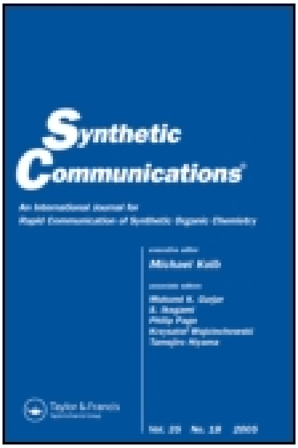

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SYNTHESIS OF SOLID ARENEDIAZONIUM NITRATES UNDER NONAQUEOUS CONDITION

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SYNTHESIS OF SOLID ARENEDIAZONIUM NITRATES UNDER NONAQUEOUS CONDITION

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ABSTRACT

Amines react with DMF-NO_2 adduct under nonaqueous condition to give solid aryl diazonium nitrate in high purity and excellent yield.

Since diazonium salts are important synthetic intermediates that have long been used in the dye and pharmaceutical industries,[1–7] their synthesis has received considerable attention. The normal method for synthesis of diazonium salts was carried out in aqueous medium and usually yielded the diazonium salts in solution[8] but this method needs low temperature and does not produce solid diazonium salts. Furthermore, the synthesis of diazonium nitrate has seldom been studied because of the strong oxidization of nitric acid. To avoid the oxidation of aromatic amines by nitric acid, Kagiyama and Tsurushima[9] recently reported a successful method using alkyl nitrites to prepare diazonium nitrates, while Wagenblast[10] reacted NO_2 in the gaseous or liquid phase with aromatic amines to obtain corresponding diazonium nitrates.

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In the course of our study on the treatment and utilization of the waste gas NO_x with organic compounds, DMF was used as an absorbent, which absorbed NO_2 gas to give a DMF-NO_2 adduct. DMF-NO_2 was found to be a new and mild oxidizing agent.[11] The structure of DMF-NO_2 may be similar to that of alkyl nitrate, which makes the oxidative power of NO_2 mild. Using this oxidizing agent with aromatic amines in DMF produces solid diazonium nitrates in excellent yield and high purity (see Table).

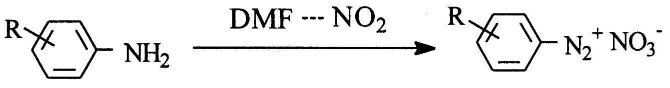


Table. Diazonium Nitrates from Aromatic Amines and DMF-NO_2 Adduct

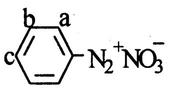
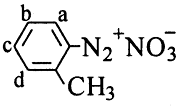
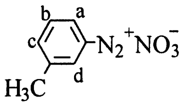
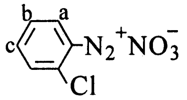
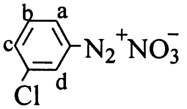
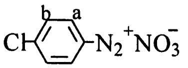
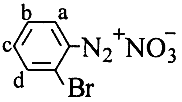
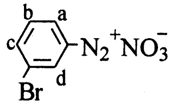
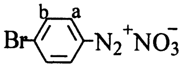
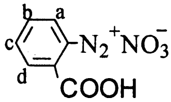
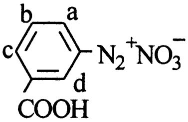
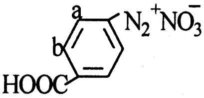
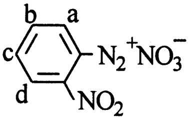
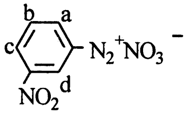
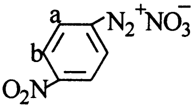
Product	Yield (%)	^{1}H NMR (δ)	IR (cm^{-1})	Microanalysis (%)(found)
	90^a	8.46(d,2H,H_a) 8.20(s,1H,H_c) 7.87(s,2H,H_b)	2293(m,sharp) 1384(vs) 826(w)	C, 43.11 (43.38) H, 3.02 (3.12) N, 25.15 (25.09)
	72^a	8.43(s,1H,H_a) 8.06(d,1H,H_c) 7.67(m,2H,H_b+H_d) 2.73(s,3H,CH_3)	2267(w,sharp) 1385(vs) 844(w)	C, 46.40 (46.79) H, 3.90 (4.01) N, 23.20 (23.91)
	78^a	8.32(s,2H,H_a+H_d) 8.05(s,1H,H_c) 7.74(s,1H,H_b) 2.46(s,3H,CH_3)	2279(m,sharp) 1384(vs) 825(w)	C, 46.40 (46.69) H, 3.90 (3.75) N, 23.20 (23.55)
	84^a	8.58(m,1H,H_a) 8.24(m,1H,H_d) 8.03 (m,1H,H_C) 7.81(m,1H,H_b)	2271(m,sharp) 1384(vs) 825(w)	C, 35.75 (34.90) H, 2.00 (1.82) N, 20.85 (20.45)
	86^a	8.61(s,1H,H_d) 8.47(d,1H,H_a) 8.27(d,1H,H_c) 7.85(t,1H,H_b)	2277(w) 1384(vs) 826(w)	C, 35.75 (35.86) H, 2.00 (1.89) N, 20.85 (20.91)
	81^a	8.53(d,2H,H_a) 7.92(d,2H,H_b)	2279(w) 1384(vs) 826(w)	C, 35.75 (35.80) H, 2.10 (1.93) N, 20.85 (21.12)

