H), 5.1 (s, 2 H), 3.9 (q, 4 H), 3-3.6 (m, 4 H), 2-1.9 (m, 2 H), 1.2 (t, 6 H); mass spectrum, *m/e* 348 (M + 1) (11%), 347 (15%), 305 (18%), 304 (99%), 303 (27%), 302 (13%), 223 (11%), 222 (100%), 204 (65%), 91 (18%).

IV. General Procedure for Preparation of Diethanolamine Heterocyclic Boronate. Ethyl heterocyclic boronate (5 mmol) prepared as described above (IIIB) was taken in 15 mL of ether. To it 0.52 mL (5.4 mmol) of diethanolamine in 5 mL of 2-propanol was added, and the reaction mixture was stirred at 25 °C for 1 h. A crystalline solid formed, was filtered, and washed with 5 mL of cold ether. The results are shown in Table VI.

Acknowledgment. This article is dedicated on his 60th year to Prof. George Zweifel, University of California, Davis, for his pioneering work on both asymmetric hydroboration and hydroboration of heterocyclic olefins.

Onium Ions. 34.[1] The Methoxydiazonium Ion: Preparation, ^{1}H, ^{13}C, and ^{15}N NMR and IR Structural Studies, Theoretical Calculations, and Reaction with Aromatics. Attempted Preparation and the Intermediacy of the Hydroxydiazonium Ion

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Abstract: Nitrous oxide is methylated with $CH_3F \rightarrow SbF_5$ in SO_2F_2 or with CH_3O^+SOClF in SO_2ClF to give the stable methoxydiazonium ion $CH_3ON_2^+$ (**1**), which was characterized by NMR (^{15}N, ^{13}C, ^{1}H) and FT IR spectroscopic studies. It is stable below −30 °C, above which it decomposes, regenerating N_2O. When reacted with aromatics, such as toluene, **1** gives only methylation products and no methoxy derivatives are formed. Spectroscopic and chemical data indicate that the mesomeric form $CH_3O—N{=}N^+$ is a significant contributor to the overall structure of **1**. Consideration of computed charge distribution (4-31 G with full geometry optimization and 4-31 G*) also supports this conclusion. Independent generation of **1** was also studied by solvolysis of methylazoxy triflate and diazotization of methoxylamine with $NO^+BF_4^-$. Preparation of the elusive hydroxydiazonium ion HON_2^+ (**4**) was attempted by protonation of nitrous oxide in superacids, but no long-lived ion could be observed. Diazotization of hydroxylamine with $NO^+BF_4^-$ gives nitrous oxide indicative of the intermediacy of **4**.

There is continued interest in non-benzenoid diazonium ions and their chemistry. The ability of electron-withdrawing substituents in stabilizing diazonium ions is well demonstrated by preparation[3] of fluorodiazonium ion salts $FN_2^+AsF_6^-$ or $FN_2^+SbF_6^-$ as well as fluorinated alkyldiazonium ions[4,5] $(CF_3)_2CHN_2^+$ and $CF_3CH_2N_2^+$ in superacidic media. The methyldiazonium ion $CH_3N_2^+$ was observed by McGarrity and co-workers[6] by protonation of diazomethane below −100 °C.

We have reported in our previous studies the generation of the aminodiazonium ion $H_2NN_2^+$ by protonation of hydrazoic acid in superacids and its use for aromatic amination.[7] Eberson, Nilsson, and Rietz reported the cyanation of aromatics via diazotization of cyanamide with isoamyl nitrite/acetic acid[8a] in a radical-type reaction. More recently, we reported that aromatics can be cyanated and nitrated with NCN_2^+ and $O_2NN_2^+$ generated via diazotization of cyanamide and nitramide, respectively, with $NO^+BF_4^-$,[8b] and we attempted with Christie fluorination of aromatics with $FN_2^+AsF_6^-$.[8b] We also reported our observation of the formation of $^{14}N^{15}N$ from diazotization of NH_3, $HN[(CH_3)_3Si]_2$, and HNCO, respectively, with $^{15}NO^+BF_4^-$, indicating intermediate formation of the parent diazonium ion HN_2^+.[9]

In continuation of our studies on non-benzenoid diazonium ions we now report our investigation of the preparation of the methoxydiazonium ion $CH_3ON_2^+$ (**1**) via methylation of N_2O with stable ion conditions in low nucleophilic solvents and its spectroscopic (by ^{1}H, ^{13}C, ^{15}N NMR and FT IR) characterization. Independent preparation of **1** by cleavage of methylazoxy triflate and diazotization of methoxylamine hydrochloride was also attempted. Our studies also included attempted preparation of the related hydroxydiazonium ion HON_2^+ (**4**).

