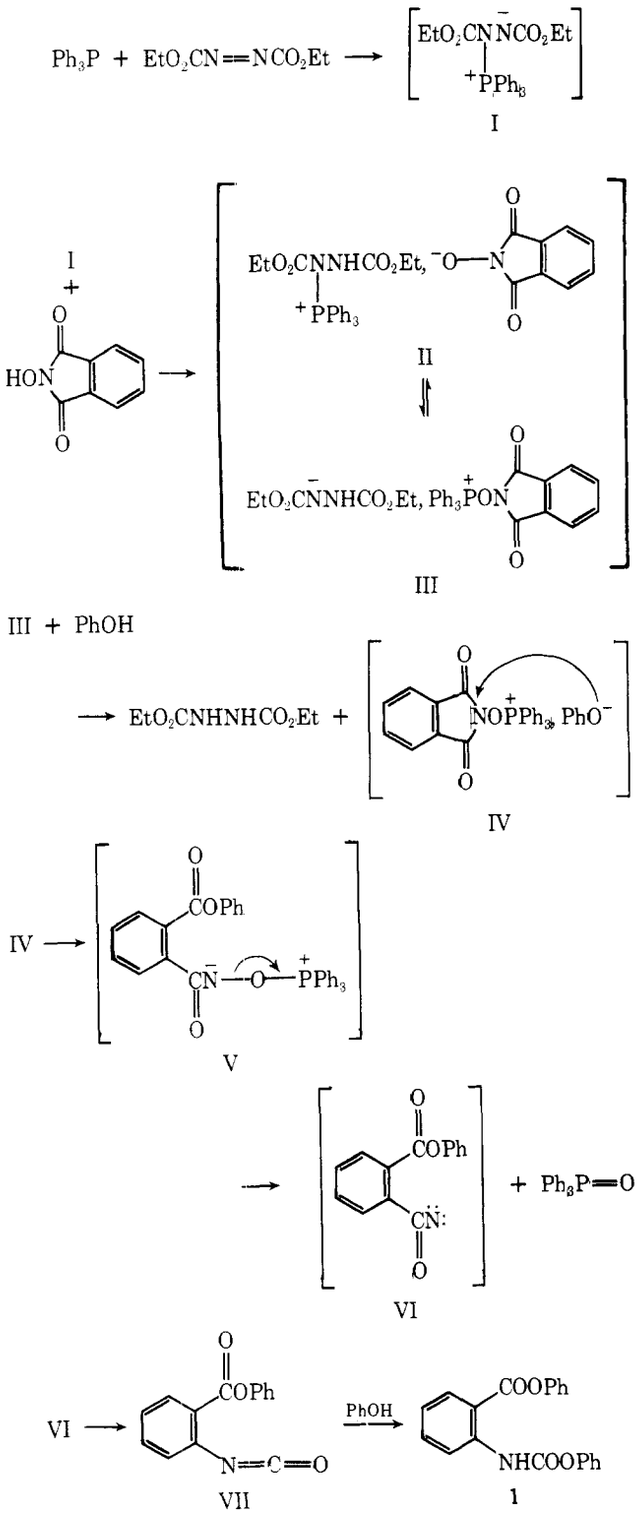
Scheme I



limits their reactivity (in case of 2,4-xylenol the reaction yield is much decreased) or it renders them completely unreactive (e.g., 2,6-di-*tert*-butyl-4-methylphenol); this behavior is quite clear in the light of the proposed mechanism.

Experimental Section

General. Melting points are uncorrected. Infrared spectra were obtained as KBr disks with a Unicam SP-200 spectrophotometer. ^{1}H-NMR spectra were recorded with a Jeol JNM-4H-100 spectrometer for $CDCl_3$ solutions (δ scale, Me_4Si = 0 ppm), silica gel G Merck was used for TLC, and silica gel 100–200 mesh Macherey-Nagel was used for column chromatography.

