

favored at the ortho position compared to the para. This observation is consistent with what is known for enolates formed from α,β -unsaturated ketones, where the kinetic product of protonation at C is the α -position.³¹

Stereospecific Tautomerizations. The rate of deuterium exchange for 5-methylphenol (**3b**) in acidic methanol- d_4 of either the available (H6) or para position (H4) is orders of magnitude slower than that of tautomerization. Yet, the diastereotopic methylene proton H1 readily exchanges. Together, these observations indicate that the tautomerization process is highly stereoselective at C4, and quite probably at C6 as well, provided that the phenol/2,4-dienone tautomerization in acid is as facile as the 2,5-dienone process for **3**. For the 2,5-dienone species **2b** or **3b**, the lack of significant coupling between R4 and the stable meta proton (H3) suggests a dihedral angle of 80–90°. Consideration of molecular models indicates that H4 is the proton syn to the osmium as shown in Figure 1 and that the additional proton enters from the face of the ring anti to the metal. Supporting this conclusion is an earlier study which indicates that hydrogenation of η^2 -anisole or η^2 -dimethoxybenzene occurs exclusively anti to pentaammineosmium(II).

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Conclusions

Osmium(II) coordination stabilizes 2,5-cyclohexadien-1-one to the degree that it reaches an equilibrium with its aromatic tautomer phenol in methanol at a ratio of 1:5; this represents approximately 10 kcal/mol stabilization in the free energy of ketonization, relative to the uncoordinated ligands. The addition of a methyl substituent accounts for 1–2-kcal variation in this free energy depending on position; by proper adjustment of alkyl substituents, the 2,4-dienone tautomer may also be observed as a major product. Starting with the phenolic isomer in basic methanol, conversion to 2,4-cyclohexen-1-one is kinetically favored over the formation of the 2,5 analogue, although the latter is the thermodynamically favored product. All tautomerization processes are stereoselective, with protonation and deprotonation occurring preferentially at the ring face opposite the metal. Preliminary results suggest that electrophiles react with phenol selectively at the para position, paralleling the thermodynamic product of ketonization. Electrochemical studies indicate that the phenol–2,5-dienone equilibrium shows little deviation from that of the free ligand on osmium(III).

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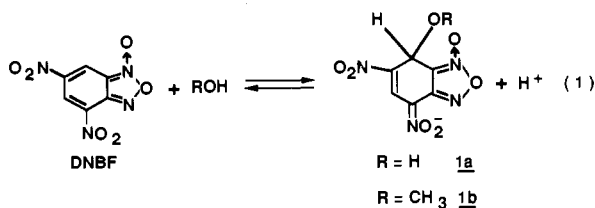
4,6-Dinitrobenzofuroxan: A Stronger Electrophile than the *p*-Nitrobenzenediazonium and H⁺ Cations

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Abstract: It is shown by means of a kinetic study of the reactions of 4,6-dinitrobenzofuroxan (DNBF) with the π -excessive heteroaromatics indole, 2-methylindole, and 1,2,5-trimethylpyrrole, producing the corresponding σ -adducts, that DNBF is a more powerful electrophile than the *p*-nitrobenzenediazonium cation and also a much stronger electrophile than the proton.

Much evidence has been recently accumulated that 4,6-dinitrobenzofuroxan (DNBF) is a neutral 10- π -electron heteroaromatic substrate which in many processes exhibits an extremely high electrophilic character. Thus, whereas the common reference electrophile, 1,3,5-trinitrobenzene (TNB), only reacts with the strong oxygen bases hydroxide and methoxide ions, DNBF undergoes facile addition of water or methanol according to eq 1



to give the hydroxide or methoxide adducts (**1a**, **1b**) which are 10¹⁰ times thermodynamically more stable than the analogous TNB adducts.^{1–6} More importantly, DNBF reacts quantitatively at room temperature with such weak carbon nucleophiles as

1,3,5-trimethoxybenzene ($\text{p}K_a = -5.7$)^{7,8} or aniline^{9,10} to afford stable anionic C-bonded σ -adducts which are formally the products of S_EAr substitution of the benzene ring.¹¹ Similar substitutions readily occur with π -excessive heteroaromatics like pyrrole,

