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Dry Diazonium Nitrates from Aromatic Amines and Tributyl Phosphate-NO_2 Adduct

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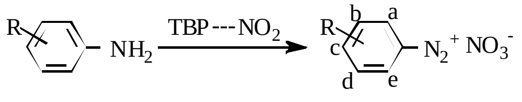
Aromatic amines reacted with TBP-NO_2 adduct to give dry aryl diazonium nitrate in high purity and yield.

INTRODUCTION

Since the discovery of diazonium compounds in 1858, more than a century has witnessed the synthesis, the high reactivity and application of these invaluable compounds. Applications of diazonium salts have long been important in both the dye and the pharmaceutical industries.[1-7] Recently, diazonium salts have also found new application in the recording, imaging, copying and printing sciences.[8-13] The most frequently employed diazonium salts in these fields are classical arenediazonium chlorides, tetrafluoroborates, hydrosulfates and dihydrophosphates.[1-4] However, studies of the diazonium nitrates have been seldom involved because of the strong oxidization of nitric acid. In order to avoid the oxidation of aromatic amines by nitric acid, N_2O_4 in $CHCl_3$ was treated with phenyl isocyanates by Backman to obtain diazonium nitrates.[14] Recently, Kagiyama and Tsurushima[15] reported a successful method using alkyl nitrites to prepare diazonium nitrates, while Wagenblast[16] reacted NO_2 in the gaseous or liquid phase with aromatic amines to obtain corresponding diazonium nitrates.

In the course of our study on the treatment and utilization of the waste gas NO_X with organic compounds, TBP (tributyl phosphate) was used as an absorbent of NO_2. The resultant absorbent product, TBP-NO_2, proved to be a selective and moderate oxidant, which can convert the aromatic methanol into corresponding aldehydes or ketones in high yields.[17] In this work, the reaction of TBP-NO_2 with aromatic amines to give arenediazonium nitrates was studied.



1a – 1o 2a – 2o

a) H	b) *o*-CH_3	c) *m*-CH_3
d) *o*-Cl	e) *m*-Cl	f) *p*-Cl
g) *o*-Br	h) *m*-Br	i) *p*-Br
j) *o*-CO_2H	k) *m*-CO_2H	l) *p*-CO_2H
m) *o*-NO_2	n) *m*-NO_2	o) *p*-NO_2

RESULTS AND DISCUSSION

When TBP-NO_2 adduct was mixed with aromatic amines in TBP, the diazonium precipitated immediately; work-up by recrystallization gave a dry and pure product. The IR peaks at 2252-2293 cm^{-1} confirm the presence of ArN_2^+, while the peaks at 1384 cm^{-1} and 825-826 cm^{-1} are assigned to the vibration of nitrate anions. Elemental analyses and ^{1}H NMR data also confirm the structures.

The arenediazonium nitrates with electron-withdrawing substituents (compounds **2j-2o**) were prepared at 10-40 °C in excellent yield. These salts prove to be very stable and can be stored at room temperature in a desiccator for a half a year without any change. The diazonium nitrates without electron-withdrawing substituents (compounds **2a-2i**) were obtained at lower reaction temperatures (10-15 °C) in good yield. Higher reaction temperature leads to the formation of tar. These salts can be stored at 10-15 °C for two months; storage at room temperature makes these salts gradually darken. When heated to about 65 °C or struck or ignited, all the dry diazonium salts explode.

As synthetic intermediates, these dry and pure diazonium nitrates are expected to be more useful than other diazonium salts. Application of these diazonium salts is under investigation.

EXPERIMENTAL SECTION

Starting materials are reagent grade and used without further purification. A FTS-40 infrared spectrophotometer was utilized to record spectra of samples. ^{1}H NMR spectra were obtained on a Bruker DPX-400 spectrometer using TMS as an internal standard. Elemental analyses were performed by PE-2400 microelemental analyser.