Results and Discussion

Methylation of Nitrous Oxide and Spectroscopic Studies. When a slow stream of nitrous oxide was passed through the strong methylating reagent $CH_3F \rightarrow SbF_5$ in SO_2F_2 or CH_3O^+SOClF/SbF_6^- in SO_2ClF[10] at −80 °C a white precipitate of **1** was

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[1] (a) For part 33 see: Olah, G. A.; Doggweiler, H.; Felberg, J. D.; Frohlich, S. *J. Org. Chem.* **1985**, *50*, 4847. (b) Presented at the 189th National Meeting of the American Chemical Society, Miami Beach, FL, April 1985.

[2] (a) Postdoctoral research fellow 1984-1985. (b) Present address: Department of Chemistry, Kent State University, Kent, OH 44242.

[3] Christie, K. O.; Wilson, R. D.; Sawodny, W. *J. Mol. Struct.* **1971**, *8*, 254 and references cited therein.

[4] Mohrig, J. R.; Keegstra, K.; Maverick, A.; Roberts, R.; Wells, S. *J. Chem. Soc., Chem. Commun.* **1974**, 780.

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[8] (a) Eberson, L.; Nilsson, R.; Reitz B. *Acta Chem. Scand.* **1972**, *26*, 3870. (b) Olah, G. A.; Laali, K.; Farnia, M.; Shih, J.; Singh, B. P.; Shack, C. J.; Christie, K. O. *J. Org. Chem.* **1985**, *50*, 1338.

[9] Olah, G. A.; Herges, R.; Felberg, J. D.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1985**, *107*, 5282.

[10] Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 5163.

[11] ^{15}N NMR parameters for N_2O were previously reported in a liquid crystal solvent; see: Schultheis, H.; Fluch, E. *Z. Naturforsch. B* **1977**, *32b*, 257.

[12] Schwarz, W.; Niederer, P.; Rieker, A. *Helv. Chim. Acta* **1981**, *64*, 488.

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Table I. ^{15}N, ^{13}C, and ^{1}H NMR Parameters of the Methoxydiazonium Ion (**1**), Its Precursors,[11] and Some Diazonium Ions

	^{15}N NMR			^{13}C NMR		^{1}H NMR
	N_α	N_β	J_{NN}	δ_{Me_4Si}	J_{CH}	δ_{Me_4Si}
CH_3F				70.3 (dq)	150.1	4.17 (d)
$CH_3F \rightarrow SbF_5$				96.8 (dq)	164.4	5.68 (d)
$O^-{-}N_\alpha{=}N_\beta^+$	232.6	148.9	8			
$CH_3O{-}N_\alpha{=}N_\beta^+$	221.7	86.8	12	47.7 (q)	162.2	4.43 (s)
$Ph{-}N_\alpha^+{\equiv}N_\beta$	223.8	316.8	<0.7[12]			
$F{-}N_\alpha{=}N_\beta^+$	214.1	189.0				
$CH_3NH{-}N_\alpha{=}N_\beta^+$		273.9		36.8		3.82[7]

Table II. IR N–N Stretching Frequencies of **1** and Phenyldiazonium Ion (cm^{-1})

	$^{14}N{=}^{14}N$	$^{15}N{=}^{15}N$	shift obsd	shift calcd
N_2O	2226[13]	2158[13]	68	63
N_2^+-OCH_3	2385	2315	70	68
N_2^+-Ph	2285			

formed, which dissolved in excess CH_3F,

By slow evaporation of the solvent, **1** crystallized in colorless needles which decomposed at −30 °C regenerating N_2O(Ft IR).

$$N_2O + CH_3F \rightarrow SbF_5 \xrightarrow[-80\ ^\circ C]{SO_2F_2} \underset{\mathbf{1}}{CH_3ON_2^+SbF_6^-}$$

The proton-decoupled ^{13}C NMR spectrum of the resulting solution showed that the $CH_3F \rightarrow SbF_5$ complex (δ_{Me_4Si} 96.8, J_{CF} = 123 Hz) disappeared at the expense of a new singlet absorption at δ_{Me_4Si} 47.7 (Table I). The proton-decoupled ^{13}C NMR spectrum confirmed the signal at 47.7 ppm to be a methyl quartet with J_{CH} = 164 Hz. The ^{1}H NMR spectrum of **1** consisting of a singlet absorption at δ_{Me_4Si} 4.43 (Table I) indicates that a considerable part of the positive charge of the molecule is localized at the methyl group.