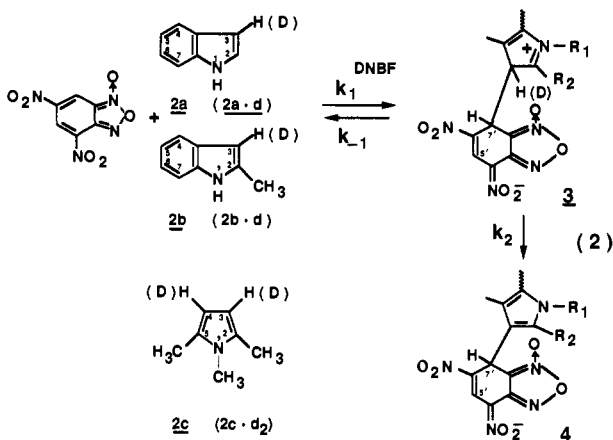
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thiophene, furan, or indole derivatives.^{7,12a} Coupling to weakly activated enolic double bonds is a process that is much more readily achieved with DNBF than with TNB.^{2,12-14}

The ease of achievement of the above reactions has led to the conclusion that DNBF may be a suitable probe to assess the reactivity of weakly nucleophilic carbon centers in general. So far, however, no quantitative assessment of the electrophilic character of this neutral heteroaromatic substrate with respect to that of such common powerful electrophiles as benzenediazonium cations has been made. In the present paper, we report the results of a kinetic study on the reactions of DNBF with three π -excessive heteroaromatics, i.e., indole (**2a**), 2-methylindole (**2b**), and 1,2,5-trimethylpyrrole (**2c**), and their related deuterated derivatives, i.e., 3-*d*-indole (**2a-d**), 3-*d*-2-methylindole (**2b-d**), and 3,4-*d*₂-1,2,5-trimethylpyrrole (**2c-d**₂), to give the adducts **4a**, **4b**, and **4c**, respectively, according to eq 2 in aqueous DMSO solutions. Our results reveal that DNBF is actually a stronger electrophile than *p*-nitrobenzenediazonium cation and also a much stronger electrophile than the proton.



Results and Discussion

Because of the low solubility of **2a-c** in aqueous solutions, the kinetics of reactions 2 were studied at 25 °C under pseudo-first-order conditions with respect to the indole or pyrrole reagent as the excess component, in two aqueous DMSO mixtures, namely 70–30 and 50–50 (v/v) H₂O–DMSO. Experiments were carried out by mixing 0.2 or 0.1 M HCl solutions of DNBF ($\sim 3 \times 10^{-5}$ M) with equal volumes of various solutions of **2a-c** (10^{-3} – 10^{-2} M) in a stopped-flow spectrophotometer. Under the final acid conditions (0.1 or 0.05 M HCl; the ionic strength was kept constant at 0.1 M by adding KCl as needed), no interference between reaction 2 and the formation of the hydroxide adduct **1a** according to eq 1 could be detected¹ and only one relaxation time corresponding to the complete formation of the adducts **4a-c** ($\lambda_{\text{max}} \sim 490$ nm) was observed.

The general expression for the observed first-order rate constant, k_{obs} , for the formation of **4a-c**, as derived under the assumption that the zwitterions **3a-c** are low-concentration intermediates, is given by

$$k_{\text{obs}} = (k_1^{\text{DNBF}} k_2 / (k_{-1} + k_2)) [\mathbf{2a-c}] = k [\mathbf{2a-c}] \quad (3)$$

In accordance with eq 3, excellent straight lines with zero intercepts were obtained in all cases when the k_{obs} values were plotted vs the indole or pyrrole concentration, with no evidence for a pH dependence of the rates (Figure 1). While confirming the nonintervention of reaction 1, the latter result also shows that protonation at C-3 of **2a** and **2b** ($\text{p}K_{\text{a}}^{\text{H}_2\text{O}}(\mathbf{2a}) = -3.46$;¹⁵ $\text{p}K_{\text{a}}^{\text{H}_2\text{O}}(\mathbf{2b})$

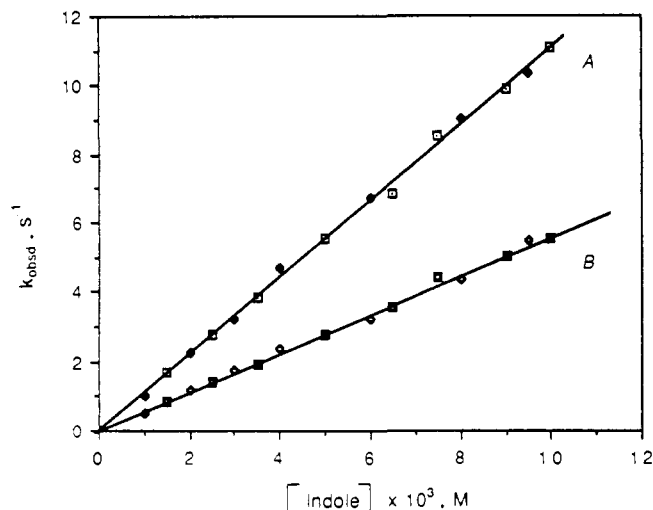
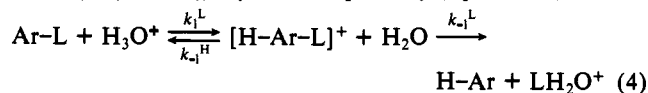


