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FACTORS AFFECTING THE OXIDATION OF BENZALDOXIME BY CERIC AMMONIUM NITRATE[1]

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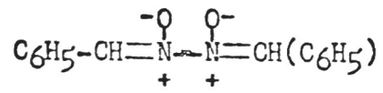
ABSTRACT

Benzaldazine N, N'-dioxide was prepared *via* chemical oxidation of benzaldoxime in methanol by ceric ammonium nitrate. Reaction variables examined were temperature, concentration of reactants and mode of addition. The highest yield (93.50%) was obtained at ambient temperature when the benzaldoxime solution was added slowly to the ceric ammonium nitrate solution. The optimum concentration was found to be a one to five molar ratio of benzaldoxime to ceric ammonium nitrate.

INTRODUCTION

The chemical oxidation of benzaldoxime can be effected using a variety of oxidizing agents. The particular products that form, as well as the yields of these products seem to depend upon the specific oxidizing agent employed. Thus oxidation by peroxytrifluoroacetic acid gives phenylnitromethane in 70% yield, (1) while reaction with alkaline ferricyanide produces benzaldazine-N, N-dioxide (1) (2).



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The same substance is produced along with furoxans, 1, 2, 4-oxadiazole-2-N-oxide and O-acyl oximes by oxidation with elemental iodine (3). When dinitrogen tetroxide is used as the oxidant at temperatures ranging from 36C to 60C, phenylnitrolic acid, diphenylfuroxan and benzaldazine-N,N-dioxide are produced(4).

Higher yields of phenylnitrolic acid were observed at higher temperatures and shorter reaction times while at lower temperatures formation of benzaldazine-N, N-dioxide predominated. The latter data indicates that temperature may also be a factor in determing reaction products in these reactions. In 1965 Chapman and Swindell oxidized benzaldoxime with ceric ammonium nitrate (5).

The benzaldazine-N,N'-dioxide product was found to be thermally unstable and decomposed readily to benzaldehyde, 3,5-diphenyl 1,2,4-oxadiazole and, presumably, nitrogen and water. Analysis by thin layer chromatography indicated that other products in smaller amounts were also formed in this decomposition. The yield of benzaldazine-N, N-dioxide was observed to vary according to the mode of addition and the concentration of reagents but no detailed investigation of the scope of these effects was made. In the present investigation an attempt was made to correlate the yield of benzaldazine-N,N'-dioxide as a function of temperature and concentration.

RESULTS AND DISCUSSION

The oxidation of benzaldoxime by ceric ammonium nitrate was carried out at three temperature ranges: 0C, 21-23C, and 45-47C. When the reaction is carried out by adding 10 ml of 0.5 M benzaldoxime in methanol to 10 ml of freshly prepared 0.5 ceric ammonia nitrate in methanol the average yield of product at 0C is 51.71%. As the temperature is increased from 0 to 21-23 the average yield of product increases to 75%. When the mode of addition was reversed, i.e., the benzaldoxime solution added in one portion to the ceric ion solution, the yields are all increased but showed the same general temperature dependence. Thus at 0C the average yield is 65%; at 21-23C, 86%; and at 45-47C, 47%. These data are recorded in Table I.

[1] Portions of this paper were abstracted from the masters thesis of D. Tsau, Tennessee Technological University, June, 1967.

