J. Am. Chem. Soc. **1983**, *105*, 5657-5660

is changed. Thus, aldehydes lead to shorter lifetimes and complications owing to acetal formation and self-quenching, while larger ketones lead to lifetime shortening owing to Norrish Type I and Type II processes. In view of these complications, it is not surprising that triplet acetone appears to be the only simple aliphatic carbonyl compound of importance in biological systems.

Experimental Section

Acetone (Fisher Spectrograde), acetaldehyde (BDH reagent), and 2-butanone (Aldrich Gold Label) were used as received. Biphenyl and 4,4′-dimethylbiphenyl were obtained from Aldrich Chemical Co. and sublimed under vacuum. Sodium dodecyl sulfate (BDH, specially pure) and Brij-35 (Aldrich) were used as received. Cetyltrimethylammonium chloride (K&K) was precipitated from the 50% methanol solution with acetone, washed several times with anhydrous ether, and dried under vacuum. Distilled water (Fisher HPLC grade) and acetonitrile (Eastman Kodak Spectro) were used as obtained.

Ultraviolet absorption spectra were recorded on a Cary 219 UV spectrometer, and fluorescence emission spectra were recorded on a Perkin-Elmer Model LS-5 spectrofluorometer with a PE Model 3600 data station.

Samples for laser flash photolysis were contained in Suprasil cells made of 7 × 7-mm^2 rectangular tubing (Vitro Dynamics). All experiments were carried out under oxygen-free conditions. Quenchers were added as aliquots of standard alcoholic solutions. Other details are similar to those reported previously.[2,16]

The samples were excited with the pulses from a Lumonics TE-861S Excimer laser, with mixtures of Xe/HCl/He as the lasing medium. Details of experimental technique and a full description of the instrument have been given elsewhere.[16]

Acknowledgment. The technical assistance of Mr. S. E. Sugamori is gratefully acknowledged. Thanks are due to Drs. P. Jacques and D. J. Lougnot for kindly providing a preprint of ref 28 and for valuable correspondence.

Registry No. SDS, 151-21-3; CTAC, 112-02-7; Brij-35, 9002-92-0; acetone, 67-64-1; acetaldehyde, 75-07-0; 2-butanone, 78-93-3; biphenyl, 92-52-4; 4,4′-dimethylbiphenyl, 613-33-2.

Onium Ions. 26.[1] Aminodiazonium Ions: Preparation, ^{1}H, ^{13}C, and ^{15}N NMR Structural Studies, and Electrophilic Amination of Aromatics

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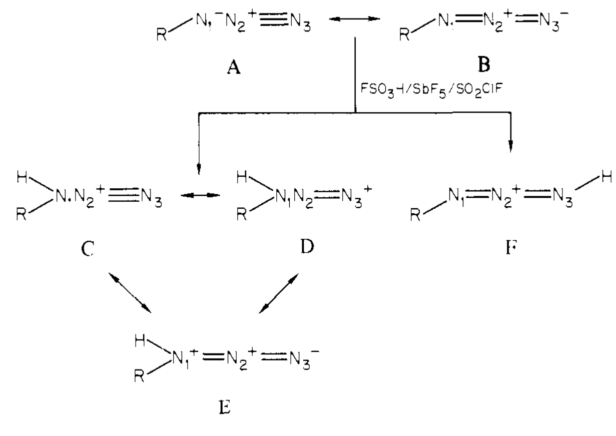
Received January 31, 1983

Abstract: Protonation of hydrazoic acid and alkyl azides with FSO_3H/SbF_5, HF/SbF_5, or HF/BF_3 results in the formation of stable aminodiazonium ions as shown by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopic studies. Molecular orbital calculations of the thermodynamics of the protonation of hydrazoic acid also support preferential formation of the aminodiazonium ion. The aminodiazonium ion was also prepared in situ from $NaN_3/AlCl_3/HCl$ or $(CH_3)_3SiN_3/AlCl_3/HCl$ [$(CH_3)_3SiN_3/HF/BF_3$]. Aminodiazonium salts were found to affect electrophilic amination of aromatics in high yields, with generally high regioselectivity and low substrate selectivity.

Aromatic diazonium ions are quite stable, isolable as salts in some cases, and important compounds in organic synthesis, such as dyestuffs.[3] However, their aliphatic counterparts[4,5] can only be obtained in strong acid solutions without elimination of nitrogen. In spite of the preparation of X-ray study of the fluorodiazonium ion (FN_2^+) as the stable hexafluroantimonate salt,[6] little is known about heteroatom-substituted diazonium ions. Schmidt[7] described the preparation and IR spectra of the hydrohexachloroantimonates of methyl azide and hydrozoic acid, and suggested them to be the aminodiazonium salts (although several IR-active absorptions were missing in the obtained IR spectra). No other study of aminodiazonium ions is known.

