The sign and magnitude of the ^1H–^{19}F couplings have been shown to be stereospecific, the present results can thus be used to shed some light on the conformations of these oligosaccharides. However a detailed discussion of the information offered by the ^1H–^{19}F couplings is beyond the scope of the present report and will be presented in a later communication.

Conclusion

This investigation presents the first detailed study of the ^1H spectra of fluorinated and nonfluorinated oligosaccharides by a new ^{13}C–^1H chemical shift correlation technique which incorporates the selective spin–flip pulses resulting in homonuclear decoupling in the ^1H dimension. This study clearly demonstrates the improved resolution and signal to noise ratio achieved by this new version of the heteronuclear chemical shift correlation spectroscopy. We have demonstrated in this and previous studies[9-11] that this technique can be applied routinely to complex molecules with great advantage. Very high magnetic field (B_0 > 7 T) is not necessary for excellent resolution in the ^1H dimension. The provision of measuring both the relative sign and magnitude of ^1H–X spin–spin coupling offered by this technique enables the measurement of these important parameters in complex molecules. Even in the case of simple molecules, it may be an attractive alternative to double resonance methods.

Acknowledgment. The NT-300 spectrometer was purchased partially through a grant from the National Science Foundation (PCM-8115599). This work is partially supported by the National Institute of Health Institutional Biomedical Research Support Grant RR07053.

Registry No. 1α, 13299-20-2; 1β, 13299-21-3; 2, 20764-63-0; 3, 92397-29-0; 4, 52523-12-3; 5, 51996-35-1; 6, 92420-18-3; 7, 92397-30-3; 8, 92397-31-4; 9, 92397-32-5; 10, 89185-94-4; 11, 89185-97-7.

Nonconventional Electrophilic Heteroaromatic Substitutions: Ring vs. Side-Chain Reactivity of 2,5-Dimethyl Five-Membered Ring Heterocycles toward Electron-Deficient Aromatics

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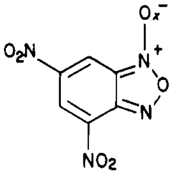
Received May 15, 1984

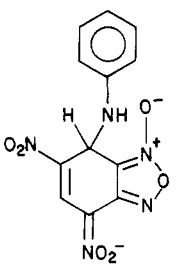
4,6-Dinitrobenzofuroxan (DNBF) and 4,6-dinitrobenzofurazan (DNBZ) behave as conventional electrophiles toward 2,5-dimethylpyrrole, 2,5-dimethylthiophene, and 2-methylbenzofuran, adding to the unsubstituted β-carbon to form the corresponding σ adducts in Me_2SO. In contrast reactions with 2,5-dimethylfuran result in electrophilic substitution of a methyl group as the only observed process. The mechanism of the latter reaction is discussed with reference to previously reported results. This leads to some reconsideration of current notions regarding the mechanism of electrophilic side-chain reactions of 2,5-dimethyl five-membered ring heterocycles. It is also concluded that DNBF and DNBZ have an electrophilic character of the same order as that of 2,4-dinitrobenzenediazonium cation.

Introduction

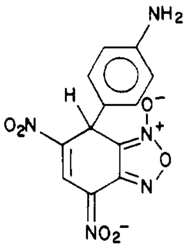
The possibility of using the extremely high electrophilic character of 4,6-dinitrobenzofuroxan (DNBF) to assess the reactivity of a number of very weak carbon nucleophiles has been recently emphasized.[1-3] This is best illustrated by the reaction of DNBF with aniline.[1,2] As expected, the nitrogen-bonded adduct 1 is formed immediately but subsequent rearrangement occurs leading to the carbon-bonded adduct 2 as the product of thermodynamic control.[4] This provides evidence that aniline can act, as do phenols,[5-7] as a carbon nucleophile in σ complex formation and related nucleophilic aromatic substitution reactions with nitroarenes.[8-10]



x = 0 DNBZ
x = 1 DNBF



1



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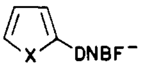

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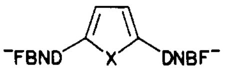
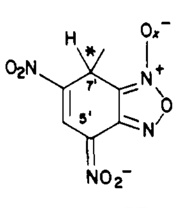


4

X = NH, S, O



x = 0 DNBZ⁻
x = 1 DNBF⁻

Also noteworthy are the reactions of DNBF with π-excessive heterocycles like furan, thiophene, and pyrrole,

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(1) Strauss, M. J.; Renfrow, R. A.; Buncel, E. *J. Am. Chem. Soc.* **1983**, *105*, 2473.

