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Lewis Acid Modification of NO as an Oxidizing Agent

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Tertiary amines $(CH_3)_2NR$, where R is phenyl or a methyl-substituted phenyl group, in the presence of nitric oxide and a Lewis acid undergo α-hydrogen cleavage concurrent with intermolecular hydrogen transfer to yield equal amounts of iminium and ammonium salts in CH_2Cl_2 as solvent. When R is a *p*- or *o*-methyl-substituted phenyl ring this facile hydrogen transfer reaction also takes place in SO_2. In CH_2Cl_2 no reaction occurs in the absence of the Lewis acid. However, in SO_2 or in $CHCl_3$ with the addition of stoichiometric amounts of SO_2 and no Lewis acid, H_2SO_3 adducts of the tertiary amines form together with minor oxidation products. Pyridine and NO in SO_2, with or without a Lewis acid present, react to form the SO_3 amine adduct. This compound crystallizes in the monoclinic space group $P2_1/n$, with $a = 5.5463$ (12), $b = 14.8124$ (11), and $c = 7.9267$ (18) Å and $\beta = 104.06$ (2)°. 1,6-Dimethyl-3,4-dihydroquinazoline-4-sulfonate, a minor product formed along with the H_2SO_3 adduct of *N,N*-dimethyl-*p*-toluidine, crystallizes in the monoclinic space group $I2/m$, with $a = 10.6728$ (4), $b = 7.0426$ (6), and $c = 15.5537$ (9) Å and $\beta = 107.635$ (4)°.

Introduction

The reactions of amines with aqueous nitrous acid are well-known and, in simple terms, can be thought of as the combination of nitrosonium ion, NO^+, with the nucleophilic amine nitrogen. Neutral nitric oxide is a weaker oxidizing agent compared to NO^+ and reacts only slowly with primary or secondary amines.[2,3] The basicity of NO is such that there is no reaction between NO and a Lewis acid such as BF_3 using conventional experimental methods.[4] A weak molecular aggregate of $NO{:}BF_3$ has been prepared by expanding a mixture of NO and BF_3 through a supersonic nozzle.[5] Not surprisingly we have found that NO does not react with *N,N*-dimethyl aromatic amines in CH_2Cl_2 as solvent. However the addition of NO to Lewis acid adducts of the same amines initiates a clean intermolecular α-hydrogen transfer reaction to give equal amounts of the corresponding ammonium and iminium salts.

The known ways of preparing iminium salts have been reviewed.[6] Hydride abstraction from tertiary amines as one method of preparing iminium salts was first reported in the reactions of diazonium fluoroborates with tribenzylamine.[7] Since then a number of iminium salts have been prepared by using various salts of the carbonium ion $(C_6H_5)_3C^+$ as the hydride acceptor.[8,9] $NOBF_4$ is also known to form an unstable addition product with tribenzylamine at low temperatures, which decomposes to the tribenzylammonium and *N,N*-dibenzyliminium tetrafluoroborate salts above −20 °C.[10] This system is considered to be analogous to nitrous acid in a nonaqueous medium and in the proposed mechanism of reaction NO^+ acts as the hydride acceptor and is then released in its reduced form as NO gas.

In view of our findings we were curious to see how an aromatic amine without a readily abstractable α-hydrogen, such as pyridine, would behave in the presence of NO and a Lewis acid. It has been reported that pyridine does not react with NO.[3] However, if pyridine is added to an excess of $NOBF_4$ or NO_2BF_4 in SO_2 as solvent the *N*-nitroso- or *N*-nitropyridinium tetrafluoroborate salts are isolated in near quantitative yields as stable crystalline solids.[11] Pyridine is also known to form 1:1 addition compounds with SO_2 and SO_3.[12] Pyridine/SO_3, a useful sulfonating agent and convenient source of SO_3, is conventionally prepared by direct reaction of SO_3 with the base[13] or by reaction with chlorosulfonic acid.[14] The SO_3 adducts of *N,N*-dimethylamines may also be prepared by the latter method.[14]

