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Full Length Research Paper

An unusual way to synthesize 1-nitronaphthalene from 1-amino-5-nitronaphthalene

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1-nitronaphthalene has unexpectedly been synthesized from 5-nitronaphthylamine using diazotization method and treatment with aqueous copper sulphate solution. Detailed UV-visible, FT-IR spectral analysis in addition to ^{1}HNMR, ^{13}CNMR studies have confirmed the product.

Key words: Nitropolycyclic aromatic hydrocarbon, 1-nitronaphthalene, 1-amino-5-nitronaphthalene, diazotization, copper sulphate for reduction, UV-visible spectrum.

INTRODUCTION

Reductive removal of amine substituent from aromatic organic molecules constitutes an important process in organic synthesis (March, 1992). Reactions involving such reductive processes are particularly useful in aromatic chemistry because of the strong directing effects associated with amine substituent. Many reagents have been suggested to replace the primary aromatic amino group by hydrogen, though no method is found to be universally applicable. The yields vary considerably with both the method and the amine used. In most of the cases deaminations are carried out using the diazotized amines. While usually the diazonium salts are not isolated, there are reports of stabilized dry diazonium salts, in one case, e.g., diazonium fluoroborate (Mitsuhashi et al., 2000).

Generally, diazotization of the primary aromatic amine followed by decomposition in presence of an appropriate reducing agent leads to the desired product. Graham and Roe have used ethanol in presence of zinc powder for different types of diazonium fluoborates (Roe and Graham, 1952) for the deamination. Sodium borohydride and hypophosphorous acid has also been preferred in recent times for the same purpose (Mitsuhashi et al., 2000). In this communication we are reporting for the first time, the deamination from one of the smallest nitropolycyclic aromatic hydrocarbons (NPAHs), 5-nitronaphthaylamine (5NNA) to produce 1-nitronaphthalene (1NN).

Nitropolycyclic aromatic hydrocarbons (NPAHs) are of current interest is due to their ubiquity and persistence in the environment and to their potential mutagenic and carcinogenic activities, which in many cases are significantly higher than those of their parents Polycyclic Aromatic Hydrocarbon (PAHs) (Tokiwa and Ohnishi, 1986; Fu, 1990). NPAHs are typically present in the atmosphere in the forms of volatile particles and aerosols, are found to be among the most hazardous environmental contaminants. On the other hand, aromatic nitro compounds are particularly versatile chemical feedstock for a wide range of industrial products, such as pharmaceuticals, agrochemicals, dyestuffs, and explosives. 1-Nitronaphthalene (1NN) can be considered one of the smallest NPAH compounds for which experimental structural information is lacking, while theoretical density functional theory (DFT) predictions have recently been reported (Librando and Alparone, 2008).

There are number of processes found to be used to synthesize 1NN. One of the most common ways is the nitration of naphthalene which normally provides more than one isomer (March, 1992). Recent methods include use of nitrite salt on SiO_2 surface under microwave irradiation (Badgujar et al., 2007) or using a catalyst in presence of nitric acid for a regeoselective conversion (Parac-vogt et al., 2004). Here we report an unusual deamiation of 5NNA using conventional diazotization and hydrolysis with aqueous $CuSO_4$ solution (Scheme 1). To

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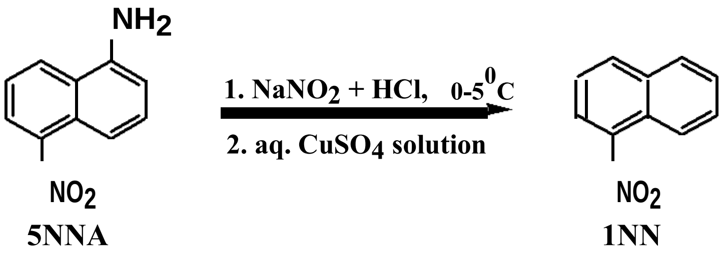


Scheme 1. Deamiation of 5NNA using conventional diazotization and hydrolysis with aqueous $CuSO_4$ solution.

the best of our knowledge there is no report of synthesis 1NN from 5NNA till date.

EXPERIMENTAL

Materials and instrumentations

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. Sodium sulfide purified (Merck India), sulphur powder purified (Merck, India), 1,5-dinitronaphthalene (97%, Sigma-Aldrich), Dimethyl formamide (GR, Merck, India), hydrochloric acid(Merck, India), sodium nitrite purified (Merck, India), copper sulphate (A.R, S.D.. Fine Chem. India) , urea (Qualigen, India), hexane (Merck, India), diethylether(GR, Merck, India), anhydrous magnesium sulphate (AR, Hi-Media, India), ethanol (GR, Merck, India), liquid ammonia (AR, Qualigen, India), and silica gel for Column 60-120 mesh (Merck, India) have been used. Infrared spectra were recorded by JASCO FT-IR-5300 spectrometer with KBr pellets in the region of 400-4000cm^{-1}. Melting points were measured with Optimelt –MPA-100. UV-visible spectra were measured by CARY 100 BIO UV- Visible Spectrophotometer, which has photometric linearity till absorbance 3. 300MHz NMR (JEOL) was used to measure the ^{1}H NMR.