(2) (a) Spear, R. J.; Norris, W. P.; Read, R. W. *Tetrahedron Lett.* **1983**, *24*, 1555. (b) Norris, W. P.; Spear, R. J.; Read, R. W. *Aust. J. Chem.* **1983**, *36*, 297.

(3) Hallé, J. C.; Simonnin, M. P.; Pouet, M. J.; Terrier, F. *Tetrahedron Lett.* **1983**, *24*, 2255.

(4) 2 has also been obtained in the zwitterionic form.[1]

(5) (a) Buncel, E.; Webb, J. G. K. *J. Am. Chem. Soc.* **1973**, *95*, 8470. (b) Buncel, E.; Jonczyk, A.; Webb, J. G. K. *Can. J. Chem.* **1975**, *53*, 3761. (c) Buncel, E.; Moir, R. Y.; Norris, A. R.; Chatrousse, A. P. *Can. J. Chem.* **1981**, *59*, 2470.

(6) Bernasconi, C. F.; Muller, M. C. *J. Am. Chem. Soc.* **1978**, *100*, 5530.

(7) (a) Shein, S. M.; Byvalkevich, O. G. *Zh. Org. Khim.* **1972**, *8*, 323. (b) Shein, S. M.; Byvalkevich, O. G.; Khmelinskaya, A. D. *Zh. Org. Khim.* **1976**, *12*, 134.

(8) Terrier, F. *Chem. Rev.* **1982**, *82*, 77.

(9) Artamkina, G. A.; Egorov, M. P.; Beletskaya, I. P. *Chem. Rev.* **1982**, *82*, 427.

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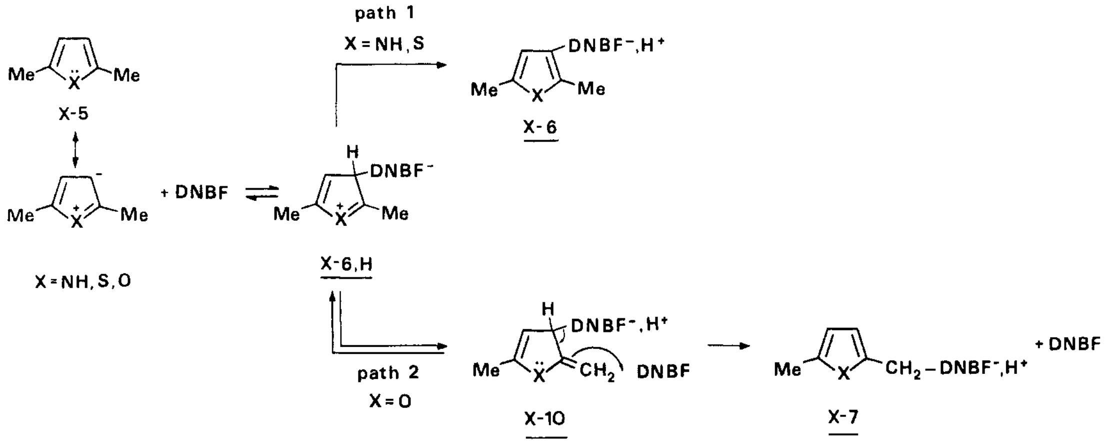
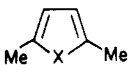
Scheme I

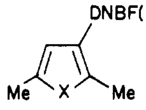


which yield the C-bonded mono- and diadducts 3 and 4, the latter forming as a 1:1 mixture of diastereomers.[3] In these cases, DNBF addition takes place at the α-position(s), in accordance with general reactivity patterns for electrophilic substitution in these five-membered ring heterocycles.[11]