Experimental Section

Chemicals. *N,N*-Dimethylaniline, *N,N*-dimethyl-*o*-toluidine, *N,N*-dimethyl-*p*-toluidine, pyridine, pyrrole, and *N*-methylpyrrole were predried over KOH and vacuum-distilled from CaH_2 or zinc dust before use.[15] Methylene chloride and $CHCl_3$ were purified,[15] distilled from P_2O_5, and stored under vacuum. SO_2, directly from the manufacturers cylinder was stored as liquid over P_2O_5 in a container with a "Teflon" high vacuum stopcock. Nitric oxide was passed through a silica gel trap at −78° to remove NO_2.[16] BF_3, BCl_3, and PF_5 were dried over P_2O_5 prior to use. 2,3-Dimethyl-2-butene was distilled under reduced pressure before use. Amine *N*-oxides were prepared according to a literature method.[17]

General Procedure. The amine (ca. 0.5 mmol) was accurately weighed into an NMR tube equipped with a Teflon-brand colinear J. Young valve so that the sequential addition of reactants was possible and each step of the reaction could be monitored by NMR spectroscopy. CH_2Cl_2 or SO_2 (0.5 mL) was condensed into the NMR tube followed by appropriate amounts of internal references ($CFCl_3$ and/or neopentane). The NMR spectra of the free amine were then recorded.

Approximately 1.5 mmol of a Lewis acid (BF_3, BCl_3, or PF_5) were weighed into the same tube and the NMR spectra of the amine acid adduct were obtained. This adduct generally formed virtually upon mixing the two reactants as was evidenced by an immediate color change of the solution in the NMR tube. Nitric oxide (1–2 mmol) was then condensed into the tube and the NMR spectra again taken. The time for the reaction to proceed to completion varied from several hours to several weeks at room temperature, depending on the amine, solvent, and Lewis acid employed.

For a preparative run the quantities of reactants were scaled up by a factor of 4 and mixed in a 10–15-mL Pyrex tube equipped

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with an NMR tube as side arm and a Teflon-brand high vacuum stopcock. After 1–2 weeks at room temeprature, all volatile species were removed by vacuum pumping to leave a red/brown viscous material. The proton resonance spectrum of this residue, redissolved in CH_2Cl_2 or SO_2, showed equal proportions of the corresponding ammonium and iminium species. Attempts to crystallize these complexes were unsuccessful. When amine, Lewis acid, and NO were mixed in equimolar proportions the reaction did not proceed to completion. For complete reaction an excess of both NO and Lewis acid was required.

On a preparative scale reactants were also mixed in $CHCl_3$ as solvent. After several days at room temperature volatile materials were evacuated slowly while keeping the reaction solution at 0 °C. A yellow crystalline material remained in the reactor which when examined under a microscope could be seen to be composed of at least two different crystal types. This material was extremely sensitive, turning into an orange oil immediately upon exposure to air or after 10 min in a drybox. Due to its sensitivity the crystals could not be further studied.

***N,N*-Dimethyl-*p*-toluidine/Lewis Acid/NO.** Reaction was complete within hours in either SO_2 or CH_2Cl_2 as solvents to yield the ammonium and iminium salts. ^1H and ^{13}C NMR data for all the species involved are listed in Table S3. Mass spectral analysis of the vapor from a reaction which had proceeded for 24 h in CH_2Cl_2 as solvent showed the presence of nitrogen gas. Separation of the dimethylammonium salt was accomplished by passing a CH_2Cl_2 solution of the two salts through a 25-cm (diameter = 10 mm) silica gel column under N_2. The ammonium salt was eluted from the column with acetonitrile. Its infrared spectrum showed strong bands at 3400 and 1081 cm^{-1} assigned to $N—H^+$ and BF_4^- stretching vibrations, respectively. The proton and carbon magnetic resonance spectra were very similar to those of the ammonium salt prepared from the amine and HBr. The amine did not react with NO alone in CH_2Cl_2 as solvent.

