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A CONVENIENT DEDIAZONIATION OF ARENEDIAZONIUM TETRAFLUOROBORATES: TRIETHYLAMINE EFFECTS ON COMPETITIVE IONIC AND RADICAL DEDIAZONIATION

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ABSTRACT: Triethylamine was very efficient in the dediazoniation of arenediazonium salt. The major product depended on the comparative molar ratio (r) of triethylamine to benzenediazonium salt. When r<0.5, anisole (ionic product) was a major, while benzene (radical product) was a major when r>1.

Dediazoniations of arenediazonium salts can be achieved by numerous reductants¹

such as hypophosphorous acid,² hot ethanol,³ triphenylphosphine,⁴ N,N-dimethyl-

formamide,⁵ rhodium complexes in dimethylformamide⁶, etc.

Recently we found out that triethylamine was very efficient in hydrodediazoniation

of arenediazonium tetrafluoroborates to give arene as shown in next page.

Herein, our method of using triethylamine in the dediazoniation reactions are

demonstrated in synthetic applications.

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 $(X=H, NO_3, Me, OMe) \xrightarrow{MeOH} X \xrightarrow{N_2} H$

For instances, we were successful in the preparation of (3-methoxyphenyl)(3'methoxycarbonylphenyl)diazene (3) from (3-methoxycarbonylphenyl)(4'-amino-3'-methoxyphenyl)diazene (1) as shown in equation 1.



When the dediazoniation of 4-nitrobenzenediazonium tetrafluoroborate in the presence of triethylamine (1 eq) was carried out in furan instead of methanol, arylation on furan ring occurred to make reaction product, 2-(4-nitrophenyl)furan (4), in moderate yield as shown in equation 2.

$$O_2 N - \bigvee - N_2^+ BF_4^- \xrightarrow{\text{NEt}_3 (1 \text{ eq})} O_2 N - \bigvee O_2 N \xrightarrow{O} (2)$$

Furan
$$4 (70\%)$$

On the other hand, we found out that the major products in the dediazoniation reaction depended upon the molar ratio (r) of triethylamine and arenediazonium tetrafluoroborate. A representative example in the case of benzenediazonium tetrafluoroborate is shown in equation 3.



The dependence of product distribution upon molar ratio of triethylamine and benzenediazonium tetrafluoroborate is shown in Table 1. As shown in Table 1, anisole was obtained as a major product when the molar ratio of triethylamine to benzenediazonium tetrafluoroborate was smaller than 0.5 (r<0.5). On the other hand, the major product was switched to benzene when the molar ratio of triethylamine to benzenediazonium tetrafluoroborate was greater than 1.0 (r>1.0). The two products, anisole and benzene, are obviously obtained by ionic and radical process, respectively.⁷ The selective formation of major product depending on the amounts of triethylamine provides a convenient synthetic method. The mechanistic aspects of this reaction are undergoing at present.

5 (mmol)	Triethylamine (mmol)	Product Distribution (%)		
		6	7	8
1	0.2	92		7
1	0.3	77		19
1	0.4	85	14	1
1	1.0	0	100	0

Table 1. Product Distribution% for the Dediazoniation of Ber	zenediazonium
Tetrafluoroborate in Methanol by Increasing Amounts of T	riethylamine.
(equation 3).	•

Experimental

General Procedure for the Preparation of Arenediazonium Tetrafluoroborate.

Arenediazonium fluoroborates were prepared according to the reported procedure.⁸ **Preparation of 1.** To the ice-cooled solution of acetonitrile (80 mL) containing 3-carbomethoxybenzenediazonium tetrafluoroborate (5.0 g, 20 mmol) was added o-anisidine (2.3 mL, 20 mmol) dissolved in acetonitrile (24 mL) for 40 min. After stirring for 2 hr at room temperature, the solution was filtered to give the compound 1 (4.49 g). On evaporating second crop (0.74 g) was obtained. Total yield: 5.18 g (92%). mp 100-102 °C (dichloromethane). MS *m/e* 285 (M⁺); ¹H Nmr (80 MHz) δ 3.96 (6 H, s, CO₂CH₃ and OCH₃), 4.27 (2 H, s, NH₂), 6.78 (1 H, d, J=8.0Hz), 7.45-7.53 (2 H, m), 7.61 (1 H, d, J=2.22 Hz), 7.97-8.10 (2 H, m), 8.49 (1 H, m); IR (KBr) 3425 (NH₂), 3320 (NH₂), 1720 cm⁻¹ (C=O).

Preparation of 2. To the flask containing water (15 mL) and conc. HCl (15 mL)

was added compound 1 (2.86 g). This solution was cooled in an ice-bath and was diazotized by adding sodium nitrite (1.04 g, 15 mmol) in cold water (5 mL). After then sodium fluoborate (2.81 g, 25.6 mmol) was added to the diazotized solution. Filtered residue was washed twice with cold water, three times with ethanol, and five times with THF to remove remaining 1. Drying in a vacuum oven gave 2 (2.81 g, 73%). mp 152 °C (dec). IR (KBr) 2250 ($-N_2^+$), 1070 cm⁻¹ (BF₄⁻).

Preparation of 3. To the methanol (50 mL) solution of compound 2 (2.80 g, 7.82 mmol) flushed with nitrogen for 30 min, was added triethylamine (1.1 mL, 10 mmol). After stirring for 1 hr, excess of methanol was evaporated and the residue was column chromatographed using benzene as eluting solvent. Yield: 1.63 g

(77%). mp 69-70 °C (EtOH). MS *m/e* 270 (M⁺); ¹H Nmr (300 MHz) δ 3.90 (3 H, s, OCH₃), 3.98 (3 H, s, CO₂CH₃), 7.07 (1 H, dd, J=8.71, 2.60 Hz), 7.43 (1 H, d, J=7.91 Hz), 7.48 (1 H, d, J=3.17 Hz), 7.57-7.63 (2 H, m), 8.09-8.17 (2 H, m), 8.58 (1 H, s).

Preparation of 4. After the furan (25 mL) solution of 4-nitrobenzenediazonium tetrafluoroborate (2.37 g, 10 mmol) was flushed with nitrogen for 10 min, triethylamine (0.7 mL) in furan (5 mL) was added. After removal of furan, the residue was column chromatographed using methylene chloride as an eluting solvent. Yield: 1.31 g (70%). mp 132 °C (ref.⁹ mp 134 °C).

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