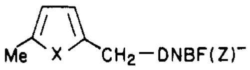
It is therefore interesting to determine whether DNBF will add to a weaker nucleophilic β-position, as do conventional electrophiles when the α-positions are blocked,[11] and we have studied the reactivity of DNBF and its deoxy furazan analogue, i.e., DNBZ, toward 2,5-dimethylpyrrole **NH-5**, 2,5-dimethylthiophene **S-5**, 2,5-dimethylfuran **O-5**,



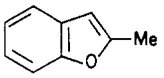
X-5
X=NH
X=S
X=O



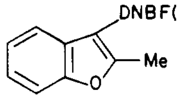
X-6(6')
X=NH
X=S



X-7(7')
X=O



8



9(9')

and 2-methylbenzofuran 8 in dimethyl sulfoxide (Me_2SO).

While the experiments with **NH-5**, **S-5**, and **8** have confirmed our expectations, we have observed side-chain electrophilic subsitution with **O-5**. Inasmuch as this reaction occurs in a nonacidic medium, some reconsideration of current notions about the mechanism of side-chain reactions of these 2,5-dimethyl five-membered ring heterocycles with strong electrophiles[12] is required.

Results

The various reactions were carried out at room temperature in Me_2SO. All the resulting complexes were identified by ^1H NMR. As shown in Scheme I, the reactions release a proton, which serves as the counterion for the anionic moiety.

The addition of **NH-5** or **S-5** to 1 equiv of DNBF (or DNBZ) in Me_2SO-d_6 resulted in the formation of the C_β adducts **NH-6** (**6'**) and **S-6** (**6'**). ^1H NMR spectra indicate that the five-membered ring of these adducts has only a single proton H_4 and two nonequivalent methyl groups. The more shielded 5-methyl group shows an allylic coupling with H_4 which is well resolved for X = S but unresolved for X = NH (Table I).

Table I. ^1H NMR Data of C_β Ring Adducts[a]

σ adducts	δ_{NH}	$\delta_{H_{5'}}$	$\delta_{H_{7'}}$	δ_{H_4}	δ_{Me_2}	δ_{Me_5}	$^4J_{H_4Me_5}$
NH-6	10.08	8.61	5.13	5.25	2.19	2.01	nr
NH-6'	10.14	8.70	5.58	5.24	2.22	2.02	nr
S-6		8.56	5.27	6.23			1
S-6'		8.67	5.73	6.21	2.45	2.21	1.1
9		8.76	5.64		2.53		
9'		8.81	6.02		2.56		

[a] δ in ppm relative to internal Me_4Si. J in Hz. Solvent Me_2SO-d_6.

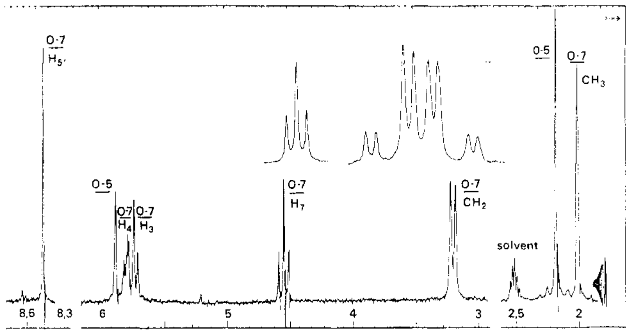


Figure 1. ^1H NMR spectrum (100 MHz) of the adduct **O-7** in the presence of an excess of **O-5** in Me_2SO-d_6 (the methyl region was recorded at a lower amplitude). The inset shows the ABX pattern recorded at 400.13 MHz.

Similarly, **8** reacts with DNBF (or DNBZ) to form the C_β adducts **9** or **9'**. ^1H NMR spectra show a progressive decrease of the signals due to the H_3 proton and to the methyl group of **8** and a concomitant increase of three singlets in a 1:1:3 ratio. These signals are assignable respectively to the $H_{5'}$, $H_{7'}$, and methyl protons of **9** (or **9'**).