General Procedure for the Preparation of TBP-NO_2 Adduct

In a typical procedure, to 21.1 g (0.3 mol) of sodium nitrite (98%) in a three-neck round bottom flask was added dropwise 18 g (0.18 mol) of conc. sulfuric acid (98%) *via* a pressure-equalized dropping funnel. The evolved NO_X gases were blown by oxygen through a condenser into a drying tower (packed with *ca*. 80 g of the mixture of phosphrous pentaoxide and quartz sand, $P_2O_5 : SiO_2 = 1 : 1$ in wt.), then through an oxidizing tower (packed with *ca*. 100 g of quartz sand carrying chromium trioxide, $CrO_3 : SiO_2 = 5 : 95$ in wt.) and finally into the bottom of an absorption tower (height 300 mm, inside diameter 15 mm, packed with glass ring). From the top of the absorption tower, 79.9 g (0.3 mol) of TBP was added dropwise to induce counterface absorption. Control of the rate of addition of TBP and of sulfuric acid and the flow of oxygen made a complete absorption of NO_2. The absorption solution collected in the bottom of the absorption tower is the TBP-NO_2 adduct.

Arenediazonium Nitrates. General Procedure

To 5.0 mmol of aromatic amine dissolved in 10 mL of TBP at 10-15 °C, was added 11 mL (40 mmol) of TBP-NO_2 immediately with vigorous stirring. The diazonium salt precipitated immediately. The crude product was filtered and washed with Et_2O. Recrystallisation by dissolving the crude product in DMF and then adding Et_2O and evaporation *in vacuo* gave pure and dry diazonium salts.

Benzenediazonium nitrate (2a)

Colorless needles; Yield: 90%; IR (KBr, cm^{-1}): 2294 (m, sharp), 1384 (vs), 825 (w); ^{1}H NMR (D-DMSO): 8.68 (d, J_{ab} = 8.8 Hz, 2H, H_a), 8.26 (t, J_{cb} = 7.6 Hz, 1H, H_c), 7.98 (t, J_{ba} = J_{bc} = 8.2 Hz, 2H, H_b). Anal. Calcd. for $C_6H_5N_3O_3$: C, 43.11; H, 3.02; N, 25.1; Found: C, 43.22; H, 3.15; N, 25.16.

o-Toluenediazonium nitrate (2b)

Colorless needles; Yield: 84%; IR (KBr, cm^{-1}): 2261 (w, sharp), 1384 (vs), 826 (w); ^{1}H NMR (D-DMSO): 8.65 (d, J_{ab} = 8.0 Hz, 1H, H_a), 8.15 (t, J_{cb} = J_{cd} = 7.6 Hz, 1H, H_c), 7.84 (d, J_{dc} = 7.6 Hz, 1H, H_d), 7.79 (t, J_{ba} = J_{bc} = 8.0 Hz, 1H, H_b), 2.74 (s, 3H, CH_3). Anal. Calcd. for $C_7H_7N_3O_3$: C, 46.40; H, 3.90; N, 23.20; Found: C, 46.61; H, 4.04; N, 23.75.

m-Toluenediazonium nitrate (2c)

Colorless needles; Yield: 86%; IR (KBr, cm^{-1}): 2279 (m, sharp), 1384 (vs), 825 (w); ^{1}H NMR (D-DMSO): 8.51 (d, J_{ab} = 7.2 Hz, 1H, H_a), 8.50 (s, 1H, H_e), 8.09 (d, J_{cb} = 8.2 Hz, 1H, H_c), 7.87 (t, J_{ba} = J_{bc} = 7.4 Hz, 1H, H_b), 2.50 (s, 3H, CH_3). Anal. Calcd. for $C_7H_7N_3O_3$: C, 46.40; H, 3.90; N, 23.20; Found: C, 46.74; H, 3.73; N, 23.48.

o-Chlorobenzene diazonium nitrate (2d)