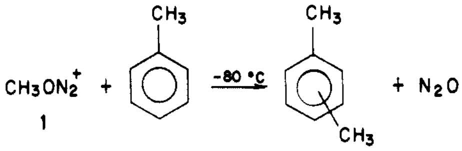
In order to gain further structural information and to rule out any N-methylation, we prepared α,β-^{15}N-labeled methoxydiazonium ion by using α,β-^{15}N-labeled nitrous oxide as starting material.

The ^{15}N NMR spectrum of labeled **1** shows a doublet for the α-nitrogen at δ_{NH_3} 221.7 and a doublet for the terminal nitrogen at δ 86.8 with J_{NN} = 12 Hz. Compared with nitrous oxide itself both signals shift upfield, by 10.9 ppm for N_α and 62.1 ppm for N_β (Table I). The assignment of the ^{15}N NMR signals to the appropriate nitrogen atoms was unambiguously proven by the preparation of singly α-labeled methoxydiazonium ion which showed a singlet absorption at δ_{NH_3} 221.7. In the ^{13}C NMR spectrum no ^{13}C–^{15}N couplings were observed, thus ruling out any N-methylation. Most remarkable are the ^{15}N MNR shifts of **1** compared with the well-known aromatic diazonium ions. In contrast to **1**, N_α of the benzenediazonium ion is more upfield than N_β (Table I). The large difference of the chemical shift of N_α in **1** and aromatic diazonium ions can hardly be due to the inductive effect of the methoxy group. Those effects are shown not to be more than 7 ppm in para-substituted benzenediazonium ions. Both the chemical shift of N_α and the unusual ^{15}N–^{15}N coupling indicate a considerable difference in the hybridization of N_α and in the nature of the N–N bond.

We also studied the infrared spectra of ion **1** and found that its N–N stretching frequency is quite different from that of the benzenediazonium ion. The FT IR spectra of **1** were recorded at −80 °C in SO_2F_2/CH_3F as solvent. In Table II the N–N stretching frequencies are compared with those of labeled and unlabeled nitrous oxide and phenyldiazonium ion.

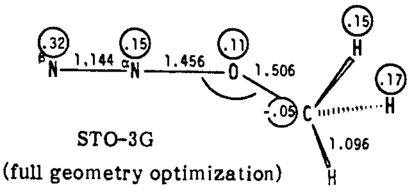
The N–N stretching of **1** appears at shorter wavelengths than in aromatic diazonium ions and close to that of molecular nitrogen itself (2397 cm^{-1}), indicating a strong N–N bond.

Reactions with Aromatics. Aromatic diazonium ions are used as reagents for the preparation of diazo compounds via electrophilic attack of the terminal nitrogen on reactive arenes. Cyano-, nitro- and aminodiazonium ions were shown to cyanate, nitrate, and aminate aromatics with loss of nitrogen, a good leaving group. The methoxydiazonium **1**, however, only methylates toluene at

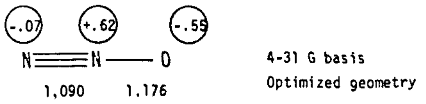


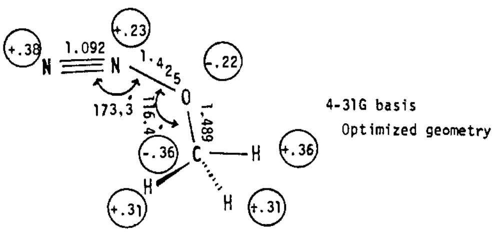
−80 °C with nitrous oxide as the leaving group. No methoxy derivatives were formed.