Under similar experimental conditions, **O-5** reacts with DNBF (or DNBZ) to give products whose ^1H NMR spectra are not consistent with structures **6** (or **6'**). The spectra of these adducts consist of six signals in a 1:1:1:1:2:3 ratio, showing that the species have two ring protons (H_4, H_5) and only one methyl group. Significantly, the 100-MHz spectrum of the DNBZ adduct exhibits a well-resolved ABX system, pointing out the presence of an asymmetrical tertiary carbon ($C_{7'}$) bonded to a methylene group (Table II). Because of the smaller inequivalence between the two diastereotopic methylene protons, the analogous ABX system of the DNBF adduct appears as an AX_2 system at

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(10) Buncel, E. "The chemistry of Amino, Nitro and Nitroso Compounds"; Patai, S., Ed.; Wiley: London, 1982; Supplement F, p 1225.

(11) (a) Jones, R. A.; Bean, G. P. "The Chemistry of Pyrroles"; Academic Press: London, 1977, p 115. (b) Marino, G. *Adv. Heterocycl. Chem.* **1971**, *13*, 235.

(12) (a) Gore, S. T.; Mackie, R. K.; Tedder, J. M. *J. Chem. Soc. Perkin Trans 1* **1976**, 1639. (b) Bartle, M. G.; Gore, S. T.; Mackie, R. K.; Mhatre, S.; Tedder, J. M. *Ibid* **1978**, 401.

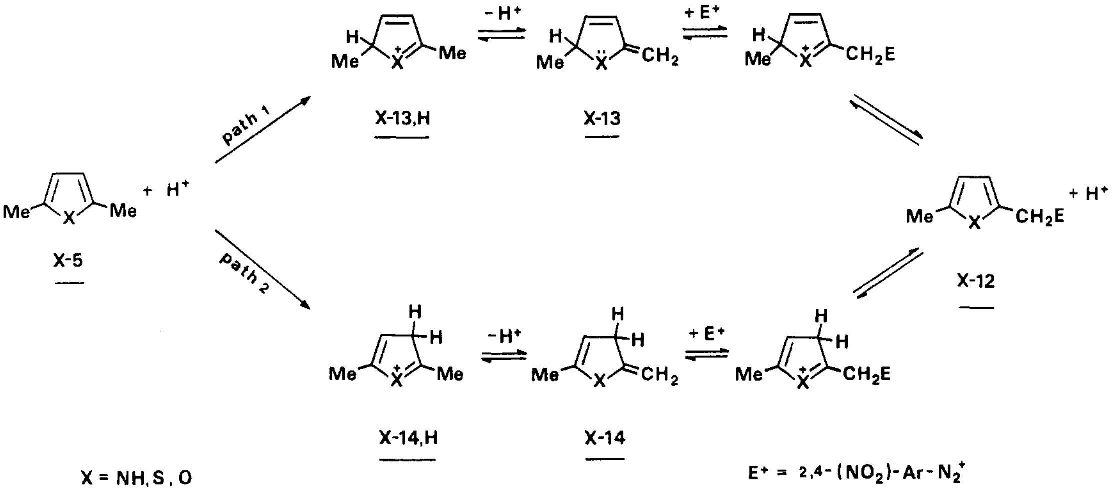
(13) Terrier, F.; Simonnin, M. P.; Pouet, M. J.; Strauss, M. J. *J. Org. Chem.* **1981**, *46*, 3537.

Table II. ^{1}H NMR Data of Side-Chain Adducts[a]

σ adducts	$\delta_{H_{5'}}$	$\delta_{H_{7'}}$ (X)	δ_{H_4}	δ_{H_3}	δ_{H_A}	δ_{H_B}	δ_{Me_5}	$^3J_{H_3H_4}$	$^4J_{H_4Me_5}$	$^4J_{H_3CH_2}$	$^2J_{H_AH_B}$	$^3J_{H_AH_{7'}}$	$^3J_{H_BH_{7'}}$
O-7	8.47	4.54	5.80	5.73	3.22	3.17	2.02	3.0	1.1	0.5_5	(−)15.0	4.2	3.6_5
O-7′	8.58	4.90	5.81	5.68	3.30	3.05	2.05	3.0	1.0	0.5	(−)14.8	6.0	3.6

[a] δ in ppm relative to internal Me_4Si. J in Hz. Solvent Me_2SO-d_6.

