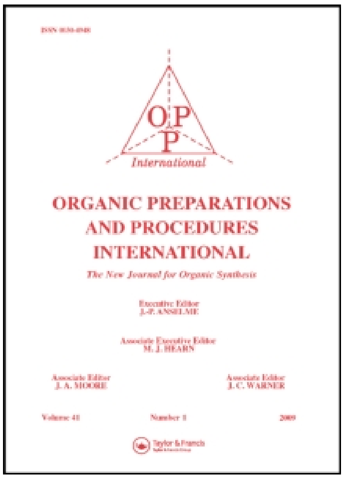

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DRY ARENEDIAZONIUM NITRATES FROM AROMATIC AMINES AND UREAS WITH NITROGEN DIOXIDE ADDUCTS OF DIOXANE AND OF TRIBUTYL PHOSPHATE

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OPPI BRIEFS

DRY ARENEDIAZONIUM NITRATES FROM AROMATIC AMINES AND UREAS WITH NITROGEN DIOXIDE ADDUCTS OF DIOXANE AND OF TRIBUTYL PHOSPHATE

Submitted by (09/05/00)

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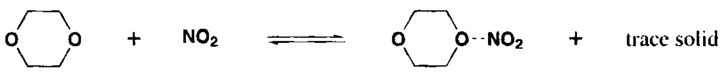
Diazonium salts are important synthetic intermediates which have long been used in the dye and pharmaceutical industries,[1-7] in imaging and recording material sciences.[8-13] Investigation of the reactivity of diazonium salts is still an active area of study.[14-18] The salts most often employed are the chlorides, tetrafluoroborates, hydrosulfates and dihydrophosphates.[1-4] However, the synthesis and applications of arenediazonium nitrates have seldom been studied because the strong oxidizing power of nitric acid makes it difficult to transform aromatic amines into the corresponding diazonium nitrates with sodium nitrite. To avoid the oxidation of aromatic amines by nitric acid, alkyl nitrites have been employed to convert aromatic amines into diazonium nitrates.[19] Reaction of phenylisocyanate with N_2O_4 in $CHCl_3$ gave phenyldiazonium nitrate,[20] while treatment of solid aromatic amines with gaseous nitrogen dioxide affords solid diazonium nitrates.[21]

During a recent study on the treatment and utilization of the waste gas NO_x with organic compounds, dioxane was used as absorbent to give a dioxane-NO_2 adduct. Like tributyl phosphate-NO_2 (TBP-NO_2),[22] PEG-NO_2 (polyethylene glycol-NO_2),[23] and DMF-NO_2 (dimethylformamide-NO_2),[24] dioxane-NO_2 is found to be a mild oxidizing agent. In the present work, dioxane-NO_2 and TBP-NO_2 are used to convert aromatic amines and arylureas respectively to give pure and dry diazonium nitrates.

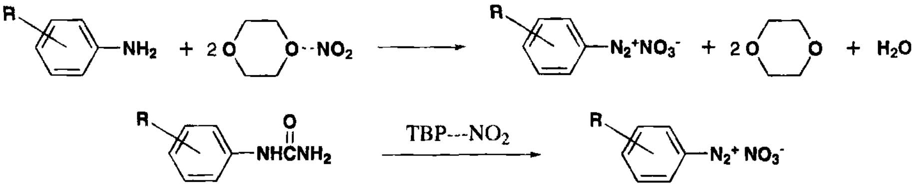


$$(CH_3CH_2CH_2CH_2O)_3P{=}O \;+\; NO_2 \longrightarrow (CH_3CH_2CH_2CH_2O)_3P{=}O\cdots NO_2$$

Comparison of the IR spectrum of the dioxane with that of the dioxane-NO_2 solution shows several new peaks at 1350 cm^{-1}, 875 cm^{-1} and 890 cm^{-1}. The 1350 cm^{-1} peak is assigned to the vibration of the NO_2 moiety of the dioxane-NO_2, which is shifted 30 cm^{-1} to the low-frequency side of NO_2. The peaks at 875 cm^{-1} and 890 cm^{-1} are ascribed to the skeletal ring vibrations of dioxane in dioxane-NO_2, which correspondingly shift 45 cm^{-1} and 50 cm^{-1} to the high-frequency side of dioxane. By comparison with the IR spectrum of TBP, there are also several new peaks in the IR spectrum of TBP-NO_2, such as 1648cm^{-1} ($\nu_{as}NO_3^-$), 1308cm^{-1} (ν_s NO_3^-) and the absorption of $\nu_{P=O}$ is shifted from 1286 cm^{-1} to 1209 cm^{-1}. However, the peak for $\nu_{P\text{-}O\text{-}C}$ and other peaks did not change. The data suggest that the dioxane-NO_2 adduct and the TBP-NO_2 adduct are formed by the weak attraction of the lone electron pair of oxygen and the positive nitrogen of NO_2. Peaks corresponding to N_2O_4 are not observed. When the ratio of NO_2 to dioxane is greater than 2 (or such a ratio is formed locally during the process of absorption), crystals corresponding to dioxane-N_2O_4 adduct form at room temperature.[25]

When the dioxane-NO_2 solution is mixed with aromatic amines in dioxane, the diazonium salts precipitate immediately. In contrast, when arylureas in TBP were treated with 8 equiv. of TBP-NO_2 at room temperature, the arylureas disappeared completely in 5 minutes. About 15 minutes later, the diazonium nitrates precipitated. Work-up with ether and recrystallization afforded dry and pure products (see Table).