Phenyl *N*-Phenoxycarbonylanthranilate (1). A solution of *N*-hydroxyphthalimide (326 mg, 2 mmol), phenol (376 mg, 4 mmol), and TPP (524 mg, 2 mmol) in 10 mL of THF was treated with 380 mg (2.2 mmol) of DEAD and left overnight at room temperature. The solvent was evaporated in vacuo, and the residue was chromatographed on silica gel column with a mixture of benzene and ether (9:1 v/v) as eluent affording 460 mg (69%) of **1**: IR 3300, 3050, 1740, 1700, 1250–1130 cm^{-1}; ^{1}H NMR (δ 7.05–7.75 (complex, 12 H, aromatic), 8.25 (dd, 1 H, J_1 = 1.5 Hz, J_2 = 8.0 Hz, aromatic), 8.6 (d, 1 H, J_3 = 7.5 Hz, aromatic), 10.8 (s, 1 H, NH).

The compounds **2, 3, 4, 5,** and **6** were obtained in the same manner.

***p*-Methylphenyl *N*-*p*-Methylphenoxycarbonylanthranilate (2):** IR 3300, 3050, 1745, 1700, 1260–1130 cm^{-1}; ^{1}H NMR δ 2.35, 2.4 (2s, 6 H, $2CH_3$), 6.95–7.35 (complex, 9 H, aromatic), 7.6 (t, 1 H, J_1 = 7.5 Hz, aromatic), 8.3 (dd, 1 H, J_2 = 1.5 Hz, J_3 = 8.0 Hz, aromatic), 8.55 (d, 1 H, J_4 = 7.5 Hz, aromatic), 10.6 (s, 1 H, NH).

***p*-Methoxyphenyl *N*-*p*-Methoxyphenoxycarbonylanthranilate (3):** IR 3350, 3020, 1760, 1695, 1260–1140 cm^{-1}; ^{1}H NMR δ 3.8, 3.85 (2s, 6 H, $2OCH_3$), 6.85–7.4 (complex, 9 H, aromatic), 7.6 (t, 1 H, J_1 = 7.5 Hz, aromatic), 8.3 (dd, 1 H, J_2 = 1.5 Hz, J_3 = 8.0 Hz, aromatic), 10.7 (s, 1 H, NH).

***p*-Bromophenyl *N*-*p*-Bromophenoxycarbonylanthranilate (4):** IR 3350, 3100, 1755, 1700, 1255–1130 cm^{-1}; ^{1}H NMR δ 7.0–7.8 (complex, 10 H, aromatic), 8.3 (dd, 1 H, $J_1 \sim 1.0$ Hz, J_2 = 8.0 Hz, aromatic), 8.55 (d, 1 H, J_3 = 7.5 Hz, aromatic), 10.5 (s, 1 H, NH).

Phenyl *N*-Phenoxycarbonyl-β-alaninate (5): IR 3300, 3050, 1745, 1720, 1695, 1280–1150 cm^{-1}; ^{1}H NMR δ 2.8 (t, 2 H, $J_1 = J_2$ = 7.5 Hz, CCH_2O), 3.6 (q, 2 H, J_3 = 7.5 Hz, CCH_2N), 5.7 (broad t, 1 H, NH), 6.9–7.55 (complex, 10 H, aromatic).

Phthalimidyl *N*-Phthalimidoxycarbonylanthranilate (6): IR 3300, 3050, 1810, 1795, 1745, 1250–1130 cm^{-1}; ^{1}H NMR δ 7.5–8.1 (complex, 10 H, aromatic), 8.33 (dd, 1 H, $J_1 \sim 1.0$ Hz, J_2 = 8.0 Hz, aromatic), 8.4 (d, 1 H, J_3 = 7.5 Hz, aromatic), 10.3 (s, 1 H, NH).

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Registry No.—DEAD, 1972-28-7; TPP, 603-35-0; *N*-hydroxyphthalimide, 524-38-9; *N*-hydroxysuccinimide, 6066-82-6; phenol, 108-95-2; *p*-methoxyphenol, 150-76-5; *p*-methylphenol, 106-44-5; *p*-bromophenol, 106-41-2.

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(7) Exceptionally, thiophenols cannot be used as nucleophilic agents in reactions with betaine, because in a strongly oxidizing medium they form sulfides as the only reaction products.

Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy. Furazans and Related Systems[1]

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Introduction

In the past few years, nitrogen-15 nuclear magnetic resonance spectroscopy, ^{15}N NMR, has shown considerable utility in solving organic structural problems.[2-4] A particular advantage of ^{15}N NMR is the large range of chemical shifts and

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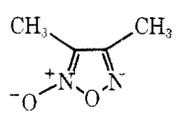
Table I. Nitrogen-15 NMR Resonances[a] for Furazans and Related Compounds

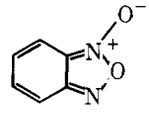
Registry no.	Compd	Solvent (concn)	^{15}N shift		^{14}N shift[b]
2518-42-5	1	Acetone (20% v/v)	+7.0	+19.1	+23[c]
		Trifluoroethanol (20% v/v)	+7.9	+21.7	
		Trifluoroacetic acid (20% v/v)	+6.3	+25.3	
480-96-6	2	Acetone (2 M); at +55 °C	+5.0		+26[d]
		Acetone (2 M); at −10 °C	−1.7	+11.8	
4975-21-7	3	Acetone (20% v/v)	−31.0		−26[c]
		Trifluoroethanol (20% v/v)	−24.5		
		Trifluoroacetic acid (20% v/v)	−13.0		
273-09-6	4	Acetone (2 M)	−42.5		−28[d]
		Trifluoroethanol (2 M)	−35.9		
		Trifluoroacetic acid (2 M)	−28.5		
273-13-2	5	Acetone (2 M)	+43.4		
		Dimethyl sulfoxide (2 M)	+44.3		
		Trifluoroethanol (2 M)	+54.4		
		Trifluoroacetic acid (2 M)	+66.1		
273-15-4	6	Acetone (2 M)	+0.8		
		Trifluoroethanol (2 M)	+19.3		
		Trifluoroacetic acid (2 M)	+62.5		
6766-90-1	7	Dimethyl sulfoxide (2 M)	+83.1		
	8	Dimethyl sulfoxide (2 M)	+113.7		

[a] In parts per million from external nitric acid (1 M 98% ^{15}N-enriched nitric acid in D_2O); positive shifts are upfield. [b] From G. Englert, *Z. Electrochem.*, **65**, 854 (1961). [c] Neat. [d] In CH_2Cl_2.

the general sensitivity of these shifts to structural changes. In this paper, we report on the insight that high-resolution ^{15}N NMR offers as to the electronic effects operating in compounds **1–8**.



1



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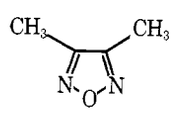

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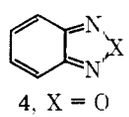
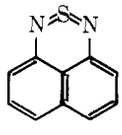


4, X = O
5, X = S
6, X = Se



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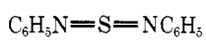


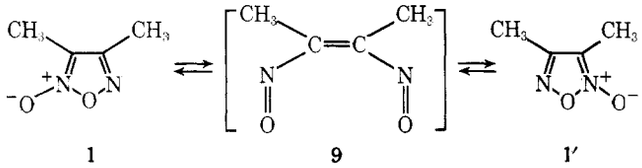
8

Although there presently appears to be no published ^{15}N NMR data on **1–8**, the ^{14}N NMR spectra of some of them have already been reported.[5] The problem with ^{14}N NMR is that nitrogen-14 has a larger nuclear quadrupole moment, which often results in large line widths and consequent uncertainties in chemical-shift measurements. In some cases, as will be shown later in this paper, these uncertainties may be greater than the chemical-shift differences which are of interest.

Results and Discussion

Nitrogen-15 chemical shifts of compounds **1–8** in various solvents, together with the extant ^{14}N NMR data, are given in Table I. These shifts will be seen to cover a relatively large range and to display rather substantial solvent dependencies.