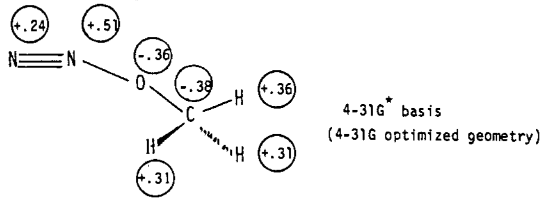
Theoretical Calculations. Ab initio quantum mechanical calculations using the STO-3G minimal basis set (with full geometry optimization) showed the N–N–O unit of **1** to be almost linear and the oxygen to form an almost tetrahedral angle with nitrogen and the methyl group. Further, the C–O bond was lengthened to 1.506 Å while the N–N bond length is 1.14 Å.



STO-3G calculations are, however, recognized as being rather poor for the description of bonding between electronegative elements. The C–O bond distance found is clearly exaggerated. Calculation of charge distribution is also difficult when electronegative atoms are bonded together. Consequently self-consistent-field quantum chemical calculations were carried out at the 4-31G split-valence basis set level in order to determine the equilibrium geomertry of $N_2OCH_3^+$ as well as the net charges of its component atoms. A full geometry optimization was carried out with the exception that the methyl group was frozen in tetrahedral geometry with CH distances taken to be 1.096 Å. The net atomic charges were further checked through a 4-31G* calculation at the 4-31G equilibrium geometry. For comparison, calculations were carried out on N_2O itself at the 4-31G level.







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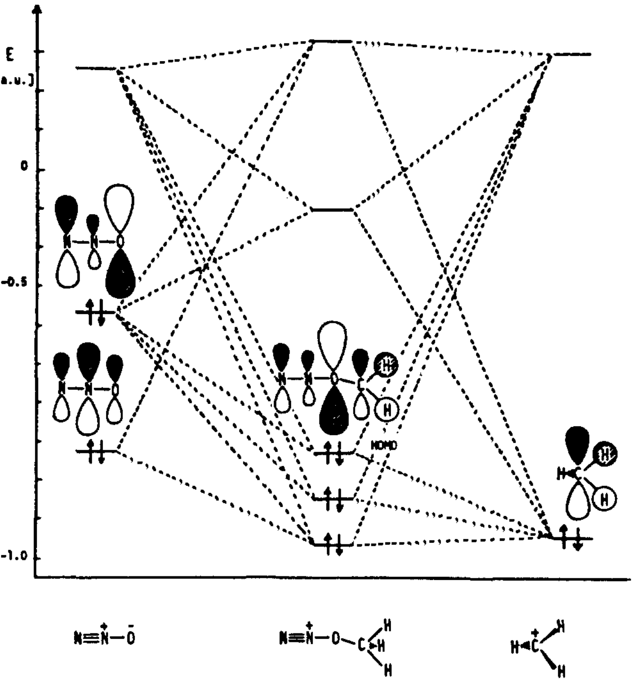
(13) Begun, G. M.; Fletcher, W. H. *J. Chem. Phys.* **1958**, *28*, 414.

Scheme I. MO Diagram of the Interaction of the π-System of Nitrous Oxide with a Methyl Cation

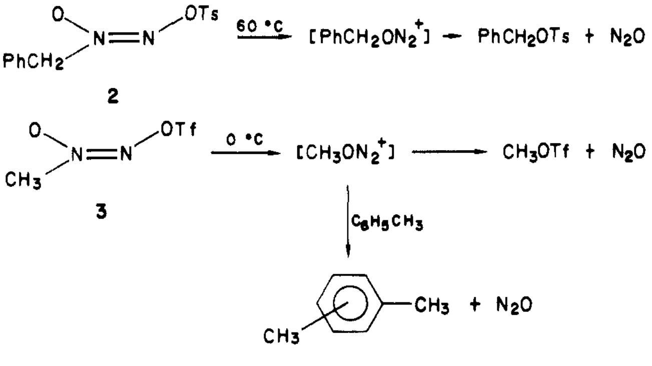


Little change was found in the N–N distance as one passes from NNO to the methoxydiazonium ion; however the NO distance increases substantially (1.176 to 1.425 Å) in response to formation of the new OC bond. This bond itself is rather weak, the equilibrium distance being 1.489 Å as compared to the more normal 1.43 Å for CO bonds of this type. The cation is almost linear (173.3°), and the NOC angle is close to tetrahedral (116.4°). The NNOC framework was found to be planar.

