SYNTHESIS OF BENZOTRIAZOLES

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Among the fluorescent bleaching agents the compounds with an aryltriazol-2-yl radical stand out due to their chemical resistance, light stability, and intense fluorescence [1-3].

One of the main methods for forming the aryltriazole ring in these compounds is the oxidation of the corresponding o-aminoazo dyes in aqueous ammonia solutions at 80-135°C by Cu(II) salts, taken in large excess [3]. The oxidation of aminoazo dyes that are difficultly soluble in water is run in aqueous pyridine, alcohol, or pyridine. Also known is the oxidation of o-aminoazo dyes with a smaller amount of Cu(II) salts (0.5-2 moles/mole of amine) in an air stream [3, 4].

Previously [5] we had shown that the oxidation by oxygen of aromatic diamines, including 2,4-diaminoazobenzene derivatives, in a pyridine—CuCl system (1-3 moles of CuCl/mole of diamine) leads to the formation of oligomeric products. While studying this reaction we found that with smaller amounts of CuCl the 2,4-diaminoazobenzene derivatives are vigorously oxidized to the corresponding benzotriazoles, whose yields, however, do not exceed 60-70% due to the polycondensation reaction that proceeds in parallel. If either an aqueous pyridine or an aqueous alcohol—pyridine solution is used the oxidation is ended in several minutes at 40-60° and the yield of the benzotriazoles reaches 90-97%.

The oxidation of o-aminoazobenzene is quite rapid even at ~ 20° and the yield of 2-phenylbenzotriazole is quantitative. The oxidation rate of o-aminoazobenzene is quite dependent on the amount of CuCl. Thus, at a CuCl concentration of 0.05 mole/mole of amino the calculated amount of O_2 is absorbed in 75 min, and the reaction is ended in 10 min if the amount of CuCl is increased to 0.5 mole. A partial replacement of the pyridine by either alcohol, DMF or dioxane has little effect on the oxidation rate.

The advantate of oxidizing o-aminoazobenzene derivatives in a CuCl—pyridine system is especially obvious when o-aminoazo derivatives with electron-acceptor substituents are oxidized. The oxidation of 2,4-diamino-4'-nitroazobenzene by O_2 in the presence of 0.4 mole of CuCl, in aqueous pyridine, at 50°, is ended in 40 min, whereas when $CuSO_4$ is used the reaction mixture is refluxed for 6-8 h [6].

As is known [7], the catalytic activity in the CuCl—pyridine system is possessed by the coordinated pyridine complex of copper, in which from 0.5 to 4 moles of pyridine is consumed for coordination. Consequently, when oxidizing o-aminoazobenzene derivatives to benzotriazoles in the presence of CuCl—pyridine there is no need to use a large amount of pyridine, except in those cases where it is the solvent. Cu(II) salts do not catalyze this reaction. Thus, only 0.1 of the calculated amount of O_2 is absorbed in 2 h when 2,4-diaminoazobenzene is oxidized in pyridine in the presence of catalytic amounts of Cu(II) salts, while the remainder of the O_2 is absorbed in 25 min if 0.3 mole of CuCl is added to this mixture. If the pyridine is replaced by NH_3 the O_2 absorption practically ends at the amount needed to oxidize the Cu(I) to Cu(II).

As a result, it was shown that the oxidation of o-aminoazo derivatives to benzotriazoles by O_2 in the CuCl—pyridine system proceeds under mild conditions in various organic solvents and their mixtures with water, which greatly expands the possible applications of this method.

EXPERIMENTAL

The oxidation of the o-aminoazobenzene derivatives was run in a closed system, composed of a glass reactor ("duck") equipped with a jacket and buret, with vigorous stirring in an O_2 atmosphere. The reaction rate was judged by the volume of absorbed O_2, which was measured in a gas buret. The end of reaction was determined by the amount of absorbed O_2 and by the disappearance of the azo dye in TLC (Silufol, 2 : 2 : 1 benzene—petroleum ether—acetone).

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The reaction mass was poured into 5% HCl solution, and the benzotriazole precipitate was filtered, washed on the filter in succession with 5% HCl solution and water, and dried.

Oxidation of o-Aminoazobenzene (I). A mixture of 1.97 g (0.01 mole) of (I) and 0.5 g (0.005 mole) of CuCl in 50 ml of pyridine was oxidized at 20°. The calculated amount of O_2 (118 ml) was absorbed in 10 min. We obtained 1.94 g (99.5%) of 2-phenylbenzotriazole, mp 109-109.5° [8]. The reaction time increased to 75 min when the amount of CuCl was decreased to 0.0005 mole.

Oxidation of 2,4-Diaminoazobenzene (II). a) The calculated amount of O_2 (124 ml) was absorbed in 30 min when a mixture of 2.12 g (0.01 mole) of (II) and 0.2 g (0.002 mole) of CuCl in 50 ml of pyridine was oxidized. We obtained 1.67 g (79.5%) of 5-amino-2-phenylbenzotriazole (III) as bright yellow crystals, mp 182-183° [6].

b) The calculated amount of O_2 (124 ml) was absorbed in 10 min when 2.12 g (0.01 mole) of (II) and 0.2 g (0.002 mole) of CuCl in a mixture of 5 ml of pyridine, 50 ml of alcohol, and 50 ml of water was oxidized at 40°. We obtained 1.93 g (91.9%) of (III).

c) The oxidation of 2.12 g (0.01 mole) of (II) in the presence of 0.04 mole of the salts ($CuCl_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$) in a mixture of 50 ml of pyridine and 30 ml of water practically does not go. Analysis of the reaction mixture by TLC disclosed the presence of traces of (III). After adding 0.3 g (0.003 mole) of CuCl to the reaction mixture the calculated amount of O_2 was absorbed in 20 min. We obtained 1.81 g (89%) of (III).

d) The oxidation of 2.12 g (0.01 mole) of (II) and 0.2 g (0.002 mole) of CuCl in aqueous alcohol—ammonia solution (15 ml of water, 50 ml of alcohol, and 20 ml of 25% NH_3 solution) does not go. The calculated amount of O_2 was absorbed in 25 min when 5 ml of pyridine was added to the mixture. We obtained 1.92 g (91%) of (III).