Figure 1. Influence of the indole concentration on the observed first-order rate constant for addition of DNBF in 30% DMSO–70% H₂O (A) and 50% DMSO–50% H₂O (B); $t = 25$ °C. (■) $[\text{H}^+] = 0.10$ M; (□) $[\text{H}^+] = 0.05$ M.

$= -0.28$)¹⁵ and at C-2 or C-3 of **2c** ($\text{p}K_{\text{a}}^{\text{H}_2\text{O}}(\text{C-3}) = -0.49$;¹⁶ $\text{p}K_{\text{a}}^{\text{H}_2\text{O}}(\text{C-2}) = +0.73$)¹⁷ was not interfering appreciably with the complexation under our experimental conditions. Determination of the second-order rate constants k from the slopes of the k_{obs} vs $[\mathbf{2a-c}]$ plots was therefore straightforward.

While exhibiting similar general features, the experiments carried out with the three deuterated indoles did not reveal a significant influence of the nature of the isotopic substitution at C-3 on the rates of formation of the adducts **4a-c**; the experimental $k^{\text{H}}/k^{\text{D}}$ ratios are 1.1 ± 0.1 , with no dependence of the substrate basicity. This shows that proton removal from the zwitterions **3** is rapid in the two aqueous solvents studied and that electrophilic attack by DNBF is the rate-limiting step of reactions 2; i.e., we have $k = k_1^{\text{DNBF}}$. The situation resembles that observed in a large number of electrophilic aromatic substitutions, in particular the diazo coupling reactions of most indole and pyrrole derivatives by benzenediazonium cations.^{11,18-21}

Values of the measured second-order rate constants k_1^{DNBF} for DNBF addition to **2a-c** in 30% and 50% DMSO–H₂O mixtures are compared in Table I with similar data ($k_1^{\text{ArN}_2^+}$) reported for electrophilic attack by *p*-nitrobenzenediazonium cation in aqueous solution. Also included for purposes of comparison are the k_1^{H} values for protonation at C- β of **2a-c** in aqueous solutions. As previously discussed, these rate constants can be safely estimated from reported protideuteration or protideuterium exchange rate data (k_{exch}) by assuming reasonable values of 18 and 7.8 for the $k_1^{\text{H}}/k_{-1}^{\text{H}}$ and $k_1^{\text{H}}/k_{-1}^{\text{D}}$ ratios, respectively (eqs 3 and 4).^{17,18,23-26}



$$k_{\text{obs}} = k_1^{\text{L}} [\text{H}_3\text{O}^+] / (1 + k_1^{\text{H}}/k_{-1}^{\text{L}}) = k_{\text{exch}} [\text{H}_3\text{O}^+] \quad (5)$$

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Table I. Relative Electrophilic Reactivities of DNBF, *p*-Nitrobenzenediazonium Cation, and the Proton in Aqueous Solution^a

electrophile	solvent	k_1 , L mol ⁻¹ s ⁻¹					
		indole (pK _a = -3.46) ^b		2-methylindole (pK _a = -0.28) ^b		1,2,5-trimethylpyrrole (pK _a = -0.49) ^{c,d}	
		2a	2a-d	2b	2b-d	2c	2c-d
DNBF	70% H ₂ O-30% DMSO	1110	940	21000	19900	48800, (24400) ^e	42000
	50% H ₂ O-50% DMSO	555	500	9900	9650	24000, (12000) ^e	20500
O ₂ N-C ₆ H ₄ -N ₂ ⁺	H ₂ O			2700	2250 ^f	1600, (800) ^e	
H ₃ O ⁺	H ₂ O	9, ^g 7.57 ^h		734, ⁱ 667 ^h		950, ^h (475) ^e	

^a $t = 25^\circ\text{C}$. ^b Reference 15. ^c Reference 16. ^d Statistically corrected pK_a = -0.79. ^e Statistically corrected k_1 values. ^f Calculated by assuming a $k_1^{\text{H}}/k_1^{\text{D}}$ ratio of 18 in protiodetritiation exchange experiments reported in ref 26. ^g Calculated by assuming a $k_1^{\text{H}}/k_1^{\text{D}}$ of 7.8 in protiodedeuteriation experiments reported in ref 26. ^h Reference 17. ⁱ Calculated from the k_1 value for **2b** by using $k_1^{\text{H}}/k_1^{\text{D}} = 1.2$, as reported in ref 18.