Scheme II



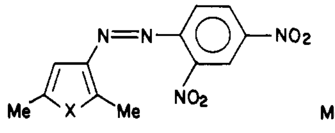
100 MHz but can be nicely observed at 400 MHz (Figure 1). Clearly, these data (Table II) are uniquely consistent with structures **O-7** and **O-7′** for the formed adducts. To our knowledge, **O-7** and **O-7′** are the first σ complexes to be formed by electrophilic substitution at a methyl hydrogen.[8]

As mentioned in the Experimental Section, the adducts **O-7** and **O-7′** could be isolated as their potassium salts.

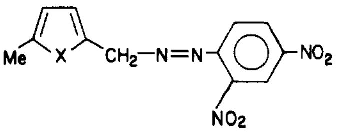
Discussion

The formation of the C_β adducts **NH-6**, **NH-6′**, **S-6**, and **S-6′** shows that DNBF and DNBZ behave as conventional electrophiles in the pyrrole and thiophene series, attacking an unsubstituted β-position when the α-positions of these heterocycles are blocked. The only reasonable pathway accounting for the formation of the aforementioned adducts is depicted in Scheme I (path 1) for the DNBF system. This involves direct attack of DNBF (or DNBZ) at C_β of the neutral molecules **NH-5** and **S-5** to give the undetected zwitterions **X-6,H** (or **X-6′,H**) which very rapidly rearrange to **X-6** (or **X-6′**) since rearomatization of the pyrrole or thiophene ring acts as a driving force for this process. A similar mechanism must account for the formation of the C_β adducts **9** and **9′** from 2-methylbenzofuran **8**. The DNBF or DNBZ attack at the unsubstituted β-carbon of **8** is consistent with the general reactivity pattern found for reactions of this compound with electrophiles.[14]

The observation of side-chain substitution to give **O-7** and **O-7′** rather than addition at the β-position to give **O-6** and **O-6′** in the reactions of DNBF and DNBZ with 2,5-dimethylfuran is obviously in marked contrast with the above results. Such unconventional behavior is not, however, totally surprising since Tedder et al. have previously reported that substitution at the methyl group occurs, together with the expected ring attack, in the reactions of various polymethylthiophenes or furans with 2,4-dinitrobenzenediazonium cation.[12] The 2,5-dimethyl derivatives **S-5** and **O-5** thus react to give **S-11** and **O-11** as well as **S-12** and **O-12**.



X-11



X-12

X = S, O

The mechanism shown in path 1 of Scheme II was proposed for these reactions which occur in *acidic media*.[12] The key point in this mechanism is that initial C protonation of the thiophene or furan ring is required to form the methylene intermediate **X-13** involved in the side-chain attack by 2,4-$(NO_2)_2$-ArN_2^+. This same methylene intermediate is involved in H/D exchange of the methyl group of **S-5** in acidic media.[12,15] A more complete mechanism for the formation of **X-12** should also include path 2, at least in the thiophene series. The observation of rapid hydrogen exchange at C_β of **S-5**[15] supports the attack of H^+ at both C_α and C_β and also the formation of the intermediate adduct **X-14,H** and consequently of **X-14**. It is also of interest to note that protonation of the pyrrole analogue **NH-5** is known to occur competitively at C_α and C_β, yielding 70% of **NH-13,H** (p*K*a = −0.70) and 30% of **NH-14,H** (p*K*a = −1.07).[16]

In our experiments, the reactions occur in the absence of any added acid, rendering formation of **X-13** or **X-14** improbable. Based on the formation of only C_β adducts of pyrrole, thiophene, and benzofuran, the most reasonable mechanism is depicted in path 2 of Scheme I. DNBF (or DNBZ) attack will occur initially at C_β of the 2,5-dimethyl derivatives but the rearomatization of the resulting undetected zwitterion **X-6,H** will be less favored in furan than