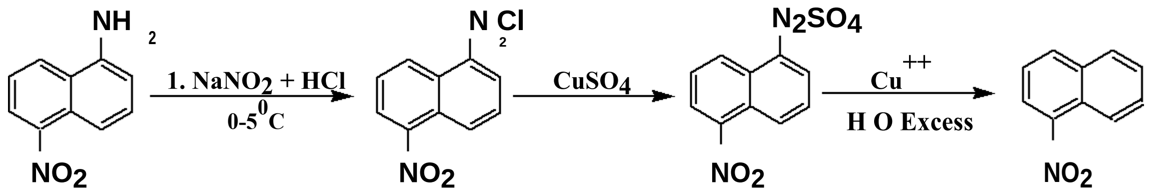
Synthesis of 1-nitronaphthalene (1NN) from 1,5-dinitronaphthalene (1,5DNN)

Synthesis of 1NN was done in the following three steps. First polysulphide solution was prepared and was used to reduced from 1,5DNN to 5-nitronaphthylamine (5NNA) following a modified reported method which gave better yield. This 5NNA was then used to synthesize 1NN.

(i) Preparation of poly sulfide solution:4.29 g (55 mmol) of Na_2S was dissolved in 50 ml water in a round bottom flask and 3.35 gm of solid sulphur (105 mmol) was added to the solution in warmed condition and stirred until clear brown colored solution was obtained. The solution was then filtered to get freshly prepare polysulphide solution for the use in subsequent step.
(ii) Preparation of 5NNA: 10 g (45.8 mmol) of 1,5-dinitronaphthalene (1,5DNN) was dissolved 150 ml of dimethyl formamide (DMF) and heated to 110-120°C to get a clear dark solution. Then the reaction mixture is diluted with 300 ml of triple distilled water. Freshly prepared polysulphide solution was added slowly with constant stirring through a addition funnel into the solution. The reaction mixture was kept stirring at 80-85°C for 3 h. The reaction mixture was then cooled down to laboratory temperature (~30°C) and filtered through the suction pump. The precipitate was washed with cold water (50 ml × 3) followed by washing with hot 2 N HCl (50 ml x 5). The filtrate was acidified with 2N HCl and cooled in ice bath. Liquid ammonia (100 ml) was then added to the filtrate. The basic solution was then kept in refrigerator for precipitation. Red precipitated was obtained which was dried over vacuum pump. Crystallization from ethanol -water (1:10) solvent mixture yielded pure 5NNA (yield:36%). The melting point was found to be 118.5°C (literature: 119°C) (Nakamura, 1942).
(iii) Synthesis of 1- nitro naphthalene(1NN) from 1-amino 5 -nitro naphthalene(5NNA): 540 mg (2.87 mmol) of recrystallised 5NNA was dissolved in 9 ml of 20% HCl followed by the addition of 60 g crashed ice. The compound was diazotized with $NaNO_2$ (203 mg dissolved in 3 ml) at 0-5°C. After the reaction was completed, excess nitrous acid was decomposed by addition of urea (13 mg). Subsequently the reaction solution was poured into $CuSO_4$ solution (5.4 g $CuSO_4$ in 30 ml water) to decompose following the literature (Roe and Graham, 1952). Abundant water was added into it followed by extraction with diethylether (50 ml x 4). The ether layer is washed further with brine and dried over anhydrous $MgSO_4$. Evaporation of solvent was done at reduced pressure (10^{-3} bar, at 40°C) which yielded yellow solid. This yellow solid was found to be mixed with some amount of unreacted stating material (5NNA), which was clearly visible as red niddle like crystal. These mixtures of solid compounds were then crystallized from 70% hexane in diethylether to get yellow crystal of 1NN. This was then further purified by column chromatography using neutral silica as bed materials and pure hexane as eluent. The product was confirmed by ^{1}HNMR, ^{13}CNMR, FT-IR, and UV-Visible spectrum as already discussed in preceding section (mp. 55.7°C, literature mp. 56-58°C) (Yin and shi, 2006). ^{1}HNMR data was found to be as follows: ^{1}H NMR ($CDCl_3$) δ 7.53, 7.55, 7.58 (t,1H, aromatic), 7.60, 7.63, 7.65 (t,1H, aromatic), 7.70, 7.73, 7.75 (t,1H, aromatic), 7.95, 7.98 (d,1H, aromatic), 8.11, 8.14 (d,1H, aromatic), 8.23, 8.25 (d,1H, aromatic), 8.56, 8.59 (d,1H, aromatic). ^{13}C NMR ($CDCl_3$ δ ppm) 123.14, 124.00, 124.13, 127.35, 128.60, 129.45, 134.64