As can be seen in Table I, the rate constants k_1^{DNBF} for reaction 2 increase with decreasing DMSO content of the H₂O-DMSO mixtures, suggesting that greater k_1^{DNBF} values would have been obtained for formation of the adducts **4a-c** if the solubilities of **2a**, **2b**, and **2c** made possible measurements in aqueous solution. Hence, Table I clearly shows that the neutral DNBF molecule is at least by a factor of 10 a stronger electrophile than the positively charged *p*-nitrobenzenediazonium cation. The difference in electrophilic reactivity is even more accentuated with the hydronium ion, e.g., $k_1^{\text{DNBF}}/k_1^{\text{H}_3\text{O}^+} \sim 50$ in the case of the pyrrole system. It is also perhaps interesting to note that the rates of electrophilic attack at the 3-position of 2-methylindole and 1,2,5-trimethylpyrrole are similar. This similarity appears to be consistent with the fact that the pK_a values for protonation of these two derivatives at C₃ are not markedly different.^{15,17}

The above results provide for the first time a quantitative demonstration that, despite its neutral character, DNBF ranks among the most powerful electrophiles known to date and call for future exploration of this unique property in other systems.

Experimental Section

Materials. 4,6-Dinitrobenzofuroxan was prepared according to the procedure of Drost: mp 172 °C (lit. 172-174.5 °C^{1,10b,12,27}). Indole (**2a**), 2-methylindole (**2b**), and 1,2,5-trimethylpyrrole (**2c**) were commercial products (Aldrich) which were purified by sublimation or distillation under vacuum.

Deuteration of **2a-c** was effected according to previously described procedures.^{18,20,22,26} 1,3-Dideuterioindole (**2a-d₂**) or, after subsequent and facile D/H exchange at the 1-position, 3-deuterioindole (**2a-d**), were prepared by subjecting **2a** to an acid-catalyzed exchange with D₂O according to the method described by Binks and Ridd,²¹ as well as by Jackson and Lynch,²⁰ or to a base-catalyzed exchange with D₂O according to the method described by Challis and Millar.²⁶ The latter method was found to afford samples with greater deuterium incorporation at C-3 (≥98% on the basis of 250-MHz ¹H NMR spectra recorded on a Bruker AM-250 spectrometer equipped with an ASPECT 3000 computer) than the former (≥94%). 1,3-Dideuterio-2-methylindole (**2b-d₂**) or 3-deuterio-2-methylindole (**2b-d**) were similarly obtained by acid- or base-catalyzed exchanges using procedures developed by Challis et al.^{18,26} The resonance of the H-3 proton was essentially absent in the NMR spectra of **2b-d** and **2b-d₂**. 3,4-Dideuterio-1,2,5-trimethylpyrrole (**2c-d₂**) was prepared by H⁺-catalyzed exchange according to the method recently described for the deuteration at C-2 of 3-ethyl-2,4-dimethylpyrrole (kryptopyrrole).²² The corresponding 250-MHz ¹H NMR spectra showed essentially complete exchange at the 3(4)-positions.

Dissolution of **2a-d₂** and **2b-d₂** in water-DMSO solutions was found to restore the NMR signals assigned to the NH protons in a few minutes, as expected from the known lability of this hydrogen atom.^{22,26} For this reason, the kinetic experiments carried out to measure the effect of isotopic substitution at C-3 on the rates of complexation of **2a** and **2b** by DNBF have been described under Results and Discussion as referring only to reactions involving **2a-d** and **2b-d** as the starting deuterated substrates. In fact, similar rates were obtained whether 1,3-dideuterio or 3-deuterio derivatives were used as starting materials.

Reactions 2 afford the adducts **4a-c** in their acid form, which is not very stable in air.²⁸ Exchanging the H⁺ counterion for a K⁺ or Na⁺

cation is therefore the classical way to isolate DNBF σ -adducts of this type as crystalline alkali salts.^{9,12} The preparation and characterization of the adduct **4a** in its acid form has, however, been reported previously.²⁸ In the present work, we have prepared **4a-c** in the form of sodium salts as described below for **4a**. A solution of 0.226 g of DNBF (1 mM) in 2 mL of dioxane and a solution of 0.117 g of indole (1 mM) in 2 mL of dioxane were mixed with stirring at room temperature. The solution immediately turned dark red and was allowed to stand for 5 min; sodium bicarbonate (0.084 g, 1 mM) in 0.5 mL of water was added with stirring to the mixture, which began to deposit crystals within 3 min. After filtration, red crystals were obtained; the crystals were washed once with cooled methanol and then with copious amounts of diethyl ether and dried thoroughly under vacuum to give 0.24 g (65%) of the sodium salt of **4a**. The sodium salts of **4b** and **4c** were obtained similarly in comparable yields.