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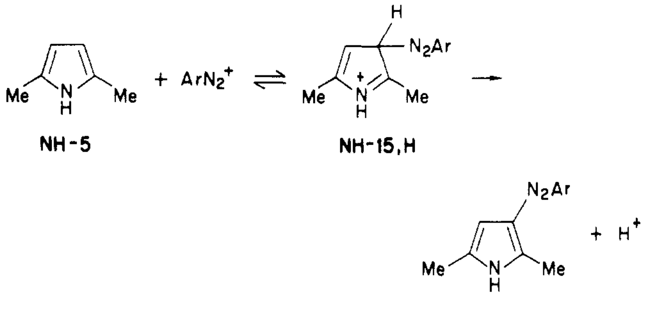
[14] Baciocchi, E.; Clementi, S.; Sebastiani, G. V. *J. Chem. Soc., Perkin Trans. 2* **1976**, 266.

[15] Alexander, R. S.; Butler, A. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1998.

[16] Whipple, E. B.; Chiang, Y.; Hinman, R. L. *J. Am. Chem. Soc.* **1963**, *85*, 26.

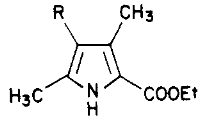
in pyrrole, thiophene, or benzofuran derivative, thus allowing the formation of the very reactive methylene intermediate **O-10** (**10′**). Ionization of the methyl group of **O-6,H** (or **O-6′,H**) to give **O-10** (**10′**) is facilitated by the strong electron-withdrawing nature of both the cationic ring and the DNBF$^-$ or DNBZ$^-$ moiety.[8,17] Formation of **O-7** (**7′**) can then occur in a concerted process involving addition of a second DNBF (or DNBZ) molecule to the methylene carbon of **O-10** (**10′**) with concomitant expulsion of the electrophilic moiety initially attached at C_β.

That the first step of the side-chain substitution leading to **O-7** (**7′**) is the attack of DNBF (or DNBZ) at Cβ of **O-5** (Scheme I) is supported by our observation that addition of triflic acid CF_3SO_3H to a Me_2SO solution of **S-5** and DNBZ does not affect the course of the reaction, i.e., **S-6′** and not **S-7′** is formed. However the most significant support comes from kinetic evidence recently gained that benzenediazonium cations reversibly add to unsubstituted C-2 and/or C-3 carbons of various pyrroles (e.g., **NH-5**) and indoles in acidic media, according to the reaction.[18,19]

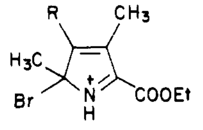


Even though intermediate adducts like **NH-15,H** rearomatize so fast that no side-chain coupling occurs in these instances, this result strongly suggests that the reactions of 2,4-$(NO_2)_2ArN_2^+$ with the thiophene and furan analogues must also proceed via initial attack of the electrophile (Scheme I) rather than via initial H^+ attack, as proposed in Scheme II.

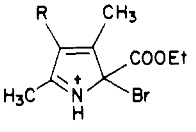
The essential feature of Scheme I is that the promoting step for side-chain substitution of **X-5** is the reversible formation of a zwitterionic σ adduct **X-6,H**. The mechanism is therefore very similar to that postulated in the side-chain substitution of various polyalkylbenzenes[20,21] and also of 2,3-dimethylbenzofuran and -thiophene[14,22] by various electrophiles, e.g., Cl^+, Br^+, I^+, NO_2^+. Based on this adduct formation, one may expect the side-chain attack of the heterocycles **X-5** to depend mainly on the nature of the electrophile and the reacting aromatic moiety rather than the acidity of the medium. Clearly a larger acidifying effect of the electrophilic moiety bonded to C-3 in **X,6H** should increase the kinetic and thermodynamic acidity of this "carbon acid", thus favoring the rate and degree of ionization of the methyl group[23,24] and therefore the formation of the reactive methylene intermediate **X-10** relative to the 3-substituted product **X-6**. On the other hand, the rearomatization of **X-6,H** is obviously related to the energy gained in the process, so that side-chain attack is expected to be more difficult in pyrrole than in thiophene than in furan derivatives. All the available experimental results are consistent with these expectations. Thus, neither DNBF or DNBZ nor benzenediazonium cations add to the methyl carbon of 2,5-dimethylpyrrole **NH-5**.[18] Similarly, the methyl groups of this derivative do not undergo hydrogen exchange, even in strong acid, showing that the cations **X-13,H** or **X-14,H** (Scheme II), which are the analogues of **X-6H**, also rearomatize faster than they can deprotonate to give the corresponding methylene intermediates.[25] Only with some 2,3,4,5-tetrasubstituted pyrroles of type **16** has side-chain substitution of a methyl group (by Cl^+, Br^+) been observed.[26,27] In these instances, the situation is not comparable to that for the **NH-5** derivative since the reactions initially give rise to cationic σ adducts such as **17a–d** which have appreciable stabilities. Consequently rearomatization of these adducts



