobenzimidazolone-2 can be obtained by a fusion process of 4-nitrophenylenediamine-1,2 and urea [6], or by nitration of benzimidazolone-2 (Scheme 1).

The technological application of the first method invokes the following problems: thermal stability of the nitro compound during the fusion process, and the availability of pure 4-nitro-1,2-phenylenediamine, which is produced by a sodium sulphide reduction of 2,4-dinitro-aniline in aq.–ethanol. Thus, methods based on the nitration of benzimidazolone-2 could be of much greater practical value. However, it should be emphasized that di- and trinitro compounds can also be formed [7] during the nitrations as a result of the high reactivity of the aromatic ring of the benzimidazolone-2 moiety towards electrophilic reagents. Pure 5-nitro-benzimidazolone-2 can be obtained by nitration of benzimidazolone-2 using a significant excess (1:14) of concentrated nitric acid [8], but the high consumption of acid raises the cost of the method, since the acid should be regenerated and purified. The literature [9] also

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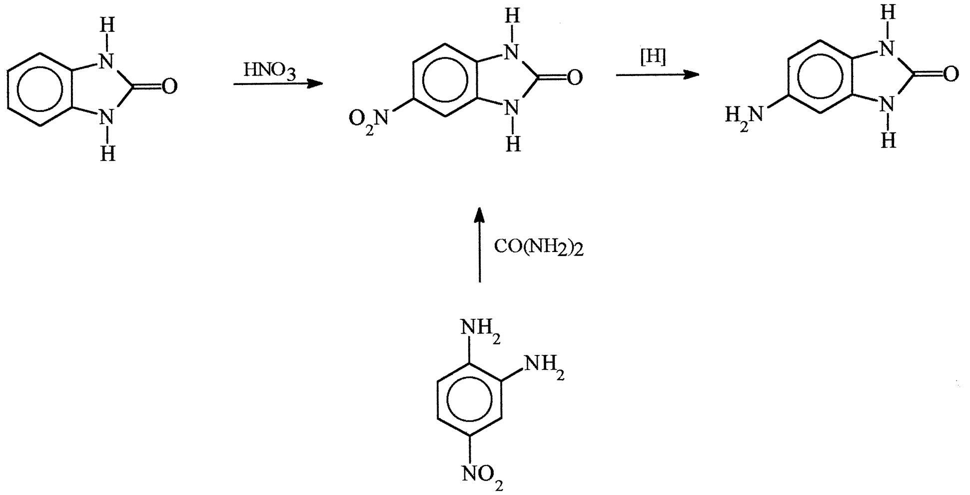

Scheme 1.

describes the nitration of benzimidazolone-2 in concentrated sulfuric acid, but investigations showed that 5,6-dinitrobenzimidazolone-2 was obtained as a by-product, even though the stoichiometric amount of nitric acid was employed in the reaction. Despite this disadvantage, the nitration process using nitric acid or mixed acid could be considered to be an advantageous method from the technological viewpoint.

The purpose of our research work was an optimization of the nitration process of benzimidazolone-2 in sulfuric acid medium, i.e. a determination of the temperature and the composition of the nitrating mixture which are needed to obtain 5-nitrobenzimidazolone-2 product which was low in dinitro and other by-product impurities.

The nitrating mixture employed can be characterized by the DVS value [dehydrating value of sulfuric acid, Eq. (1)], or by the concentration of waste sulfuric acid [Eq. (2)]:

$$\mathrm{DVS} = \frac{m_{H_2SO_4}}{m_{H_2O}} = \frac{[H_2SO_4]\%}{[H_2O]\%} \quad (1)$$

$$[H_2SO_4]\% = \frac{\mathrm{DVS} \times 100}{1 + \mathrm{DVS}} \quad (2)$$

$m_{H_2SO_4}$, $[H_2SO_4]\%$—weight and concentration (wt%) of H_2SO_4 used
m_{H_2O},$[H_2O]\%$—weight and concentration (wt%) of H_2O at the end of reaction (water introduced with substrates and formed during the reaction).

The optimal composition of the nitrating mixture should correspond to such a DVS value which is needed for the complete reaction of benzimidazolone-2, but at the same time the mixture should not further nitrate the initially formed 5-nitrobenzimidazolone-2.

2. Experimental

In order to determine the optimal conditions of the nitration reaction, selected values of DVS were chosen and suitable compositions of the nitrating mixtures were calculated. The mixtures were then employed in the nitration reactions carried out at 5, 10 and 15°C. Temperatures lower than 15°C were not considered, owing to the additional cost of cooling. The products of the reactions were isolated and analysed to determine the concentration of the 5,6-dinitrobenzimidazolone-2 by-product. The method is outlined in the following scheme:

DVS → composition of a nitrating mixture →
$HNO_3(\%)/H_2SO_4(\%)/H_2O(\%)$
→ nitration →
→ analytical control →
→ choice of a nitrating mixture

The nitrating mixtures consisted of 96% sulfuric acid and 63% nitric acid; benzimidazolone-2 was prepared by fusion of *o*-phenylenediamine with urea [10].