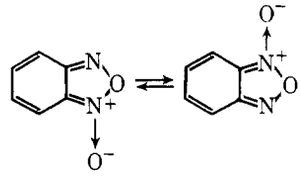
Dimethylfurazan 2-oxide (**1**) in acetone shows two resonances about 12 ppm apart at room temperature. The free energy of activation ($\Delta G^{\ddagger}$) for valence tautomerism of **1**, presumably by way of the dinitrosoalkene **9**, is known from many studies to be 34 kcal/mol,[6] and two different ^{15}N resonances are expected. The lower field ^{15}N resonance of **1** is almost insensitive to the nature of the solvent used, while the higher field line moves to still higher fields by 2.6 and 6.2 ppm in 2,2,2-trifluoroethanol and trifluoroacetic acid, respectively. Because the ^{15}N resonance of dimethylfurazan (**3**) is also solvent dependent (see Table I), the resonance at +19.1 ppm has been assigned to the nitrogen atom with the lone pair of electrons, and the resonance at +7.0 ppm to the *N*-oxide nitrogen of **1**.



1 **9** **1′**

The ^{15}N NMR of a 2 M solution of benzofurazan 1-oxide (**2**) in acetone at room temperature did not give a usable signal, even after a 20 h accumulation of free-induction decays. The other compounds reported here usually gave useful spectra after 2–3 h under the same conditions. When the temperature was raised to about 55 °C, a relatively broad line appeared at 5 ppm upfield from the nitric acid resonance. Lowering the temperature to about −10 °C results in two fairly sharp resonances equally spaced from the line observed at high temperature. The separation between the two resonances of **2** at −10 °C in acetone (13.5 ppm) was a little larger than that found for **1**.

Observation of two different resonances for benzofurazan 1-oxide below 0 °C is in agreement with the unsymmetrical structure, as indicated by much other physical data.[7] The free-energy barrier for valence tautomerism of benzofurazan 1-oxide (**2a** ⇌ **2b**) has been reported from many NMR measurements to be 14 kcal/mol.[7] This $\Delta G^{\ddagger}$, in combination with the chemical-shift difference of the two ^{15}N resonances of **2** at −10 °C, gives a predicted coalescence temperature of about 20 °C, which is in full accord with our observations.



2a **2b**

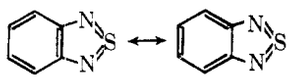
The lower field ^{15}N resonance of **2** was assigned to the *N*-oxide nitrogen by analogy with **1**.

The ^{15}N chemical shifts of **1** and **2** are at about 45 ppm higher field than those of dimethylfurazan and benzofurazan in the same solvent (see Table I). Comparable upfield shifts for ^{15}N resonance of pyridines upon N-oxidation have also been observed.[8]

Furazans and furazan oxides are weak bases (the pK_a values of **2** and **4** are −8.3 and −8.4, respectively[9]) and are not protonated in trifluoroacetic acid ($pK_a = -2.5$[10]), but are expected to be extensively hydrogen bonded to this solvent. The relatively small solvent shifts (6–18 ppm) observed for **1–4** are in agreement with this conclusion. The influence of trifluoroacetic acid on the ^{15}N chemical shift of 2,1,3-benzothiadiazole (**5**) is only slightly larger than that observed for compounds **1–4.** On the other hand, substantial upfield shifts are observed for the ^{15}N resonance of 2,1,3-benzoselenadiazole (**6**) in trifluoroethanol and trifluoroacetic acid (18.5 and 61.7 ppm, respectively). The solvent shift of 61.7 ppm observed in trifluoroacetic acid seems to be too large to be accounted for by hydrogen bonding and therefore is attributed to protonation.

Replacement of the oxygen in benzofurazan by sulfur to give 2,1,3-benzothiadiazole (**5**) leads to a large upfield shift of about 85 ppm. Interestingly, the ^{15}N chemical shift of 2,1,3-benzoselenadiazole (6) appears only 43 ppm upfield from that of benzofurazan. The unexpectedly high-field position of the ^{15}N resonance of **5** indicates that the type of bonding between sulfur and nitrogen may well be different from that between oxygen and nitrogen (and selenium and nitrogen as well). Participation of 3d orbitals of sulfur to form sulfur diimide type resonance structures **5a** and **5b** is one possible explanation. Similar resonance is highly unlikely for benzofurazan, and the 4d orbitals of selenium may not be easily involved (because of the large difference in sizes of nitrogen and selenium orbitals) for this type of π bonding.