Colorless needles; Yield: 80%; IR (KBr, cm^{-1}): 2273 (m, sharp), 1384 (vs), 826 (w); ^{1}H NMR (D_2O): 8.60 (d, J_{ab} = 8.6 Hz, 1H, H_a), 8.20 (t, J_{cb} = J_{cd} = 8.0 Hz, 1H, H_c), 8.00 (d, J_{dc} = 8.2 Hz, 1H, H_d), 7.83 (t, J_{ba} = J_{bc} = 8.4 Hz, 1H, H_b). Anal. Calcd. for $C_6H_4ClN_3O_3$: C, 35.75; H, 2.00; N, 20.85; Found: C, 34.96; H, 1.82; N, 20.46.

m-Chlorobenzene diazonium nitrate (2e)

Colorless needles; Yield: 82%; IR (KBr, cm^{-1}): 2305 (w), 1384 (vs), 826 (w); ^{1}H NMR (D_2O): 8.60 (s, 1H, H_e), 8.49 (d, J_{ab} = 8.0 Hz, 1H, H_a), 8.25 (d, J_{cb} = 8.4 Hz, 1H, H_c), 7.88 (t, J_{ba} = J_{bc} = 8.4 Hz, 1H, H_b). Anal. Calcd. for $C_6H_4ClN_3O_3$: C, 35.75; H, 2.00; N, 20.85; Found: C, 35.81; H, 1.89; N, 20.93.

p-Chlorobenzene diazonium nitrate (2f)

Colorless needles; Yield: 83%; IR (KBr, cm^{-1}): 2276 (w), 1384 (vs), 826 (w); ^{1}H NMR (D_2O): 8.52 (d, J_{ab} = 8.8 Hz, 2H, H_a), 7.93 (d, J_{ba} = 8.8 Hz, 2H, H_b). Anal. Calcd. for $C_6H_4ClN_3O_3$: C, 35.75; H, 2.10; N, 20.85; Found: C, 35.78; H, 1.96; N, 21.02.

o-Bromobenzene diazonium nitrate (2g)

Colorless needles; Yield: 84%; IR (KBr, cm^{-1}): 2267 (m, sharp), 1384 (vs), 826 (m); ^{1}H NMR (D_2O): 8.61 (d, J_{ab} = 8.0 Hz, 1H, H_a), 8.16 (d, J_{dc} = 8.4 Hz, 1H, H_d), 8.10 (t, J_{cd} = J_{cb} = 7.8 Hz, 1H, H_c), 7.88 (t, J_{ba} = J_{bc} = 7.8 Hz, 1H, H_b). Anal. Calcd. for $C_6H_4BrN_3O_3$: C, 29.29; H, 1.64; N, 17.08; Found: C, 28.91; H, 1.79; N, 17.30.

m-Bromobenzene diazonium nitrate (2h)

Colorless needles; Yield: 85%; IR (KBr, cm^{-1}): 2276 (m, sharp), 1384 (vs), 826 (w); ^{1}H NMR (D-DMSO): 8.90 (s, 1H, H_e), 8.69 (d, J_{ab} = 8.4 Hz, 1H, H_a), 8.38 (d, J_{cb} = 8.2 Hz, 1H, H_c), 8.02 (t, J_{ba} = J_{bc} = 8.4 Hz, 1H, H_b). Anal. Calcd. $C_6H_4BrN_3O_3$: C, 29.29; H, 1.64; N, 17.08; Found: C, 29.41; H, 1.48; N, 17.18.

***p*-Bromobenzene diazonium nitrate (2i)**

Colorless needles; Yield: 86%; IR (KBr, cm^{-1}): 2274 (s), 1384 (vs), 826 (m); ^{1}H NMR (D_2O): 8.42 (d, J_{ab} = 9.2 Hz, 2H, H_a), 8.12 (d, J_{ba} = 9.2 Hz, 2H, H_b). Anal. Calcd. $C_6H_4BrN_3O_3$: C, 29.29; H, 1.64; N, 17.08; Found: C, 29.51; H, 1.76; N, 17.25.