The nitration reactions were carried out at the chosen temperatures by adding powdered benzimidazolone-2 to the nitrating mixtures with DVS values of 10; 5; 4; 3.5 (5% excess of nitric acid was used). The weight of the excess sulfuric acid was determined to be 120 g in order to satisfy good stirring conditions. The resulting nitro compounds were isolated by pouring the reaction mixture into ice-water, filtering the precipitated solid, washing with water, then with aq. $NaHCO_3$, and again with water, finally and drying at 50–60°C. The purity of the products was monitored by TLC using Al_2O_3 coated plates (Merck, 60F 254, Type E) and ethanol as eluent; the chromatograms were observed in UV light.

Standard samples of 5-nitrobenzimidazolone-2 ($R_f = 0.80$) and 5,6-dinitrobenzimidazolone-2 ($R_f = 0.20$) were prepared according to known procedures [7,8]. The conditions of the nitration reactions and the results obtained are given in Table 1.

5-Aminobenzimidazolone-2 was prepared by reduction of pure 5-nitrobenzimidazolone-2 according to Bechamp's method. The product was isolated from the hot reaction mixture through basification with NaOH, filtration of ferric oxides, active charcoal purification and neutralization with hydrochloric acid. The separated amine was filtered, washed with water and dried at 100°C. The content of the pure amine in the product was determined by dissolution of a sample of the product in dilute hydrochloric acid and titration with 0.1 M $NaNO_2$ solution.

3. Conclusions

The results of our investigations showed that the preparation of pure 5-nitrobenzimidazolone-2 by the nitration of benzimidazolone-2 is feasible, providing that the appropriate DVS value is chosen; this value should be in the range 3.5–4.5. With lower values, the reaction slows down and does not go to completion. Higher values lead to products containing considerable amounts of 5,6-dinitrobenzimidazolone-2.

Table 1
Parameters and results of the nitration reaction of benzimidazolone-2

DVS	$[H_2SO_4]\%$	Reaction temperature (°C)	Composition of the nitrating mixture			Yield (%)	Melting point (°C)	Presence of 5.6-dinitrobenzimidazolone-2
			H_2SO_4 (%)	HNO_3 (%)	H_2O (%)			
10	90.0	10	91.6	2.8	5.6	90.4	303–305	[a]
5	83.3	10	83.3	2.8	13.3	96.0	305–306	[a] (traces)
4	80.0	10	80.6	2.8	16.6	97.1	307–308	[b]
3.5	77.7	10	78.3	2.8	18.9	97.0	307–308	[b]
3	75.0	10	75.6	2.8	21.6	[c]		
8	88.9	5	89.6	2.8	7.6	96.2	304–305	[a]
5	83.3	5	83.9	2.8	13.3	97.0	307–308	[b]
4	80.0	5	80.6	2.8	16.6	97.2	307–308	[b]
4	80.0	15	80.6	2.8	16.6	97.0	307–308	[b]

[a] 5,6-dinitrobenzimidazolone-2 found in the reaction product.

[b] Chemically pure compound.

[c] Reaction not completed, unreacted benzimidazolone-2 found.

The nitration of benzimidazolone-2 can be carried out using a DVS value within the given range, at a temperature of 5–15°C. At temperatures higher than 20°C, oxidation products, as well as polynitro compounds, are formed.

For technological purposes a more convenient version of the nitration method can be employed. The method consists in the addition of nitric acid to the solution of benzimidazolone-2 in sulfuric acid while keeping DVS value within the chosen limits [11].

Our investigation has shown that Bechamp method is useful for the reduction of the resulting nitro compound to the corresponding amine. This amine was employed in the synthesis of benzimidazolone pigments having a high degree of purity [12]. According to the literature [13] 5-nitrobenzimidazolone-2 can be also reduced in water using a Pd/SiO_2 catalyst.

It should be stated that the method developed by us is fully suitable for industrial application. The synthesis of 5-aminobenzimidazolone-2 can be illustrated by the following example.

Powdered benzimidazolone-2 (13.4 g) was added in small portions to a nitrating mixture consisting of 32.6 g of water, 200 g of 96% sulfuric acid and 10.2 g of 63% nitric acid, while stirring at 10–15°C over a period of about 0.5 h. Stirring was continued for 0.5 h and then the mixture was poured into 600 ml of chipped ice. The precipitated product was filtered, washed with water, 5% aq. $NaHCO_3$ and finally with water until the washings were neutral. After drying at 50–60°C 17.2 g of 5-nitrobenzimidazolone-2 was obtained (96%). M.P.: 307–308°C.

Some of the nitro compound (17.9 g) was added in small portions to a boiling mixture containing 25 g of Fe dust, 60 ml of water and 0.5 ml of hydrochloric acid, while stirring intensively over a period of 1 h. After completion of the reduction, water was initially added to give 200 ml of total volume of the reacting mixture, and then 13 ml of 30% NaOH and 0.5 g of sodium dithionite were added at 50–60°C. Ferric oxides were filtered and the filtrate was acidified by adding hydrochloric acid. The resulting precipitate was filtered, washed with water and dried at 100°C to give 13.3 g of 5-aminobenzimidazolone-2 which contained 99.6% of the pure amine. Yield: 89.2%.

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