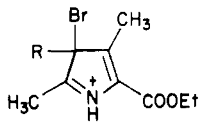
16



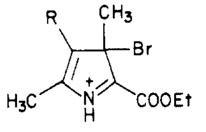
17a



17b



17c



17d

either to revert to **16** or to give the corresponding substituted products occurs at a much slower rate than deprotonation of the α-methyl group, favoring the side-chain bromination or chlorination.

In the case of 2,5-dimethylthiophene, DNBF and DNBZ only add to the ring C_β carbon whereas 2,4-$(NO_2)_2$-ArN_2^+ reacts, as does H^+, at both ring and methyl positions.[12a,15] A significant result, however, is that benzenediazonium cations less activated than 2,4-$(NO_2)_2$-ArN_2^+ do not couple with the methyl group of **S-5**.[12a] In the less aromatic furan series, DNBF or DNBZ exclusively react at the methyl group as does 2,4-$(NO_2)_2$-ArN_2^+ under some experimental conditions.[12b] Again, less activated benzenediazonium cations attack only at the ring C_β carbon.[12b,29]

In conclusion, we wish to point out that the coupling of DNBF or DNBZ to the methyl group of **O-5** provides a new and striking illustration of the remarkable electrophilic character of these electron-deficient aromatics. Assuming that Scheme I is the correct mechanism, the side-chain substitution of **O-5** implies that the electrophilic character

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of DNBF and DNBZ is of the same order as that of H$^+$ or 2,4-dinitrobenzenediazonium cation.

Experimental Section

4,6-Dinitrobenzofuroxan was prepared by the procedure of Drost,[31] mp 172 °C (lit.[31] mp 172 °C). 4,6-Dinitrobenzofurazan was prepared through reduction of DNBF by triphenylphosphine in xylene,[32,33] mp 131 °C (lit.[32] mp 129–132 °C). 2,5-Dimethylpyrrole, -thiophene, and -furan were commercially available products (Aldrich) which were purified according to standard procedures.

As those formed from other nucleophiles,[1,2b,13,32] the DNBF and DNBZ adducts formed in this work are all very sensitive explosives and extremely difficult to handle under normal conditions. However, we succeeded in isolating the adducts as their potassium salts by adding potassium acetate and methylene chloride to the Me$_2$SO solutions. The red crystals thus obtained did not melt but decomposed at about 180–200 °C with gas evolution. Dissociation of these salts in Me$_2$SO-d_6 gave NMR spectra identical with those recorded in the "in situ" generation of the adducts in their "acid" form. Also, the visible spectra were typical of C-bonded DNBF and DNBF adducts: $\lambda_{\max}$ 500 nm, $\epsilon \simeq 30\,000$ M^{-1} cm^{-1} in Me$_2$SO.[1,13]

Definitive evidence that the adducts **O-7** and **O-7′** were isolated as the potassium salts comes from mass spectra experiments performed with the FAB (Fast Atomic Bombardment) technique. For instance, we obtain for the parent peaks of **O-7′**: M = 305 (negative ion) and M = 383 (negative ion, 2K$^+$).