***o*-Carboxybenzene diazonium nitrate (2j)**

Colorless needles; Yield: 94%; IR (KBr, cm^{-1}): 2280 (m), 1384 (vs), 826 (w); ^{1}H NMR (D_2O): 8.58 (d, J_{ab} = 8.0 Hz, 1H, H_a), 8.29 (d, J_{dc} = 7.6 Hz, 1H, H_d), 8.20 (t, J_{cb} = J_{cd} = 7.6 Hz, 1H, H_c), 7.97 (t, J_{ba} = J_{bc} = 7.8 Hz, 1H, H_b). Anal. Calcd. for $C_7H_5N_3O_5$: C, 39.82; H, 2.39; N, 19.90; Found: C, 39.91; H, 2.32; N, 19.78.

***m*-Carboxybenzene diazonium nitrate (2k)**

Colorless needles; Yield: 95%; IR (KBr, cm^{-1}): 2284 (m), 1385 (m), 826 (w); ^{1}H NMR (D-DMSO): 9.02 (s, 1H, H_e), 8.69 (d, J_{ab} = 8.0 Hz, 1H, H_a), 8.65 (d, J_{cb} = 8.4 Hz, 1H, H_c), 7.98 (t, J_{ba} = J_{bc} = 8.2 Hz, 1H, H_b). Anal. Calcd. for $C_7H_5N_3O_5$: C, 39.82; H, 2.39; N, 19.90; Found: C, 39.90; H, 2.28; N, 19.72.

***p*-Carboxybenzene diazonium nitrate (2l)**

Colorless needles; Yield: 91%; IR (KBr, cm^{-1}): 2290 (s), 1384 (vs), 825 (w); ^{1}H NMR (D_2O): 8.61 (d, J_{ab} = 8.8 Hz, 2H, H_a), 8.35 (d, J_{ba} = 8.8 Hz, 1H, H_b). Anal. Calcd. for $C_7H_5N_3O_5$: C, 39.82; H, 2.39; N, 19.90; Found: C, 39.95; H, 2.18; N, 19.79.

***o*-Nitrobenzene diazonium nitrate (2m)**

Light yellow needles; Yield: 88%; IR (KBr, cm^{-1}): 2275 (m), 1384 (s), 826 (w); ^{1}H NMR (D_2O): 8.98 (d, J_{ab} = 8.4 Hz, 1H, H_a), 8.80 (d, J_{dc} = 8.4 Hz, 1H, H_d), 8.53 (t, J_{cb} = J_{cd} = 8.0 Hz, 1H, H_c), 8.35 (t, J_{ba} = J_{bc} = 8.0 Hz, 1H, H_b). Anal. Calcd. for $C_6H_4N_4O_5$: C, 33.97; H, 1.90; N, 26.42; Found: C, 33.97; H, 1.79; N, 26.65.

***m*-Nitrobenzene diazonium nitrate (2n)**

Light yellow needles; Yield: 92%; IR (KBr, cm^{-1}): 2292 (m), 1384 (vs), 825 (w); ^{1}H NMR (D-DMSO): 9.63 (s, 1H, H_e), 9.05 (d, J_{ab} = 8.4 Hz, 1H, H_a), 8.99 (d, J_{cb} = 8.6 Hz, 1H, H_c), 8.25 (t, J_{ba} = J_{bc} = 8.4 Hz, 1H, H_b). Anal. Calcd. for $C_6H_4N_4O_5$: C, 33.97; H, 1.90; N, 26.42; Found: C, 34.10; H, 1.42; N, 26.46.

***p*-Nitrobenzene diazonium nitrate (2o)**

Light yellow needles; Yield: 90%; IR (KBr, cm^{-1}): 2298 (w), 1386 (s), 826 (w); ^{1}H NMR (D-DMSO): 8.94 (d, J_{ab} = 7.2 Hz, 2H, H_a), 8.72 (d, J_{ba} = 7.2 Hz, 2H, H_b). Anal. Calcd. for $C_6H_4N_4O_5$: C, 33.97; H, 1.90; N, 26.42; Found: C, 33.82; H, 1.69; N, 26.51.

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Key Words

Diazonium nitrates; Aromatic amines; TBP-NO_2.

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