Addition of 2,3-dimethyl-2-butene to a CH_2Cl_2 solution containing equal amounts of the ammonium and iminium salts resulted in the complete disappearance of ^1H NMR signals attributed to the iminium salt, while resonances arising from the ammonium salt remained unchanged. New signals appeared in the NMR spectrum consistent with a Diels–Alder alkene addition to the *N,N*-dimethyl-*p*-toluidine iminium ion.

When BCl_3 is employed as Lewis acid in CH_2Cl_2 as solvent the reaction proceeds cleanly to the ammonium and iminium salts, but at a slower rate than with BF_3. There is a reaction between BCl_3 and SO_2 precluding the use of SO_2 as solvent in this case.

When PF_5 is employed as Lewis acid in CH_2Cl_2 as solvent the reaction is clean and relatively fast. A ^{19}F NMR spectrum of this sample showed a broad peak at −74.00 ppm assigned to the fluorines of the rapidly exchanging species PF_5 and PF_6^- and a doublet at −88.27 ppm (J = 1068 Hz) from POF_3. The observed reaction can be described by eq 1. All volatile species were

$$2CH_3C_6H_4N(CH_3)_2 + 3PF_5 + NO \rightarrow CH_3C_6H_4NH(CH_3)_2{}^+PF_6^- + CH_3C_6H_4NCH_3(=CH_2)^+PF_6^- + POF_3 + {}^1/_2N_2 \quad (1)$$

evacuated from this sample and the resulting orange residue was redissolved in CH_2Cl_2. The only lines remaining in the fluorine resonance spectrum were a sharp doublet at −71.88 ppm (J = 717 Hz) from PF_6^-. The infrared spectrum of the orange residue had peaks at 3160 ($N—H^+$), 3100 ($=CH_2$), 1650 ($C=N$), and 835 (PF_6^-). In SO_2 as solvent, after several days in solution, the signals of the ammonium and iminium salts gradually decreased in intensity while numerous new peaks appeared in the ^1H NMR spectra.

***N,N*-Dimethyl-*o*-toluidine/BF_3/NO.** The amine was completely converted to the corresponding ammonium and iminium salts after 2–3 days in SO_2 as solvent. With CH_2Cl_2 as solvent the conversion also proceeded cleanly but required 8–14 days, depending upon the relative concentrations of the reactants. The ^1H and ^{13}C spectral data are listed in Table S4.

***N,N*-Dimethylaniline/BF_3/NO.** The concentration dependence of the rate of product formation in CH_2Cl_2 was similar to that for the *o*-toluidine in the same solvent. The ^1H and ^{13}C NMR spectral data are listed in Table S5. In SO_2 the iminium and ammonium salts were formed together with minor compounds believed to be ring-substituted oxidation or sulfonation products.

Pyridine/BF_3/NO. The reactants were mixed as in the general procedure with SO_2 as solvent. The ^1H and ^{13}C NMR spectra of the resulting compounds are listed in Table S6. The pyridine SO_3 adduct was isolated as a white powder in 40% yield by evaporating all volatiles from an SO_2 solution of pyridine and NO which had been allowed to react at room temperature for 2 h. The adduct was recrystallized from the mixed solvent system CH_2Cl_2/SO_2 as white needles and characterized by an X-ray crystal structure.

***N,N*-Dimethyl-*p*-toluidine/NO in SO_2.** NO (6.3 mmol) was added to *N,N*-dimethyl-*p*-toluidine (3.5 mmol) dissolved in 5 mL of SO_2 to immediately give a dark orange/red solution. After 3 h at room temperature the ^1H and ^{13}C NMR spectra of this solution were assigned to one new product, the H_2SO_3 adduct, along with 13% each of the iminium and ammonium salts. Volatile materials were evaporated from the reaction flask under vacuum and the remaining red oil was pumped in vacuo for several hours. Attempts to crystallize this oil from benzene, methylene chloride, *n*-hexane, methanol, and various mixtures of these solvents were not successful, but minor products, observed in the initial ^1H NMR spectrum were removed by these procedures. For the reasons given in the Discussion section this oil is assigned as the H_2SO_3 adduct of the toluidine. Yield: 74%. Anal. Calcd for $C_9H_{15}N\ SO_3$: C, 49.75; H, 6.96; N, 6.45; S, 14.76. Found: C, 49.61; H, 6.74; N, 6.72; S, 14.40. The chemical shifts are listed in Table S7.