^{1}H NMR spectra were recorded on a Varian XL-100-12 WG spectrometer, using the C.W. mode. The temperature of the probe was 31 ± 2 °C. Chemical shifts were measured with Me$_4$Si as an internal reference. The spectrum of **O-7** was also recorded at 400.13 MHz on a Bruker WM 400 spectrometer, using the F.T. mode.

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Registry No. **NH-5**, 625-84-3; **S-5**, 638-02-8; **O-5**, 625-86-5; **NH-6**, 91949-36-9; **NH-6′**, 91949-37-0; **S-6**, 91949-38-1; **S-6′**, 91949-39-2; **O-7**, 91949-40-5; **O-7′**, 91949-41-6; **8**, 4265-25-2; **9**, 91949-42-7; **9′**, 91949-43-8; DNBF, 5128-28-9; DNBZ, 5128-28-9.

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Solvolytic Rearrangements of 2,2-Dianisyl-1-tolylvinyl Bromide and (*E*)- and (*Z*)-1,2-Dianisyl-2-tolylvinyl Bromide[1]

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The solvolysis of 2,2-dianisyl-1-tolylvinyl bromide (**3-Br**) in AcOH–AgOAc, AcOH–NaOAc, or 2,2,2-trifluoroethanol (TFE)–2,6-lutidine gave complete rearrangement to (*E*)- and (*Z*)-1,2-dianisyl-2-tolylvinyl acetates or 2,2,2-trifluoroethyl ethers, respectively, while a similar solvolysis of **3-Br** in 60% EtOH–2,6-lutidine gave 86% rearranged 1,2-dianisyl-2-tolylethanone and 14% unrearranged 2,2-dianisyl-1-tolylethanone. Solvolyses of 1,2-dianisyl-2-tolylvinyl bromide (**4-Br**) in AcOH–AgOAc, AcOH–NaOAc, TFE–2,6-lutidine, or 60% EtOH–2,6-lutidine all gave structurally unrearranged products derived from the 1,2-dianisyl-2-tolylvinyl cation (**4**). Degenerate rearrangements arising from 1,2-tolyl shifts in cation **4** were observed by using isotopically labeled (*E*,*Z*)-1,2-dianisyl-2-tolyl[2-^{14}C]vinyl bromide ((*E*,*Z*)-**4-Br-2-**^{14}*C*) as reactant. Reaction of (*E*,*Z*)-**4-Br-2-**^{14}*C* in AcOH–AgOAc resulted in only about 0.5% scrambling of the label from C-2 to C-1 in the reaction product. For solvolyses of (*E*,*Z*)-**4-Br-2-**^{14}*C* in TFE–2,6-lutidine, without or with the presence of added Et$_4$NBr, extensive scramblings of the label from C-2 to C-1 were observed in both the reaction product and the recovered, unconsumed reactant, indicating the occurrence of repeated cycles of ionizations, 1,2-tolyl shifts, and returns to covalent reactant. At complete reaction, the trifluoroethanolysis of (*E*)- or (*Z*)- or a 1:1 mixture of (*E*)- and (*Z*)-**4-Br-2-**^{14}*C* gave essentially the same extent of scrambling in the reaction product, the mean value being 25.5% scrambling or 51% rearrangement.

Introduction

The solvolytic rearrangement of triarylvinyl bromides and triflates has been extensively studied in recent years.[2] In various investigations, all the degenerate and nondegenerate β-aryl rearrangements which accompany the solvolysis of the eight triarylvinyl substrates with various combinations of *p*-anisyl (An) and phenyl (Ph) groups (listed on p 397, ref 2a) have been studied.[2] Quantitative relationships between the rate of migration of the β-aryl group (k_r) and the capture rate by the solvent (k_{SOH}) or added nucleophiles have been established. An important factor which determines the k_{SOH}/k_r ratios in the triarylvinyl cations is the relative ability of various aryl groups in stabilizing the cations and the bridged transition states for their rearrangements. Consequently, the much higher positive charge stabilizing ability of anisyl compared with phenyl results in a large preference for one reaction route over others. For example, in the solvolysis of 2,2-

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