TABLE I

Influence of Temperature and Order of Addition of Reactants on Percentage Yield

Order of Addition of Reactants	Temperature	Grams of Ceric Ammonium Nitrate	Grams of Benzaldoxime	Experimental Yield (grams)	Theoretical Yield[a] (grams)	Per Cet Yield
Ceric Ammonium nitrate to benzaldoxime	0°C	2.7434[b]	0.6138	0.3062	0.5871	52.16
	0°C	2.7284[b]	0.6138	0.3012	0.5838	51.59
	0°C	2.7322[b]	0.6138	0.3007	0.5847	51.43
Benzaldoxime to ceric ammonium nitrate	0°C	2.7523[c]	0.6138	0.3816	0.5916	64.50
	0°C	2.7368[c]	0.6138	0.3826	0.5883	65.21
	0°C	2.7366[c]	0.6138	0.3829	0.5882	65.09
Ceric Ammonium nitrate to benzaldoxime	21-23°C	2.7331[b]	0.6138	0.4485	0.5849	76.69
	21-23°C	2.6873[b]	0.6138	0.4270	0.5750	74.25
	21-23°C	2.6902[b]	0.6138	0.4344	0.5757	75.46
Benzaldoxime to ceric ammonium nitrate	21-23°C	2.7343[c]	0.6138	0.5026	0.5877	85.51
	21-23°C	2.7365[c]	0.6138	0.5081	0.5882	86.38
	21-23°C	2.7452[c]	0.6138	0.5116	0.5901	86.70
Ceric Ammonium nitrate to benzaldoxime	45-47°C	2.7373[b]	0.6104	0.2906	0.5857	49.61
	45-47°C	2.7290[b]	0.6104	0.2820	0.5840	48.29
	45-47°C	2.7323[b]	0.6104	0.2918	0.5847	49.91
Benzaldoxime to ceric ammonium nitrate	45-47°C	2.7121[d]	0.6165	0.2828	0.5928	47.70
	45-47°C	2.7206[d]	0.6165	0.2743	0.5947	46.12
	45-47°C	2.7195[d]	0.6165	0.2830	0.5944	47.61

a. based on the amount of ceric ammonium nitrate used. b. purity of ceric ammonium nitrate was 97.66%. c. purity of ceric ammonium nitrate was 98.11%. d. purity of ceric ammonium nitrate was 98.77%.

In addition to studying the effect of temperature on the yield, the effect of varying concentrations, i.e. molar ratios, was also investigated. The highest yields, 93-94%, were obtained by adding the benzaldoxime to the ceric ammonium nitrate. The ratio of oxime to ceric ion was 1:5. As the molar ratio was decreased, the yield also decreased in a regular manner down to 81.5% when a molar ratio of 1:0.25 of oxime to ceric ion was used. These data are recorded in Table II.

TABLE II

The Yield of Benzaldazine N, N'-Dioxide with Varying Molar Ratios of Benzaldoxime and Ceric Ammonium Nitrate at Room Temperature

Molar ratio benzaldoxime to ceric ammonium nitrate	Grams of ceric ammonium nitrate	Grams of benzaldoxime	Experimental yield (grams)	Theoretical Yield[a] (grams)	Per Cent yield
1:0.25	0.7174[b]	0.6057	0.1255	0.1542	81.38
	0.7203[b]	0.6057	0.1268	0.1548	81.90
	0.7187[b]	0.6057	0.1262	0.1545	81.64
1:0.5	1.4036[b]	0.6057	0.2542	0.3017	84.26
	1.5908[b]	0.6057	0.2837	0.3420	82.97
	1.3675[b]	0.6057	0.2380	0.2940	80.97
1:1	2.7343[b]	0.6138	0.5026	0.5877	85.51
	2.7365[b]	0.6138	0.5081	0.5882	86.38
	2.7452[b]	0.6138	0.5110	0.5901	86.70
1:5	13.6949[c]	0.6137	0.5728	0.6086[d]	94.12
	13.7458[c]	0.6137	0.5631	0.6086[d]	92.54
	13.7768[c]	0.6137	0.5711	0.6086[d]	93.84

a. based on the amount of ceric ammonium nitrate used. b. purity of ceric ammonium nitrate was 98.11%. c. purity of ceric ammonium nitrate was 97.66%. d. based on the amount of benzaldoxime used.

From the experimental results it is apparent that temperature has an important role in influencing the yield of benzaldazine—N,N'-dioxide. The fact that the yield at 47C is lower than the yield obtained at room temperature can be explained by noting that the benzaldazine—N,N'-dioxide is thermally unstable.[6] It may be assumed that a portion of the product decomposes and that this decomposition results in a lower yield of product. The decrease in yield as the temperature is lowered from room temperature to 0C, however, is not as readily explained. That this is not simply a kinetic phenomenon is demonstrated by allowing the reaction mixture to warm to room temperature before isolating the product. No significant change in yield was noted in this experiment. One explanation that might be offered is that a completing reaction is taking place (Fig. 1).

