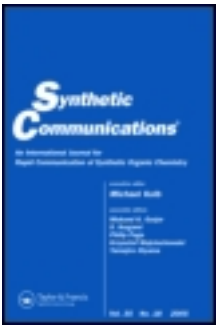

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An Efficient Procedure for the Preparation of 1-Nitroanthraquinone

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AN EFFICIENT PROCEDURE FOR THE PREPARATION OF 1-NITROANTHRAQUINONE

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Abstract: A novel and efficient method is developed for the selective mono nitration of anthraquinone (1). A mixture of fuming nitric acid, sulfuric acid and phosphoric acid in carbon tetrachloride is introduced as a new nitrating system for the high yield preparation of 1-nitroanthraquinone.

INTRODUCTION

1-Nitroanthraquinone is one of the most important anthraquinone derivatives used for the synthesis of various drugs, dyestuff intermediates and, especially, aminoanthraquinone[1]. Although 1-nitroanthraquinone can be synthesize by various methods[36-39], the direct nitration of anthraquinone is increasingly prefferd.

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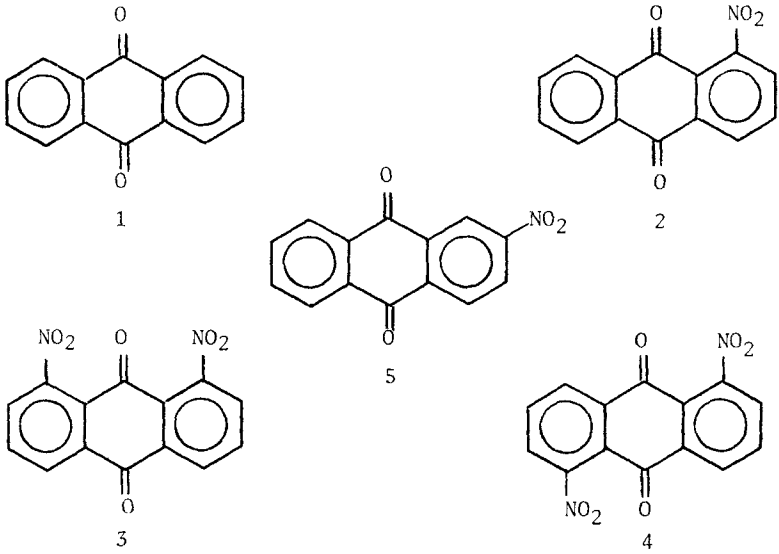
However, the direct nitration affords a mixture of isomers including 1-nitroanthraquinone (2), 2-nitroanthraquinone (5) and dinitroanthraquinones (3,4), as well as, unreacted starting material 1[2-26] (Scheme 1).

Purification methods have been studied extensivly and fairly pure 1-nitroanthraquinone has been prepared by treating the crude product of direct nitrations with different reagents[27-35]. Although several procedures were reported[2-39] for the synthesis

Scheme 1



of 1-nitroanthraquinone (2), we found them not sufficiently effective for its selective preparation.

This paper describes a novel method for the selective preparation of 1-nitroanthraquinone in a one pot reaction.

RESULTS AND DISCUSSION

Initially, a classical procedure[40] was selected and accordingly the commercially available anthraquinone was nitrated with a mixture of 33% nitric acid and 67% sulfuric acid to give 1-nitroanthraquinone (2, 60%). Other isomers were also produced and about 25% of anthraquinone remained unreacted. However, when fuming nitric acid was used, inplace of nitric acid, and the ratio of anthraquinone to fuming nitric acid was raised to 1:2.5, the reaction was completed after 30 min, and 70% 1-nitroanthraquinone (2)and 30% of isomers 3 and 4 were obtained. When the above reaction was carried out in a series of organic solvent using different conditions, it was found that CCl_4 has a pronounced effect on the selective preparation of 2($55^{o}C$, 30 min., 75%). At this point, it was decided to optimize the condition for the selective nitration of anthraquinone at room etmperature.

Numerous effert was performed and it was found that changing the molar ratio of nitrating reagent (HNO_3/H_2SO_4) has effect on the selective preparation ofthe desired compound 2. The results are summerized in Table 1 and exhibits that the best molar ratio for anthraquinone/fuming HNO_3/H_2SO_4 is 1:7:7 respectively.

Since aq. phosphoric acid containing HNO_3 has already been used for the nitration of a series of aromatic hydrocarbons[8,11,41] it was decided to examine the effect of phosphoric acid on the nitration of anthraquinone. Therefore, a mixture of fuming HNO_3, H_2SO_4 and H_3PO_4 was prepared in such away that their mole ratio

Table 1. Effect of change in mole ratio of Fum. HNO_3 and H_2SO_4 on nitration of anthraquinone in CCl_4.