As with a number of alkali salts of DNBF σ -adducts, the crystals obtained for **4a-c**, Na⁺ were not found to melt at $t \leq 320^\circ\text{C}$. Attempts to obtain satisfactory elemental analysis have failed. However, dissolution of the three salts in DMSO-*d*₆ gave NMR spectra identical to those recorded in the *in situ* generation of the acid form of the adducts in this solvent. Also, the visible spectra were typical of C-bonded σ -adducts of DNBF, exhibiting a strong maximum at $\lambda_{\text{max}} \sim 490\text{ nm}$ ($\epsilon \sim 30000\text{ M}^{-1}\text{ cm}^{-1}$) in H₂O-DMSO mixtures.

NMR (DMSO-*d*₆) (Internal Reference Me₄Si). **4a (2a)** ¹H NMR $\delta_{\text{H}_2} = 7.35$ (7.33), $\delta_{\text{NH}} = 11.09$ (11.08) ³J_{H₂-NH} = 2.6 Hz (2.8), $\delta_{\text{H}_5} = 8.71$, $\delta_{\text{H}_7} = 5.64$; ¹³C NMR $\delta_{\text{C}_2} = 125.57$ (125.24), $\delta_{\text{C}_3} = 109.22$ (101.09), $\delta_{\text{C}_5} = 130.04$, $\delta_{\text{C}_7} = 31.63$. **4b (2b)** ¹H NMR $\delta_{\text{CH}_3} = 2.47$ (2.38), $\delta_{\text{NH}} = 10.98$ (10.88), $\delta_{\text{H}_5} = 8.70$, $\delta_{\text{H}_7} = 5.61$; ¹³C NMR $\delta_{\text{C}_3} = 104.27$ (99.25), $\delta_{\text{C}_5} = 129.92$, $\delta_{\text{C}_7} = 30.68$. **4c (2c)** ¹H NMR $\delta_{\text{H}_4} = 5.31$ ($\delta_{\text{H}_{3,4}} = 5.58$), $\delta_{\text{CH}_{3(1)}} = 3.28$ (3.30), $\delta_{\text{CH}_{3(2)}} = 2.19$, $\delta_{\text{CH}_{3(5)}} = 2.01$ ($\delta_{\text{CH}_{3(2,5)}} = 2.11$), $\delta_{\text{H}_5} = 8.59$, $\delta_{\text{H}_7} = 5.17$; ¹³C NMR $\delta_{\text{C}_3} = 112.79$, $\delta_{\text{C}_4} = 103.37$ ($\delta_{\text{C}_{3,4}} = 104.50$), $\delta_{\text{C}_5} = 129.50$, $\delta_{\text{C}_7} = 31.24$.

Definitive evidence that the adducts **4a-c** were isolated as the sodium salts comes from mass spectral experiments performed with the FAB technique. For instance, we obtain for the parent peaks of **4a**, Na⁺: M = 342 (negative ion) and M = 388 (negative ion, 2Na⁺).

Kinetic Measurements. Stopped-flow determinations were performed on a Durrum stopped-flow spectrophotometer, the cell compartment of which was maintained at 25 ± 0.3 °C. All kinetic runs were carried out in triplicate under pseudo-first-order conditions with a DNBF concentration of ca. 3 × 10⁻³ M and indole or pyrrole concentrations in the range 10⁻³-10⁻² M. In a given experiment, the rates were found to be reproducible to ±2-3% and to be similar whether the process was followed by monitoring the increase in absorbance at $\lambda_{\text{max}} = 490\text{ nm}$ of the adducts **4a-c** or the decrease in absorbance at $\lambda_{\text{max}} = 415\text{ nm}$ of the parent DNBF substrate as a function of time. The visible absorption spectra of the final solutions were in all cases identical to those recorded by dissolving samples of the isolated sodium salts of the adducts in the appropriate H₂O-DMSO mixture.

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Registry No. **4a**-Na, 138208-06-7; **4b**-Na, 138208-07-8; **4c**-Na, 138208-08-9; 4,6-dinitrobenzofuran, 5128-28-9; indole, 120-72-9; 2-methylindole, 95-20-5; 1,2,5-trimethylpyrrole, 930-87-0; *p*-nitrobenzenediazonium cation, 14368-49-1.

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