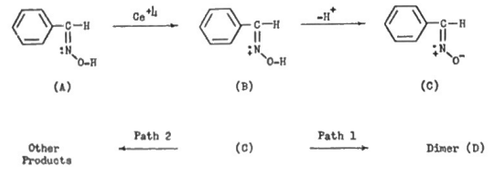

Figure 1

The nature of the alternate reaction path (path 2), if it in fact exists, is still speculative and only guesses can be made as to what products can arise from this source. It is obvious that further research is necessary in order to elucidate the nature of the alternate reaction path(s).

Experimental Section

Preparation of benzaldoxime solution. Benzaldoxime (Eastman Organic Chemicals, Distillation Products Industries) was recrystallized twice from diethyl ether. This material was used to prepare 0.5 M solutions of benzaldoxime in methanol (Fisher Certified Reagent).

Purity of ceric ammonium nitrate. The purity of ceric ammonium nitrate markedly affects the yield of benzaldazine N,N'-dioxide. The purity of the original commercial compound was found to be 86.84% which is too low to give adequate results. Relatively pure ceric ammonium nitrate can be easily prepared by recrystallization from nitric acid.[6] One hundred grams of commercial ceric ammonium nitrate was dissolved in 270 milliliters of boiling concentrated nitric acid and twenty grams of ammonium nitrate was added. The solution was cooled in ice-water, filtered and the residue dried for one hour at 110°C. The purity of the commercial and recrystallized ceric ammonium nitrate was determined by titrating ceric ammonium nitrate against ferrous ammonium sulfate (primary standard, 99.85%) using Ferroin as an indicator.[7] The commercial product was found to be 86.84% pure, while four different batches of the recrystallized compound were 96.95, 97.66, 98.11 and 98.77% pure.

Reaction of benzaldoxime with ceric ammonium nitrate to yield benzaldazine N,N'-dioxide. Ten milliliters of 0.5 M solution of benzaldoxime in absolute methanol was pipetted into seven-tenths gram of a purified ceric ammonium nitrate dissolved in ten milliliters of absolute methanol. After the reaction was completed the mixture was cooled in an ice-water bath for two and one-half minutes. The white residue was filtered, washed with thirty milliliters of ether, dried in air, and weighed.

The product was identified by a carbon, hydrogen and nitrogen analysis determined using a Coleman Nitrogen Analyzer, Model 29 and Coleman Carbon-Hydrogen Analyzer Model 33. Analysis. Calculated. $C_{14}H_{12}N_2O_2$:
C, 70.00; H, 5.00; N, 11.67. Found:
C, 70.03; H, 4.99; N, 11.75.
The product melted at 104-108C.

The effect of the different molar ratios. The reaction was repeated using different molar ratios of ceric ammonium nitrate and benzaldoxime. As the molar ratio of ceric ammonium nitrate to benzaldoxime is increased, the yield also increases. A large excess of ceric ammonium nitrate converts benzaldoxime into benzaldazine N,N'-dioxide in high yield. The results are shown on Table I.

The effect of temperature upon the yield of benzaldazine N, N'-dioxide. Using a one to one molar ratio of benzaldoxime to ceric ammonium nitrate, the oxidation was performed at 0C and 45-47C. Ten milliliters of 0.5 M benzaldoxime and ten milliliters of freshly prepared 0.5 M ceric ammonium nitrate were placed in a water bath at the desired temperature (0C, 45-47C) and allowed to reach equilibrium. The benzaldoxime solution was added in one portion to the ceric ammonium nitrate solution and thoroughly mixed. The empty flask which contained the benzaldoxime solution was rinsed immediately with thirty milliliters of methanol and this methanol also added to the ceric ammonium nitrate solution. The solid mixture was cooled in ice-water, filtered, washed with ether, air-dried and finally to 45-47C, the yield decreases to 47.14%, whereas at 0C, the average yield is 65.2%. The data and results of these experiments are shown in Table II.

The reaction was repeated at 0, 21-23C, 47-47C using the same procedure, except that the ceric ammonium nitrate was added to the benzaldoxime solution. The average yield of product at 0C is 51.73%. As the temperature is increased from 0C to room temperature, the average yield increases to 75.47%. At 45-47C the average yield decreases to 49.27%. The data and results are also shown in Table II.

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