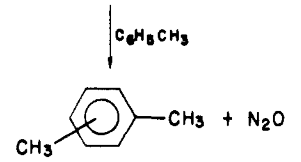
The positive charge is calculated to be localized on the ends of the molecule while the carbon and oxygen atoms form the negatively charged center of a rather ionic sandwich. The 4-31G* basis set results, while qualitatively similar, are even more ionic than those for 4-31G. This concentration of negative charge in close proximity to the β-nitrogen atom is probably responsible (at least in part) for its unusually shielded NMR absorption at $\delta(^{15}N)$ 86.8 (the electrons of the lone pair being in orbitals with less s-character and/or higher bond order between N_α and N_β, as compared to aromatic diazonium ions). The large $^{15}N-^{15}N$ coupling constant (J_{NN} = 12 Hz) seems also to confirm the low s-character of the lone pair of N_β. ^{15}N NMR shifts are, however, well recognized not to be affected by electron density alone.[14]

In carbocations hyperconjugation with a methyl group leads to stabilization. In the case of the methoxydiazonium ion, however, the antibonding orbital is occupied and thus weakens the bond (Scheme I). The weak C–O bond explains the observed chemical behavior of **1** as a powerful methylating agent.

Independent Methods To Generate 1. Maskill and Jencks recently reported on the solvolysis of benzylazoxy tosylate (**2**) and considered the intermediate of the reaction to be the benzyloxydiazonium ion.[15] In order to be able to carry out the reaction at lower temperatures at which the methoxydiazonium ion (**1**) is shown to be stable and thus an observable intermediate, we prepared and studied the cleavage of methylazoxy triflate (**3**). Triflate is a better leaving group than tosylate, and in fact **3** solvolyzed at a much lower temperature than **2**. Although the temperature (0 °C) was not low enough to observe **1** directly, its decomposition to nitrous oxide and methyl triflate as well as the trapping with toluene to form xylenes suggest the intermediacy of **1**. A further independent preparation of **1** was carried out via diazotization of methoxylamine hydrochloride with $NO^+BF_4^-$.



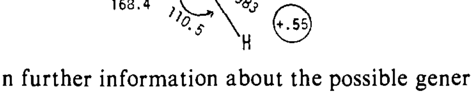
$$CH_3ONH_2{\cdot}HCl + \overset{+}{NO}BF_4^- \rightarrow [CH_3O\overset{+}{N_2}] + N_2O \rightarrow HNB_4 + CH_3OH$$



As before, **1** was not stable under the reaction conditions and decomposed to nitrous oxide or in the presence of toluene gave xylenes. The results, however, indicate the intermediacy of **1**. Diazotization of methoxylamine in aqueous solution with sodium nitrite also gives nitrous oxide, but in the presence of toluene no methylation to xylenes takes place. The aqueous medium may prevent methylation of toluene or in this case instead of the methoxydiazonium ion (**1**) the methyl ester of hyponitrous acid may be formed, which decomposes in a concerted step to nitrous oxide.[16]

Attempted Preparation of the Hydroxydiazonium Ion 4. Since nitrous oxide can be methylated we also attempted its protonation to form the hydroxydiazonium ion (**4**). Dissolving doubly ^{15}N-labeled nitrous oxide in the strongest superacids known such as SbF_5/HF (1:1) and SbF_5/FSO_3H (4:1) in SO_2ClF gave no observable shift in the ^1H and ^{15}N NMR spectra. Similarly, the FT IR spectra failed to show any absorptions besides those of nitrous oxide and the acid system (SbF_5/HF in SO_2F_2) even at −100 °C. When the solution was reacted with aromatics, such as toluene, no hydroxylation was observed. The data would seem to indicate that even if protonation of nitrous oxide would take place, the protonated ion is only present in a very low concentration or more probably undergoes fast exchange and thus is not observable.

The calculated (4-31 G) geometry and charge distribution in HON_2^+ (**4**) are similar to those in **1**.



$$H_2NOH\ HCl + \overset{+}{NO}BF_4^- \rightarrow [N_2^+OH] \rightarrow N_2O + HBF_4$$

4

$$\not\downarrow C_6H_5CH_3$$

To gain further information about the possible generation of the hydroxydiazonium ion (**4**) we also carried out a study of the diazotization of hydroxylamine with $NO^+BF_4^-$.[17] The reaction

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[14] See: Levy, G. C.; Lichter, R. L. In "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy"; Wiley-Interscience: New York, 1979; p 97.