RESULTS AND DISCUSSION

The deamination of amino group through diazotization followed by aqueous $CuSO_4$ treatment is not reported in literature though use of zinc powder and ethanol is known (Roe and Graham, 1952). Here, during the process of synthesizing 5-nitronaphthol (Ishii et al., 1976), from 5-nitronaphthylamine (5NNA), we have unexpectedly got 1-nitronaphthalene (1NN) . Since 1-5-dinitronaphthalene (1,5DNN) is easily and cheaply available compared to 5NNA, we have started with 1,5DNN. One of the nitro groups in 1,5DNN is selectively reduced by usual method (March, 1992), using freshly prepared polysulphide



Scheme 2. Detail pathway of the diazotized 5NNA using $NaNO_2$/HCl at 0 to 5°C.

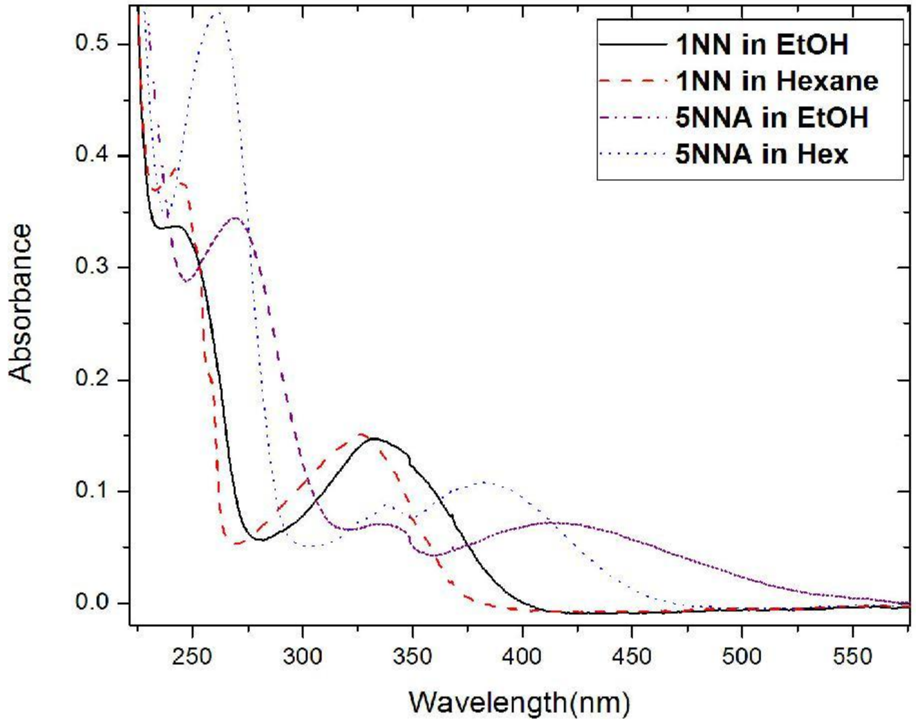


Figure 1. UV-Visible spectra of 1NN and 5NNA in hexane and ethanol at room temperature.

solution as described in experimental section to get 5NNA. 5NNA is then diazotized using $NaNO_2$/HCl at 0 to 5°C. When aqueous copper sulphate solution was added to the diazotized solution and stirred for 30 min at laboratory temperature (27 to 30°C), 1NN resulted in good to moderate yield. The reaction was repeated for three times and found to be consistence. Scheme 2 shows detail pathway of the reaction and it appears that this reductive deamination was facilitated due to the presence of the transition metal catalyst ($CuSO_4$). The product was yellow in color in contrast to the orange color crystal that we expected if the product was 1-hydroxy-5-nitronaphthalene (Ishii et al., 1976). The identity of this yellow crystal was established by melting point, ^{1}HNMR, FT-IR as well as by UV- Visible spectrum. This analysis shows that the product is indeed 1-nitronaphthalene. Since these niddle shaped yellow crystals were very thin, it was not possible to determine the structure by single crystal x- ray crystallographic study. In fact, the reason for absence of the crystal structure in literature of this molecule is due to the lack of formation of good crystal suitable for x-ray studies.