***N,N*-Dimethyl-*p*-toluidine/NO/SO_2 in $CHCl_3$.** If 3 mmol each of *N,N*-dimethyl-*p*-toluidine, SO_2, and NO are mixed together in 5 mL of $CHCl_3$ no apparent reaction takes place, even after several days at room temperature. From this clear orange solution less than 8 mg of residue remained after all volatile materials were removed in vacuo. However, if a 2:1 ratio of (SO_2, NO):amine is used a reaction does occur.

In a reaction vessel with a side arm SO_2 (6.5 mmol) was added to *N,N*-dimethyl-*p*-toluidine (3.2 mmol) dissolved in 5 mL of $CHCl_3$, producing a color change in the solution from pale yellow to a reddish orange. NO (6.6 mmol) was then condensed into this reaction mixture, the color of the solution deepening slightly upon mixing. After $2^1/_2$ days at room temperature yellow crystals had precipitated from the now dark burgundy red solution. The liquid was decanted into the empty side arm and all volatile materials were evacuated, leaving sticky yellow crystals in one arm of the reactor and a red oil in the other arm. The side arm containing the crystals was sealed under vacuum and subsequently broken open. The air-stable crystals were quickly washed with $CHCl_3$ and dried in vacuo. Their weight was 15 mg, corresponding to a 2% yield. An X-ray crystal structure determination of this minor product showed it to be 1,6-dimethyl-3,4-dihydroquinazoline-4-sulfonate. The chemical shift values are listed in Table S7. An ^1H NMR spectrum of the major product of this reaction, the red oil, showed it to be the same H_2SO_3 adduct previously isolated from the interaction of NO with *N,N*-dimethyl-*p*-toluidine in SO_2.

Magnetic resonance spectra were obtained on a Bruker AM 400 spectrometer at a magnetic field strength corresponding to 400 MHz for protons. Carbon and proton chemical shifts are reported with respect to tetramethylsilane, although neopentane was used as an internal reference since it is inert with respect to the compounds studied. A correction of 0.92 ppm was applied for protons and 31.4 ppm for ^{13}C. Fluorine resonance shifts are reported with respect to internal $CFCl_3$. Infrared spectra were obtained as CH_2Cl_2 solutions or on KBr pellets on Beckman Acculab 4 and Perkin-Elmer 683 infrared spectrometers. Elemental analyses were performed by Mr. Hector Sêguin of the National Research Council of Canada.

X-ray reflection intensities of the pyridine SO_3 adduct were measured with graphite-monochromatized Mo Kα radiation, (λ(Mo Kα_1) = 0.70932 Å), using the Enraf-Nonius diffractometer $\theta/2\theta$ scan technique with the NRCCAD control program.[18] For an approximately 0.07 × 0.1 × 0.2 mm crystal a total of 816 unique reflections were measured ($2\theta_{max}$ = 45), of which 538 reflections were considered significant with $I_{net} > 2.5\sigma(I_{net})$. Absorption correction was not necessary (μ = 0.43 mm^{-1}). The cell parameters were obtained by least-squares refinement of the setting angles

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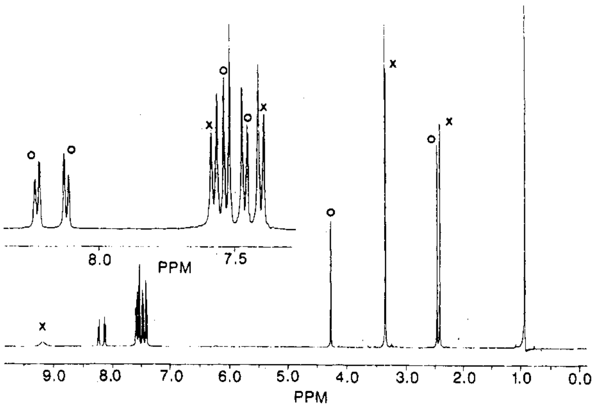


Figure 1. Proton resonance spectrum of the reaction mixture of *N*,*N*-dimethyl-*p*-toluidine, BF_3, and NO in SO_2: ammonium salt = O, iminium salt = X.