[15] Maskill, H.; Jencks, W. P. *J. Chem. Soc., Chem. Commun.* **1984**, 944 and references cited therein.

[16] Boese, A. B., Jr.; Jones, L. W.; Major, R. T. *J. Am. Chem. Soc.* **1931**, *53*, 3530.

[17] Diazotization of $HONH_3^+$ with $NaNO_2$ in aqueous solution gives hyponitrous acid which decomposes in one step to nitrous oxide and water. Wislicenius, W. *Chem. Ber.* **1893**, *26*, 772. Buckholz, J. R.; Powell, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 509.

even at low temperature (−80 °C) results in the formation of N_2O without the observation of the intermediate ion **4**. When the reaction was carried out in the presence of aromatics, such as toluene, again no hydroxylation was observed. This is to be expected. If **4** reacts analogously to methoxydiazonium ion (**1**), it should only protonate toluene, and since the protonation is reversible toluene is regenerated during workup. Whereas the diazotization of hydroxylamine represents an independent way to generate **4**, there is not sufficient stability in the ion to be observable, and its chemical behavior indicates that it is only a protonating agent. The alternative attack of NO^+ on oxygen, i.e.,

$$HONH_2{\cdot}HCl \xrightarrow{NO^+BF_4^-} ONONH_2{\cdot}HCl$$

would lead to the possible formation of NO_2^+, but no nitration of aromatics was observed.

Conclusions

We were able to prepare the hitherto elusive methoxydiazonium ion (**1**) by methylation of N_2O under stable ion conditions and studied its structure by ^1H, ^{13}C, and ^{15}N NMR as well as by FT IR spectroscopy. The spectroscopic data and its chemical behavior as a strong methylating reagent indicate its differing nature from usual diazonium ions. According to ab initio calculations the experimental data can be best explained by strong hyperconjugation of the methyl group with the π-system of nitrous oxide. Representing the methoxydiazonium ion in terms of valence bond structures, **1b** and **1c** are significant contributors to the overall structure of the ion.

$$\underset{\mathbf{1a}}{[N{\equiv}N^+{-}O{-}CH_3} \leftrightarrow \underset{\mathbf{1b}}{N^+{=}N{-}O{-}CH_3} \leftrightarrow \underset{\mathbf{1c}}{N_2OCH_3^+]}$$

Attempted protonation of nitrous oxide gave no observable hydroxydiazonium ion (**4**). Diazotization of hydroxylamine with $NO^+BF_4^-$ resulted in formation of N_2O, indicative of intermediate formation of **4**.

Experimental Section

Materials. The methylating reagents $CH_3F \rightarrow SbF_5$ and CH_3O^+SOClF/SbF_6^- were prepared by reported methods.[10] $^{15}N^{15}NO$ and $N^{15}NO$ were generated by pyrolysis of $^{15}NH_4$, $^{15}NO_3$, and NH_4. $^{15}NO_3$ (99%) was obtained from MSD Isotopes, Division of Merck Frosst Canada Inc., Montreal. ^{15}N and ^{13}C NMR spectra were recorded on a Varian FT80 spectrometer. ^1H NMR spectra were recorded on an IBM 270 and the IR spectra on a Perkin Elmer 1550 FT IR spectrometer.

Preparation of Methoxydiazonium Ion 1. Methylation of Nitrous Oxide. A slow stream of nitrous oxide was passed through a solution of $CH_3F \rightarrow SbF_5$ in SO_2F_2 or a solution of CH_3O^+SOClF/SbF_6^- in SO_2ClF at −78 C. Salt **1** precipitated as a white solid, which was redissolved in an excess of CH_3F. By slow evaporation of CH_3F **1** crystallized as colorless needles. The α and the α,β-^{15}N-labeled methoxydiazonium ions were prepared by using α- and α,β-labeled N_2O as starting material. The NMR spectra were taken at −100 °C in the solvent mixture SO_2F_2/CH_3F and the FT IR spectra in SO_2F_2/CH_3F at −80 °C. The IR vibrations for labeled compounds (Table II) were calculated from the unlabeled compounds by assuming the same bond strength and a quasi diatomic vibration.