Table. Continued

Product	Yield (%)	^{1}H NMR (δ)	IR (cm^{-1})	Microanalysis (%)(found)
	80[a]	8.63(d,1H,H_a) 8.15 (m,2H,H_c+H_d) 7.83(t,1H,H_b)	2273(m,sharp) 1384(vs) 826(m)	C, 29.29 (28.83) H, 1.64 (1.78) N, 17.08 (17.30)
	82[a]	8.72(s,1H,H_d) 8.54(d,1H,H_a) 8.41(d,1H,H_c) 7.78(t,1H,H_b)	2278(m,sharp) 1384(vs) 826(w)	C, 29.29 (29.45) H, 1.64 (1.49) N, 17.08 (17.18)
	87[a]	8.42(d,2H,H_a) 8.17(d,2H,H_b)	2276(s) 1384(vs) 826(m)	C, 29.29 (29.49) H, 1.64 (1.75) N, 17.08 (17.23)
	91[a]	8.59(d,1H,H_a) 8.30(d,1H,H_d) 8.22(t,1H,H_c) 7.95(t,1H,H_b)	2286(m) 1384(vs) 825(w)	C, 39.82 (39.89) H, 2.39 (2.27) N, 19.90 (19.78)
	93[a]	9.07(s,1H,H_d) 8.73(m,2H,H_a+H_c) 8.00(t,1H,H_b)	2291(m) 1385(m) 825(w)	C, 39.82 (39.90) H, 2.39 (2.26) N, 19.90 (19.72)
	92[a]	8.65(d,2H,H_a) 8.35(d,1H,H_b)	2290(s) 1384(vs) 826(w)	C, 39.82 (39.92) H, 2.39 (2.18) N, 19.90 (19.79)
	90[b]	8.97(d,1H,H_a) 8.81(d,1H,H_d) 8.53(t, 1H, H_c) 8.34(t, 1H,H_b)	2276(m) 1384(s) 826(w)	C, 33.97 (33.95) H, 1.90 (1.81) N, 26.42 (26.61)
	92[b]	9.43(t,1H,H_d) 8.96(m,1H,H_a) 8.90(m,1H,H_c) 8.17(t,1H,H_b)	2289(m) 1384(vs) 826(w)	C, 33.97 (34.10) H, 1.90 (1.49) N, 26.42 (26.45)
	91[b]	8.87 (d,2H,H_a) 8.71 (d,2H,H_b)	2290(w) 138(s) 826(w)	C, 33.97 (33.82) H, 1.90 (1.69) N, 26.42 (26.50)

[a]Crystallized as colorless needle; [b]light yellow needle.

When aromatic amines in DMF were reacted with 8 equiv. of DMF-NO_2, a lot of gas evolved off. Adding ether to the solution, the diazonium nitrates precipitated through a liquid phase. The arenediazonium nitrates with electron-withdrawing substituents were very pure without recrystallization, but the diazonium nitrates without electron-withdrawing substituents should be recrystallized with DMF-Et_2O. The IR peaks at 2252–2293 cm^{-1} confirmed the existence of ArN_2^+, while the peaks at 1384 cm^{-1} and 825–826 cm^{-1} belong to the nitrate ions. The IR, microanalysis, and ^1H NMR data all confirmed that the products were diazonium nitrates.

The arenediazonium nitrates with electron-withdrawing substituents prove to be very stable and could be stored at room temperature for a half year without any change. These salts were prepared at 10°–40°C in excellent yield. While the diazonium nitrates without electron-withdrawing substituents should be stored at 10°–15°C, after two months (or storage at room temperature) these salts gradually darken. These salts were obtained at lower reaction temperatures (10°–15°C) in good yield. Higher reaction temperature leads to the formation of tar. Furthermore, when heated to about 65°C, struck, or ignited, all these diazonium salts explode. Maybe these diazonium nitrates can be considered as useful synthetic intermediates as other diazonium salts.

EXPERIMENTAL

Starting materials were reagent grade and used without further purification. IR spectra were obtained on a FTS-40 infrared spectrophotometer. ^1H NMR spectra were recorded on a Bruker DPX-400 spectrometer using TMS as an internal standard. Elemental analyses were carried out on a PE-2400 microelemental analyzer.

DMF-NO_2 Adduct

In a typical procedure, 21.1 g (0.3 mol) of sodium nitrite (98%) in a three-neck round-bottom flask was added dropwise to 18 g (0.18 mol) of conc. sulfuric acid (98%). The resulting NO_x was oxidized and blew by O_2 into the bottom of a drying tower (packed with the mixture of phosphorus pentaoxide and quartz sand), an oxidizing tower (packed with the quartz sand carrying chromium trioxide to guarantee all NO oxidized into NO_2), an absorption tower (packed with glass ring) successively. At the top of the absorption tower, 21.93 g (0.3 mol) of DMF was dropped downwards through a dropping funnel. The counter-face absorption of NO_2 by DMF gave the adduct DMF-NO_2.

Arenediazonium Nitrates

Three mmol of aromatic amines dissolved in 6 mL DMF was added to 1.86 mL (24 mmol) of DMF-NO_2 immediately with vigorous stirring. Gases evolved. About 5 m later, to the solution was added 20 mL ether, then it became two layers. The solution was stirred until the diazonium salts precipitated completely. The diazonium nitrates were filtered and washed with Et_2O, then dissolved in DMF, and added Et_2O to the DMF solution. Collection, washing with Et_2O, and vacuum drying obtained the pure diazonium nitrates.

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