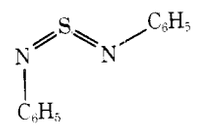
To help determine the importance of resonance structures **5a** and **5b** for 2,1,3-benzothiadiazole (**5**), we have obtained ^{15}N



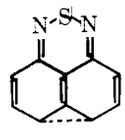
5a **5b**

NMR spectra of two sulfur diimides, namely naphtho[1,8-*cd*][1,2,6]thiadiazine-2-S^{IV} (**7**) and *N,N'*-diphenylsulfur diimide (**8**) (see Table I). The ^{15}N chemical shifts of **7** and **8** are at even higher fields than those of **4,** which lends support to the postulation of the sulfur diimide type resonance forms **5a** and **5b.**

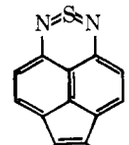
N,N'-Diphenylsulfur diimide (**8**) is known from dynamic NMR spectroscopy to have an unsymmetrical structure (**8a**), and the free-energy barrier ($\Delta G^{\ddagger}$) for its symmetrization is only about 11 kcal/mol.[11] Thus, at room temperature, the time-averaged ^{15}N spectrum of **8** should be observed and the single ^{15}N resonance is consistent with this conclusion. The ^{15}N chemical shift of diphenylsulfur diimide (**8**) is 30 ppm toward higher field than that of **7.** This relatively large difference may be due solely to the possibility of *Z,Z*, *Z,E*, and *E,E* configurations for **8,** but only *Z,Z* for **7.** However, it may be that resonance as exemplified by structure **7a** with a formal bond between the 4,5 carbons contributes to the hybrid and, if this is so, one might well expect a lower field ^{15}N shift for **7** than for **8.** Structure **7a** is consistent with the fact that **7** readily undergoes 1,11-cycloadditions with substances such as dimethyl acetylenedicarboxylate to give compounds of type **10.**[12]



8a



7a



10

Experimental Section

Compounds **1,**[13] **2,**[14] **3,**[15] **4,**[16] **5,**[17] **7,**[18] and **8**[19] were prepared as previously described. Compound **6** was obtained from Aldrich and used without further purification. Reagent grade acetone, dimethyl sulfoxide, trifluoroethanol, and trifluoroacetic acid were employed as solvents.

The natural-abundance ^{15}N spectra were obtained at a frequency of 18.25 MHz with a Bruker WH-180 pulse spectrometer that has been described in detail elsewhere.[20] With 25 mL of 2 M solutions in 25-mm o.d. spinning sample tubes, useful spectra could usually be obtained with accumulation times of 2–3 h, a 45° pulse angle, 4K data points, 3000-Hz spectrum width, and a pulse interval of 30 s. A 5-mm concentric tube containing a 1 M solution of 98% ^{15}N-enriched nitric acid in D_2O provided both the external reference standard and the field-frequency lock. The protons were decoupled at a power of 4 W by the gating technique.[21] The sample temperatures for normal spectra were about 30 °C. Chemical shifts are reported in parts per million from $H^{15}NO_3$ with a precision of about ±0.1 ppm.

Registry No.—(*Z,Z*)-**8,** 66085-13-0; (*Z,E*)-**8,** 66085-14-1; (*E,E*)-**8,** 66085-15-2.

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(21) Gated proton decoupling was employed to quench the NOE. In this technique, the proton decoupler is on only during data acquisition (1.3 s) following the observing pulse, and is off for a relatively long time (30 s) between the end of one data acquisition period and the start of the next.

Improvements in the Osmium-Catalyzed Oxyamination of Olefins by Chloramine-T

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We have reported that Chloramine-T (**1**) reacts with olefins in the presence of an osmium catalyst to afford vicinal hydroxy *p*-toluenesulfonamides (**2**).[1] This catalytic procedure was a

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