Great caution must be exercised because all these compounds may explode easily.



The arenediazonium nitrates with electron-withdrawing substituents (NO_2, CO_2H) were prepared at 10-40° in excellent yield. These salts proved to be very stable and may be stored at room temperature in a desiccator for a half year without any change. The diazonium nitrates without electron-withdrawing substituents were obtained at lower temperatures (10-15°) in good yield. Higher reaction temperature leads to the formation of tar. While these salts can be stored at 10-15° for two months, storage at room temperature leads to gradual darkening. *When heated to about 65°, struck or ignited, the dry diazonium nitrates explode.* The IR absorption at 2252-2295 cm^{-1} indicates the presence of $ArN{\equiv}N^+$, while the peaks at 1384 cm^{-1} and 825-826 cm^{-1} can be assigned to the nitrate ion. The microanalysis and ^1H NMR data confirm the structures (see Table).

Table 1. Diazonium Nitrates from Aromatic Amines and Ureas

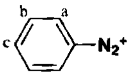
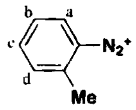
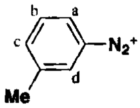
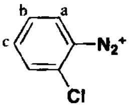
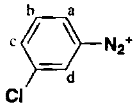
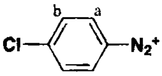
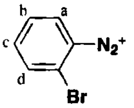
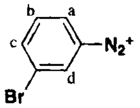
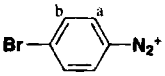
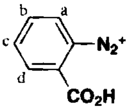
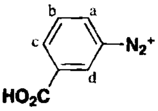
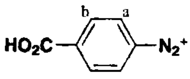
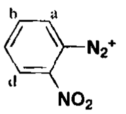
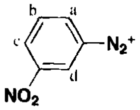
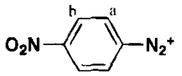
Diazonium Nitrates	Yield (%) Amines	Yield (%) Ureas	^{1}H NMR (δ)	IR (cm^{-1})	Microanalysis (Found)
	81^a	80^a	8.49(d,2H,H$_a$) 8.22(s,1H,H$_c$) 7.89(s,2H,H$_b$)	2295(m,sharp) 1384(vs) 825(w)	C, 43.11 (43.42) H, 3.02 (3.17) N, 25.15 (25.05)
	80^a	67^a	8.40(s,1H,H$_a$) 8.07(d,1H,H$_c$) 7.69(m,2H,H$_b$+H$_d$) 2.72(s,3H,CH$_3$)	2261(w,sharp) 1385(vs) 844(w)	C, 46.40 (46.81) H, 3.90 (4.02) N, 23.20 (23.90)
	82^a	81^a	8.30(s,2H,H$_a$+H$_d$) 8.04(s,1H,H$_c$) 7.76(s,1H,H$_b$) 2.47(s,3H,CH$_3$)	2279(m,sharp) 1384(vs) 825(w)	C, 46.40 (46.72) H, 3.90 (3.67) N, 23.20 (23.59)
	84^a	74^a	8.60(m,1H,H$_a$) 8.20(m,1H,H$_d$) 8.00(m,1H,H$_c$) 7.83(m,1H,H$_b$)	2270(m,sharp) 1384(vs) 826(w)	C, 35.75 (35.92) H, 2.00 (1.79) N, 20.85 (20.21)
	86^a	89^a	8.60(s,1H,H$_d$) 8.49(d,1H,H$_a$) 8.25(d,1H,H$_c$) 7.88(t,1H,H$_b$)	2287(w) 1384(vs) 826(w)	C, 35.75 (35.90) H, 2.00 (1.87) N, 20.85 (20.94)
	82^a	84^a	8.51(d,2H,H$_a$) 7.94(d,2H,H$_b$)	2287(w) 1384(vs) 826(w)	C, 35.75 (35.79) H, 2.10 (1.91) N, 20.85 (21.04)
	88^a	69^a	8.61(d,1H,H$_a$) 8.13(m,2H,H$_c$+H$_d$) 7.88(t,1H,H$_b$)	2263(m,sharp) 1384(vs) 826(m)	C, 29.29 (28.71) H, 1.64 (1.81) N, 17.08 (17.31)
	92^a	88^a	8.73(s,1H,H$_d$) 8.52(d,1H,H$_a$) 8.40(d,1H,H$_c$) 7.80(t,1H,H$_b$)	2278(m,sharp) 1384(vs) 826(w)	C, 29.29 (29.48) H, 1.64 (1.45) N, 17.08 (17.20)
	91^a	86^a	8.41(d,2H,H$_a$) 8.12(d,2H,H$_b$)	2273(s) 1384(vs) 826(m)	C, 29.29 (29.57) H, 1.64 (1.77) N, 17.08 (17.27)
	99^a	--	8.58(d,1H,H$_a$) 8.29(d,1H,H$_d$) 8.20(t,1H,H$_c$) 7.97(t,1H,H$_b$)	2286(m) 1384(vs) 825(w)	C, 39.82 (39.92) H, 2.39 (2.29) N, 19.90 (19.75)
	99^a	89^a	9.05(s,1H,H$_d$) 8.70(m,2H,H$_a$+H$_c$) 8.00(t,1H,H$_b$)	2290(m) 1385(m) 825(w)	C, 39.82 (39.93) H, 2.39 (2.17) N, 19.90 (19.69)
	96^a	92^a	8.61(d,2H,H$_a$) 8.35(d,1H,H$_b$)	2292(s) 1384(vs) 826(w)	C, 39.82 (39.98) H, 2.39 (2.14) N, 19.90 (19.73)