The electronic spectra of 1NN is presented in Figure 1 along with 5NNA for comparison. The major, though expected difference is the existence of a broad band for 5NNA at longer wavelength which is absent in 1NN. Since in 5NNA, both donor (- NH_2) and acceptor (-NO_2) groups are connected through resonance via naphthalene group, a charge transfer band appears (at 380 nm in hexane). When the donor group is removed in 1NN, this charge transfer band disappears completely. This is a clear spectroscopic proof (in addition to FT-IR, ^{1}HNMR) that deamination took place. That the broad band is of charge transfer character is also evident from the fact the band shows a drastic Stokes shift (red shift) in ethanol, a polar and protic solvent as shown in Figure 1.

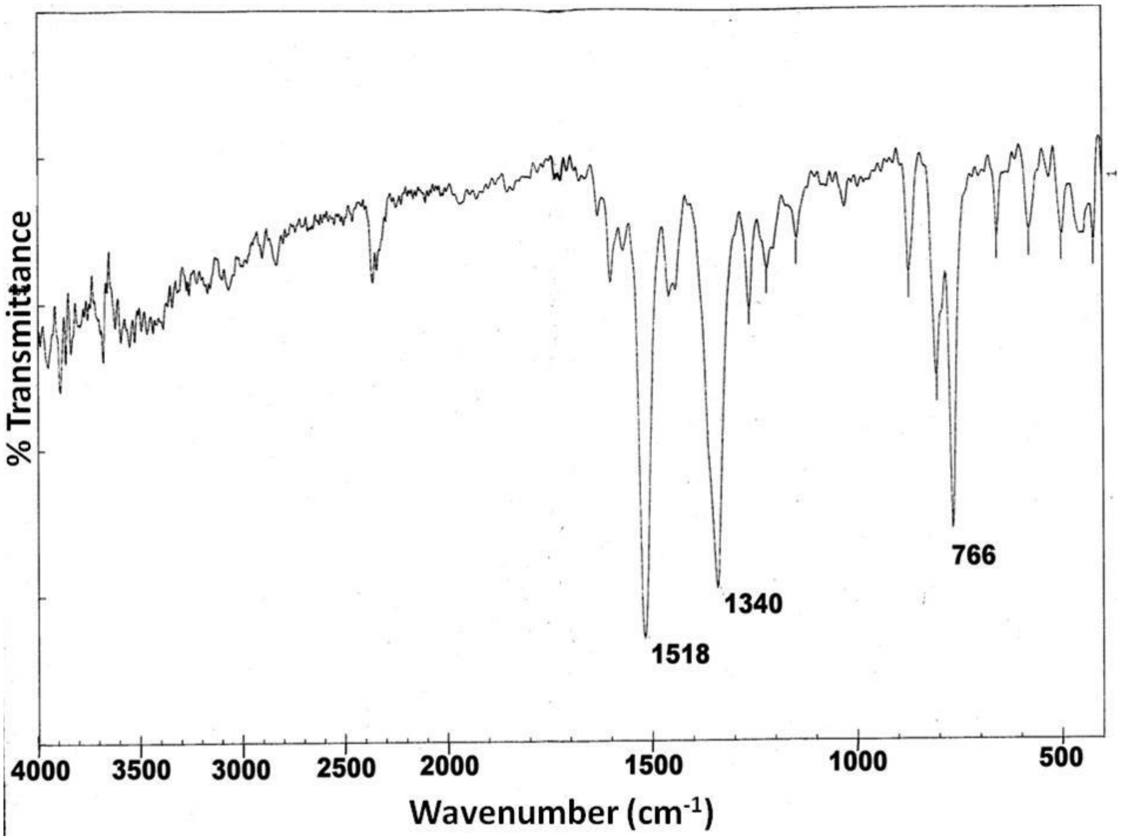


Figure 2. IR spectrum of 1NN in region of 400 – 4000 cm^{-1}, recorded using KBr plate.

In addition to UV-visible spectrum, we have also analyzed the IR spectrum of 1NN in-depth and is presented in Figure 2. As expected, there is no peak in the region of 3000 to 4000 cm $^{-1}$ reconfirming the absence of amino group in 1NN. The strong vibrational band at 766 cm^{-1} is due to the out of plane bending of aromatic C-H coupled with NO $_2$ bending. While the symmetric stretching of NO$_2$ and stretching of C -N bond appears at 1340 cm^{-1}, strongest IR absorption appears at about 1518 cm^{-1} which is due to in-plane bending of aromatic C-H and naphthalene ring stretching.

Conclusion

We have presented here a facile but an unexpected way to synthesis, 1-nitronaphthalene from 5-nitronaphthyl-amine, a very important class of compound having considerable applications. While diazotization of an aro-matic amino compound followed by hydrolysis generally provides the hydroxyl substituted product, we have obtained deaminated product using aqueous CuSO $_4$ solu-tion. The detail of UV-visible and FT-IR spectrum of the product, 1-nitronaphthalene have been reported which establish the confirmation of the product beyond doubt.

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