Oxidation of 2,4-Diamino-5-methylazobenzene (IV). A mixture of 1.13 g (0.05 mole) of (IV) and 0.2 g (0.002 mole) of CuCl in a mixture of 5 ml of pyridine and 80 ml of 50% alcohol was oxidized at 60°. The calculated amount of O_2 was absorbed in 10 min. We obtained 1.08 g (96.4%) of 5-amino-6-methyl-2-phenylbenzotriazole as white crystals, mp 214-216°.

Oxidation of 2,4-Diamino-5-butoxyazobenzene (V). The calculated amount of O_2 was absorbed in 3 min when 1.42 g (0.05 mole) of (V) was oxidized under analogous conditions. We obtained 1.38 g (98.6%) of 5-amino-6-butoxy-2-phenylbenzotriazole, mp 152.7-154° Found: C 67.88; H 6.47; N 19.9%. $C_{16}H_{18}N_4O$. Calculated: C 68.06; H 6.43; N 19.85%.

Oxidation of 2,4-Diamino-4'-nitroazobenzene (VI). A mixture of 5.1 g (0.02 mole) of (VI) and 0.8 g (0.008 mole) of CuCl in a mixture of 100 ml of pyridine and 50 ml of water was oxidized at 50°. The calculated amount of O_2 (280 ml) was absorbed in 40 min. We obtained 5 g (97%) of 5-amino-2-(4'-nitrophenyl)benzotriazole, mp 328-329° [6].

Oxidation of Congo Red (VII). A mixture of 1.3 g (0.002 mole) of (VII) and 0.2 g (0.002 mole) of CuCl in 30 ml of a 1 : 1 : 1 pyridine—alcohol—water mixture was oxidized at 55° for 5 min. We isolated 1.2 g (93%) of the Na salt of biphenylene-4,4'-bis(2-naphthyl-(1,2)-triazole-5-sulfonic acid), R_f 0.6 (Silufol, 30 : 12 : 2 : 6 n-amyl alcohol—methanol—25% NH_4OH—water), which coincides with the R_f of an authentic specimen, synthesized as described in [9].

Oxidation of 2-Amino-1-phenylazonaphthalene (VIII). The oxidation of 0.62 g (0.0025 mole) of (VIII), obtained by coupling phenyldiazonium chloride with β-naphthylamine, in 20 ml of chlorobenzene was run at 60° in the presence of 0.13 g (0.0013 mole) of CuCl and 1.5 g (0.025 mole) of pyridine. The oxidation was ended in 3 min. We obtained 0.61 g (100%) of 2-phenylnaphtho-(1,2)-triazole, mp 105.5-107° [10]. The oxidation time increased to 15 min when either the temperature was lowered to 20° or the amounts of CuCl and pyridine were respectively decreased to 0.00025 mole and 0.0025 mole.

Analogous results were obtained when either DMF, dioxane or pyridine was used as the solvent.

CONCLUSIONS

o-Aminoazobenzene derivatives are vigorously oxidized by O_2 to the corresponding benzotriazoles when CuCl—pyridine is used as the catalytic system.

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COMPARATIVE STUDY OF ACTIVITY OF H$^+$ FORM OF TYPE Y, MORDENITE, AND ZSM-5 ZEOLITES IN TOLUENE DISPROPORTIONATION REACTION

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The catalytic properties in the toluene disproportionation reaction have been studied predominantly on the type Y and mordenite zeolites [1]. The activity is markedly affected by the structure of the zeolite, the SiO_2/Al_2O_3 ratio, the nature of the acid centers, the presence of a transition metal, etc. Special attention has been given recently to ultrahigh silica zeolites of the ZSM type, which are promising catalysts for a whole series of processes [2, 3]. According to the data in [4-6], these catalysts can also be used as efficient catalysts in the toluene disproportionation reaction. At the same time, the information in the scientific literature on this problem is scanty [7]. In the present paper a comparative study was made of the catalytic activity of the H form of the type Y, mordenite, and ZSM zeolites in the toluene disproportionation reaction.

A comparison of the data on the conversion of toluene at 420°C reveals that on the studied catalysts the reaction proceeds almost completely toward disproportionation (selectivity 80-90%). Under these conditions (Fig. 1) zeolite HY exhibits the highest catalytic activity, which decreases quite rapidly with time.

The HZSM and HM specimens are less active than HY, and they show a close initial degree of conversion (~ 5%). It should be mentioned that zeolite HM is gradually deactivated, while HZSM retains the original activity.

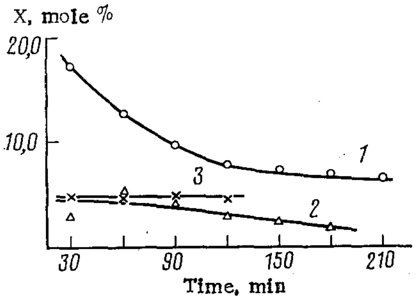

Fig. 1. Catalytic activity as a function of the experiment time at 420°C: 1) HY; 2) HM; 3) HZSM.

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