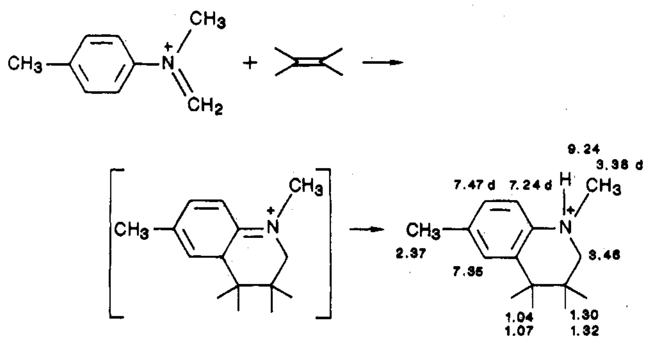
of 36 reflections with $2\theta > 30°$. The crystal is in the monoclinic space group $P2_1/n$ with $a = 5.5463$ (12), $b = 14.8124$ (11), and $c = 7.9267$ (18) Å and $\beta = 104.06$ (2)°. The structure was solved with MULTAN,[19] and H atoms were located from a subsequent D-map. The structure was refined with full matrix least squares (heavier atoms anisotropically, H atoms isotropically). The final results are $R_f = 0.041$ and $R_w = 0.047$ for the significant data ($R_f = 0.082$ and $R_w = 0.083$ for all data) with unit weights. All calculations were performed with the NRCVAX system of programs.[20] Scattering factors were taken from the International Tables for X-ray Crystallography.[21] The final atomic positional parameters and the equivalent isotropic temperature factors are listed in Table S8. The distances and angles for the atoms numbered as in Figure S1 are listed in Table S9. The anisotropic thermal parameters and final structure factors are included as supplementary material in Table S1. All bond lengths and angles have normal values.

X-ray intensities for the quinazoline were measured with Cu Kα radiation ($\lambda = 1.54056$ Å) and data were analyzed in the same manner as for the pyridine adduct. For an approximately 0.10 × 0.30 × 0.30 mm crystal a total of 1154 unique reflections were measured, of which 754 were considered significant. The cell parameters were obtained from the setting angles of 26 reflections with 2θ in the range 81° to 94°. The crystal is in the monoclinic space group $I2/m$, with $a = 10.6728$ (4), $b = 7.0426$ (6), and $c = 15.5537$ (9) Å and $\beta = 107.635$ (4)°. The final results are $R_f = 0.054$ and $R_w = 0.051$ for the significant data ($R_f = 0.078$ and $R_w = 0.061$ for all reflections) with unit weights. The final atomic positional parameters and the equivalent isotropic temperature factors are listed in Table S10. The distances and angles for the atoms numbered as in Figure S2 are listed in Table S11. The anisotropic thermal parameters and final structure factors are included as supplementary material in Table S2. All bond distances and angles for this compound are within the normal range.

Discussion

These results clearly show that NO is capable of specifically oxidizing Lewis acid adducts of *N*,*N*-dimethyl aromatic amines although NO and the uncomplexed amines do not react in CH_2Cl_2 as solvent under the same mild conditions. Since the evidence for these conclusions is primarily from NMR spectroscopy, a sample proton resonance spectrum with its interpretation is shown in Figure 1. The chemical shifts presented in this figure are typical of those listed in the supplementary tables. Except for the iminium salt all spectral assignments for the reaction mixtures were confirmed with spectra taken on the pure materials. The nature of the anion (BF_4^-, BCl_4^-, PF_6^-) does not appreciably affect the chemical shifts of the products. Changing from CH_2Cl_2 to SO_2 as solvent only has an appreciable effect on the chemical shifts of the ipso, ortho, and para carbons of the free amines. This is reasonable if there is some complexing of these amines with SO_2.