Cleavage of Methylazoxy Triflate. Methylazoxy triflate was prepared from the ammonium salt of methylazoxy ion which was synthesized according to a modified procedure of Stevens[18] as follows: Methylmagnesium bromide (50 mL, 3 N) was diluted with 450 mL of dry ether, and NO was passed slowly through for 1 h. Excess of NO was removed in a stream of nitrogen and the solution was cooled to 0 °C. HCl (2 N, 100 mL) was added and after the mixture was shaken the ether phase was separated and saturated with NH_3. At 0 °C the ammonium salt of methylazoxy ion precipitates. To complete the crystallization part of the solvent was removed under vacuum. The salt was filtered off, washed with CH_2Cl_2, and dried in a stream of NH_3. The yield is 5 g (36%). The compound is very hygroscopic and should be stored under nitrogen while refrigerated.

Ammonium salt (300 mg) was dispersed in 10 mL of liquid SO_2, 0.542 mL of triflic anhydride was added, and the mixture was refluxed for 15 min. The solution was concentrated to about 3 mL, and ammonium triflate byproduct was filtered off. SO_2 was removed in a stream of nitrogen at −30 °C. The yellow oily residue of methylazoxy triflate (**3**) was dissolved in methylene chloride: ^{13}C NMR δ 51.74 (CH_3), J_{CH} = 149 Hz; ^1H NMR δ 4.12.

The triflate **3** starts to decompose at 0 °C to form nitrous oxide (FT IR) and methyl triflate (^1H and ^{13}C NMR). In the presence of toluene (5:1) xylenes were formed (90% based on methylazoxy triflate). Under the same conditions methyl triflate does not react with toluene to form xylenes.[19]

Diazotiazation of Methoxylamine Hydrochloride. Methoxylamine hydrochloride was reacted with $NO^+BF_4^-$ in nitromethane in the presence of a threefold excess of toluene at 0 °C. The yield of xylenes was 21% (GC). N_2O was detected by FT IR and methanol by ^1H and ^{13}C NMR spectroscopy.

Attempted Protonation of Nitrous Oxide. ^{15}N NMR Study. One millimole of $^{15}N^{15}NO$, generated by pyrolysis of 82 mg of $^{15}NH_4{}^{15}NO_3$, was passed into a solution of 1.084 g (5 mmol) of SbF_5 and 100 mg (5 mmol) of HF in 2 mL of SO_2ClF or a solution of 4.336 g (20 mmol) of SbF_5 and 500 mg (5 mmol) of FSO_3H in 2 mL of SO_2ClF at −80 °C. The ^{15}N NMR spectra were compared with a solution of N_2O in neat SO_2ClF. No difference in the chemical shift of N_α and N_β or the ^{15}N–^{15}N coupling constant could be observed (Table I).

IR Study. A solution of 1 mmol of N_2O in 5 mmol of SbF_5, 5 mmol of HF, and 2 mL of SO_2F_2 at −80 °C was prepared. The FT IR spectrum was recorded at −100 °C, with AgCl windows. Beside unprotonated N_2O (Table II) and the solvent acid system no new absorptions could be observed.

Diazotization of Hydroxylamine. Hydroxylamine and hydroxylamine hydrochloride were reacted with $NO^+BF_4^-$ in CH_2Cl_2 at −80 °C. N_2O was formed and detected by FT IR.

Reaction of 1 with Toluene. A solution of 1 mmol of doubly ^{15}N-labeled **1** in SO_2ClF/CH_3F was mixed with a solution of 1 mmol of toluene in SO_2ClF at −80 °C. While toluene was added the absorptions of N_α (221.7 ppm) and N_β (86.8 ppm) of **1** disappeared and the absorptions of $^{15}N^{15}NO$ (232.6 and 148.9 ppm) became visible. The reaction mixture was quenched in $NaHCO_3$/ice, extracted with ether, and analyzed by GC. The yield of xylenes was >98%.

Calculational Methods. The restricted Hartree–Fock ab initio calculations were performed with split-level basis sets[20] with use of Pople's Gaussian 82 program.[21]

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Registry No. $1{\cdot}SbF_6^-$, 100571-61-7; **3**, 100571-62-8; N_2O, 10024-97-2; toluene, 108-88-3; methoxylamine hydrochloride, 593-56-6; hydroxylamine, 7803-49-8.

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