Table 1. Continued...

Diazonium Nitrates	Yield (%) Amines	Ureas	^{1}H NMR (δ)	IR (cm^{-1})	Microanalysis (%)(found)
	96^b	--	8.99(d,1H,H$_a$) 8.80(d,1H,H$_d$) 8.53(t,1H,H$_c$) 8.34(t,1H,H$_b$)	2275(m) 1384(s) 826(w)	C, 33.97 (33.97) H, 1.90 (1.78) N, 26.42 (26.68)
	100^b	90^b	9.46(t,1H,H$_d$) 8.99(m,1H,H$_a$) 8.90(m,1H,H$_c$) 8.16(t,1H,H$_b$)	2292(m) 1384(vs) 826(w)	C, 33.97 (34.12) H, 1.90 (1.39) N, 26.42 (26.45)
	100^b	93^b	8.86(d,2H,H$_a$) 8.70(d,2H,H$_b$)	2293(w) 1386(s) 826(w)	C, 33.97 (33.79) H, 1.90 (1.66) N, 26.42 (26.51)

a) Crystallized as colorless needles b) Crystallized as light yellow needles

EXPERIMENTAL SECTION

All solvents and reactants were reagent grade and were used without further purification. The oxidizing agent employed in the oxidizing tower was prepared in the following manner: 5 g of CrO_3 was dissolved in 4 g water then 95 g of quartz sand (20-30 mesh) was added. The mixture was stirred thoroughly and dried at 120° to give the quartz sand carrying chromium trioxide. IR spectra were obtained on a FTS-40 infrared spectrophotometer, ^{1}H NMR spectra were recorded on a Bruker DPX-400 spectrometer using TMS as an internal standard. Microanalyses were performed on a PE-400 microelemental analyzer.

Dioxane-Nitrogen Dioxide and Tributyl Phosphate-Nitrogen Dioxide Adduct.- To 35.2 g (0.5 mol) of sodium nitrite (98%) in a three-neck round-bottom flask (see the set-up previously described in this Journal[26]) was added dropwise 30 g (0.3 mol) of conc. sulfuric acid (98%) *via* a constant pressure funnel. The evolved gases were then blown by a stream of oxygen (most of the NO was converted into NO_2 at the same time) through a condenser into a drying tower (packed with *ca.* 80 g of the mixture of phosphorus pentoxide 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) and finally into a flask connected to an absorption tower [height 300 mm, inside diameter 15 mm, packed with glass rings (2 mm x 4 mm)]. When the gases reached to the bottom of the oxidizing tower, 44.1 g (0.5 mol) of dioxane was added dropwise through a constant pressure funnel to the absorption tower to rinse the glass rings. The NO_2 gas then entered the absorption tower and counterface absorption was effected. Control of the rate of addition of dioxane and of sulfuric acid and the flow of oxygen allows the complete absorption of NO_2 (the proper rate may be determined if the upper space of the constant pressure funnel is colorless). Once the addition of sulfuric acid was complete, the gas-producing flask was heated until the color of NO_2 was no longer evident. The oxygen was blown in for a little longer to drive any residual NO_2 completely into the absorption flask and tower. The absorption solution collected in the bottom flask of the absorption tower is the dioxane-NO_2 adduct.

The same apparatus and procedure were used to prepare the TBP-NO_2 adduct.

Arenediazonium Nitrates from Amines and from Arylureas. General Procedure.- To a solution of 5.0 mmol of aromatic amine in 10 mL of dioxane (or a solution of 5.0 mmol of arylurea in 10 mL TBP) was rapidly added 4.25 mL (50 mmol) of the dioxane-NO_2 adduct [or 11 mL (40 mmol) of TBP-NO_2] with vigorous stirring. For those aromatic amines and arylureas with electron-withdrawing groups such as -NO_2 or -CO_2H, the reaction temperature was held between 10-40°. For other aromatic amines and arylureas the reaction were performed at 10-15°. The diazonium salts precipitated immediately. The crude product was collected by suction and dissolved in DMF. Upon addition of Et_2O to the DMF solution, the salts precipitated as crystals, which were collected and washed with Et_2O and dried under vacuum to dryness to give the pure diazonium salts. *Temperatures higher than 65°, striking or igniting these salts must be avoided; they explode!*

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