Scheme I



The vinylic protons of the iminium salts $(CH_3)(R)N{=}CH_2^+$ give a characteristic pair of doublets in their ^{1}H NMR spectra. For example, when R is the *p*-methyl-substituted phenyl group these doublets occur at 8.12 and 8.22 ppm with a geminal coupling constant of 6.8 Hz. The doublet at lower field is further split into a pair of quartets ($J = 1.48$ Hz) by long-range proton coupling to the *N*-methyl group. The high field vinylic doublet is also split into partially resolved quartets ($J = 0.72$ Hz). Although no long-range coupling constants have been reported across a carbon–nitrogen double bond there is considerable data for such coupling across carbon–carbon double bonds.[22] The coupling of the proton trans to a methyl group is usually greater than the cis proton so we can tentatively assign the lowest field signal to the vinylic hydrogen trans to the *N*-methyl group. ^{13}C–^{14}N spin coupling is only observed for the CH_2 carbon in the iminium salt. Since such coupling is usually averaged to zero by rapid quadrupole relaxation of nitrogen the present observation suggests a symmetric electric field environment about nitrogen in the iminium salts.

Further evidence to support the identity of the iminium salt is the disappearance of the NMR spectral lines attributed to this salt and the appearance of signals consistent with its Diels–Alder addition product when 2,3-dimethyl-2-butene is added to the reaction mixture. Similar reactions have been reported to proceed very readily.[23] Proton resonance shifts of the product are shown in Scheme I.

No intermediates were observed in the course of the amine oxidation with BF_3 and NO even at temperatures as low as −60 °C so the reaction mechanism remains speculative. One possibility is the transient existence of an *N*-oxide intermediate since it is known that iminium salts can be prepared by the cleavage of the N—O bond in amine oxides. For example, mild treatment of trimethylamine *N*-oxide with trifluoroacetic anhydride in CH_2Cl_2 leads to the *N*,*N*-dimethylformaldiminium trifluoroacetate salt $(CH_3)_2N{=}CH_2^+CF_3CO_2^-$.[24] Analogous iminium salts have been prepared from dimethylarylmethylamine *N*-oxides.[25]

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When we took a sample of *N,N*-dimethylaniline *N*-oxide and exposed it directly to an excess of PF_5 or BF_3 in CH_2Cl_2 the iminium and ammonium salts did not form. An orange crystalline solid precipitated from the solution leaving no dissolved proton containing species. The proton resonance spectrum of the orange solid dissolved in SO_2 was interpreted as that of the Lewis acid adduct of the *N*-oxide. It was noted that at room temperature there was not fast inversion on the NMR time scale about the nitrogen of the *N*-oxide adduct. By −40 °C this inversion was sufficiently slowed that two separate *N*-methyl proton signals were observed. On exposure to the atmosphere the orange crystals deliquesed to a colorless oil while giving off white fumes. Since the behavior of the *N*-oxide Lewis acid adduct was different than that observed in the amine/NO/Lewis acid systems, an *N*-oxide mechanism was ruled out and these reactions were not further pursued.