Mole ratio of Anthraquinone/Fum. HNO_3 / H_2SO_4	Time h	Temperature °C	Products
1 : 1 : 1.95	0.5	55	1(25%),2(60%),3+4(15%)
1 : 1.2 : 1.95	0.5	55	1(20%),2(65%),3+4(15%)
1 : 1.8 : 1.95	0.5	55	1(15%),2(65%),3+4(20%)
1 : 2 : 1.95	0.5	55	1(15%),2(60%),3+4(25%)
1 : 2.2 : 1.95	0.5	55	1(10%),2(65%),3+4(25%)
1 : 2.4 : 1.95	0.5	55	1(5%),2(70%),3+4(25%)
1 : 2.5 : 1.95	0.5	55	2(75%),3+4(25%)
1 : 3 : 1.95	0.5	55	2(65%),3+4(35%)
1 : 3.5 : 1.95	0.5	55	2(60%),3+4(40%)
1 : 2.5 : 1.95	72	25	1(20%),2(60%),3+4(20%)
1 : 3.75 : 2.92	24	25	2(70%),3+4(30%)
1 : 5 : 3.92	20	25	2(70%),3+4(30%)
1 : 6.25 : 4.9	1.5	25	2(70%),3+4(30%)
1 : 7 : 5.9	1	25	2(70%),3+4(30%)
1 : 7.5 : 5.9	1	25	2(70%),3+4(30%)
1 : 7 : 4.5	168	25	1(10%),2(70%),3+4(20%)
1 : 7 : 5.5	72	25	2(70%),3+4(30%)
1 : 7 : 5.9	1	25	2(70%),3+4(30%)
1 : 7 : 6	0.5	25	2(60%),3+4(40%)
1 : 7 : 7	1	25	2(75%),3+4(25%)
1 : 7 : 7.8	2.5	25	2(70%),3+4(30%)

be equal to 7 : 7 : 2 respectively. Addition of this mixture to a suspension of anthraquinone (1) in CCl_4 afforded 1-nitroanthraquinone (2, 90%) after 6 h at room temperature. It should be noted that the addition of anthraquinone (1) suspension to the above acidic mixture cause a reduction in the selective production of compound 2 (80%). In the absence of CCl_4 the selectivity for the preparation of 2 was lost 15%. The effect of change in mole ratio of H_3PO_4 on the nitration of anthraquinone and the effect of temperature on the best reaction conditions are summarized in Table 2. These results clearly indicate a remarkable effect of H_3PO_4 in the selective nitration of anthraquinone. However, in the presence of H_3PO_4 the reaction is time consuming (2, 90%, 6 h,Table 2 entry 2), in comparison to the reaction in the absence of H_3PO_4 (2, 75%, 1 h, Table 1 entry 20). Therefore we conclude that the addition of H_3PO_4 to the reaction medium decrease the rate of the reaction in the expence of a considerable enhancement in the reaction selectivity.

EXPERIMENTAL

Products were characterized by comparison with authentic samples (IR, ^{1}H-NMR spectra, thin layer chromatography, melting point). Yields are based on materials isolated from column chromatography or TLC.

Preparation of 1-nitroanthraquinone (2).

To a suspension of anthraquinone (4 g, 0.016 mole) in CCl_4 (100 ml), in a roundbottomed flask, equipped with a magnetic

Table 2. Effect of change in mole ratio of phosphoric acid on nitration of anthraquinone in CCl_4.

Mole ratio of Anthraquinone/Fum. HNO_3 / H_2SO_4/H_3PO_4	Time h	Temperature °C	Products
1 : 7 : 7 : 1.5	2	25	2(80%),3+4(20%)
1 : 7 : 7 : 2	6	25	2(90%),3+4(10%)
1 : 7 : 7 : 2.2	96	25	2(75%),3+4(25%)
1 : 7 : 7 : 2.5	168	25	1(20%),2(75%),3+4(10%)
1 : 10.5 : 10.5 : 3	11	25	2(50%), 3+4(50%)
1 : 14 : 14 : 4	20	25	2(40%),3+4(60%)
1 : 7 : 7 : 2	1.5	45	2(80%),3+4(20%)
1 : 7 : 7 : 2	2.5	60	2(80%),3+4(20%)

stirrer, a mixture of acids (6 ml fuming HNO_3, 7.6 ml H_2SO_4 and 2.2 ml H_3PO_4) was added at room temperature and stirred for 6 h. The reaction mixture was poured into a beaker containing 200 g of crushed ice. The precipitate was filtered off and washed with water to afford 1-nitroanthraquinone (2, 4.5 g, 90%) as a yellow solid, m.p. 228-230 (lit [2] 233). ν_{max} (KBr): 3090(S), 1680(S),

1590(S), 1530(W), 1450(S), 1375(S), 1320(S), 1280(M), 1150(W), 1000(S), 980(S), 800(S), 710(S), cm^{-1}. ^1H NMR($CDCl_3$): 7.69(t, $\underline{J}$=4 Hz, 2H, C_6-H + C_7-H); 7.88(t, $\underline{J}$=4 Hz, 1H, C_3-H); 8.28(dd, $\underline{J}_1$= 7 Hz, $\underline{J}_2$=2 Hz, 2H, C_4- H + C_8-H); 8.5(dd, $\underline{J}_1$=7 Hz, $\underline{J}_2$=2 Hz, 1H, C_2-H) ppm.

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