Although there is no reaction between NO and *N,N*-dimethyl-*p*-toluidine in the absence of BF_3 in CH_2Cl_2 as solvent, with SO_2 as solvent there is oxidation of the organic compound to yield some colored materials and water, or a Bronsted acid equivalent. This Bronsted acid combines with the SO_2 and the amine to give the H_2SO_3 adduct which resists further attack. Identification of the adduct comes from elemental analysis and NMR and infrared spectroscopy. In addition a minor product, 1,6-dimethyl-3,4-dihydroquinazoline-4-sulfonate, which must arise from interaction of the amine with some oxidation product, has been positively identified by X-ray crystallography and NMR and infrared spectroscopy. Small percentages of the previously identified iminium and ammonium salts are also produced. Presumably these arise from Bronsted rather than Lewis acid catalyzed attack of NO on the amine. The NMR results for the H_2SO_3 adduct, listed in Table S7, are consistent with those of the other amine adducts listed in Table S3. This compound is considered to be an adduct rather than a quaternary HSO_3^- ammonium salt since no proton–proton coupling to the *N*-methyl groups was observed in its ^1H NMR spectrum and a doublet from the small amount of ammonium salt produced was distinct. The infrared spectrum of the pure H_2SO_3 adduct has bands at 1120, 1030, and 612 cm^{-1} from the SO_3 grouping, at 2920 and 1460 cm^{-1} from the CH_3 groups, and at 3025 from the OH group. For comparison the pyridine/SO_3 adduct has bands at 1300, 1080, and 690 cm^{-1} from the SO_3 and the quinazoline/SO_3 adduct has bands at 1290, 1060, and 638 cm^{-1} from the SO_3 grouping and at 2965 from the methyl groups.

In view of the reaction of *N,N*-dimethyl aromatic amines with BF_3 and NO, it was of interest to see if an aromatic amine without a readily abstractable α-hydrogen, such as pyridine, would also react under similar conditions. No reaction was observed between NO and pyridine in CH_2Cl_2 as solvent, but in SO_2 solution the pyridine/SO_3 adduct formed. BF_3 and pyridine in SO_2 solution immediately form the pyridine/BF_3 adduct. When NO is added to this system the BF_3 adduct is slowly converted to the SO_3 adduct.

Since the α-hydrogen transfer reaction of *N,N*-dimethyl aromatic amines occurs in CH_2Cl_2 when both NO and a Lewis acid are present, one can state that the incorporation of an oxidized sulfur species is not necessary for the reaction to proceed. In SO_2 as solvent essentially complete iminium/ammonium salt formation only occurs in the presence of a Lewis acid. We therefore believe that this reaction exemplifies Lewis acid catalyzed NO oxidation of these tertiary amines. A noninteracting solvent such as CH_2Cl_2 is the solvent of choice in the study of such reactions. Without the Lewis acid, SO_2 and NO have the potential to behave as oxidizing agents themselves, as evidenced by the formation of the pyridine/SO_3 adduct, and by the reaction of *N,N*-dimethyl-*p*-toluidine, NO, and SO_2 to give a mixture of oxidation products.

It is worth noting that both carbon–nitrogen bonds N1–C2 and N3–C2 in the dihydroquinazoline are about the same length (1.309 and 1.303 Å) as in the N1–C2 bond of fully aromatic quinazoline itself, 1.307 Å.[26] This suggests that there is double-bond character in the N3–C2 bond, which would put a positive charge on N3 and a negative charge on the SO_3 group. The implied zwiterionic character of the N3–S bond is completely consistent with it being considerably shorter at 1.753 Å than the corresponding bond in the pyridine/SO_3 adduct at 1.829 Å.

We have also examined the behavior of pyrrole and *N*-methylpyrrole when mixed with a Lewis acid and NO in both CH_2Cl_2 and SO_2 as solvents. In every case a black insoluble film was produced. As this film exhibited a very low electrical conductivity it was considered unlikely to be a polypyrrole. Due to their insolubility these reaction products were not studied further. No reaction was observed between nitric oxide and the BF_3 adducts of trimethylamine or triethylamine in CH_2Cl_2 as solvent.

Supplementary Material Available: Figures S1 and S2 showing the atom numbering schemes and structure for $C_5H_5NSO_3$ and $C_{10}H_{14}N_2SO_3$, respectively; tables giving the anisotropic thermal parameters, the atomic positions, equivalent isotropic temperature factors, and bond distances and angles for $C_5H_5NSO_3$ and tables giving similar information for $C_{10}H_{14}N_2SO_3$ (Tables S2, S10, and S11); proton and carbon chemicals shifts are listed in Tables S3–S7 (17 pages); final structure factors for $C_5H_5NSO_3$ and $C_{10}H_{14}N_2SO_3$ (15 pages). Ordering information is given on any current masthead page.

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