Scheme I



Results and Discussion

Protonation of Hydrazoic Acid and Alkyl Azides. We now achieved clear unequivocal protonation of methyl and ethyl azides, as well as hydrazoic acid under superacidic stable ion conditions. Considering the mesomeric structures of azides (A ⇌ B), protonation could take place on N-1 or N-3 leading either to ami-

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Table I. ^{15}N NMR Parameters of Aminodiazonium Ions and Their Azide Precursors[a]

	azide RN_3			aminodiazomium ion $RHNN_2^+$		
R	δ(N-1)	δ(N-3)	$^1J_{NH}$	δ(N-1)	δ(N-3)	$^1J_{NH}$
H	53.58	204.00	70.2[b]	68.61	266.15	100.0
CH_3	59.35	207.90		73.93	273.92	107.3
C_2H_5	74.12	210.97		85.59	277.46	105.1

[a] Chemical shift ($\delta(^{15}N)$) in ppm from anhydrous, external ammonia, coupling constants (J_{NH}) in hertz. [b] Reference 10.

nodiazonium ions (C ⇄ D) or iminodiazenium ion (F) (Scheme I). Slow addition of the azide solutions in SO_2ClF at −78 °C to an equally cold mixture of $FSO_3H/SbF_5/SO_2ClF$ gave clean solutions whose ^1H, ^{13}C, and ^{15}N NMR studies clearly indicated formation of the corresponding aminodiazonium ions ($NHRN_2^+$).

Protonation of hydrazoic acid was also carried out in $HF/SbF_5/SO_2ClF$ or $HF/BF_3/SO_2ClF$ superacid media but the latter solutions were studied mostly in regard to their aminating ability (vide infra).

^{15}N NMR Spectroscopy. For the ^{15}N NMR studies we used azides 99% enriched with ^{15}N in the 1- and 3-positions, easily prepared from $NaNN^{15}N$ by known methods.[8,9] Table I summarizes the observed ^{15}N NMR parameters of the studied aminodiazonium ions and their azide precursors.

The ^{15}N chemical shifts of the precursor azides were in good agreement with literature data.[10] The observation of two ^{15}N resonances in the ^{15}N NMR of protonated hydrazoic acid ruled out the symmetrical iminodiazenium ion structure (F) for these species. The ^{15}N chemical shifts of protonated alkyl azides is also close to that of the protonated hydrazoic acid indicating that the proton resides on N-1 leading to aminodiazonium ion. The site of protonation of the azides is also proven by their proton-coupled ^{15}N NMR spectra. Protonated hydrazoic acid shows a triplet for N-1 and the protonated alkyl azides a doublet, whereas N-3 remains as a singlet.

N-1 in the aminodiazonium ion is only slightly deshielded (11.4–15 ppm), but N-3 shows a very large downfield shift of more than 62 ppm compared to the neutral precursors, indicating a substantial positive charge on N-3 (mesomeric structure D). These differences in the chemical shifts between the azides and the aminodiazonium ions ($\Delta\delta(^{15}N\text{-}3) = 62.15\text{–}66.49$ ppm) are the largest so far reported between a neutral and protonated species in ^{15}N NMR spectroscopy.[11,12] In the benzenediazonium ions the $\delta(^{15}N)$ of the corresponding diazonium nitrogen were found between 316 and 323 ppm,[13] 40–50 ppm deshielded from the presently studied ions ($\delta(N\text{-}3) = 266\text{–}277.5$ ppm). The chemical shift range of $\delta(^{15}N\text{-}1)$ (68.6–85.6 ppm) in these aminodiazonium ions strongly indicates the contribution of the mesomeric form E to the overall structure of these ions. The ^{15}N chemical shifts of N-1 are considerably deshielded from those in simple aliphatic amines (10–40 ppm) but are somewhat comparable to those of anilines (50–70 ppm),[14] where the nonbonded electron pair is also involved in conjugation with a π system. Furthermore, the $^1J_{NH}$ spin–spin coupling provides evidence for the sp^2 hybridization of N-1 in the aminodiazonium ions. The coupling constant $^1J_{NH}$ increases from 70 Hz in hydrazoic acid to a range of 100–107.3 Hz in the aminodiazonium ions upon protonation. The relationship between s character at nitrogen and one bond N–H coupling constants is given by eq 1.[15]

$$\%s = 0.43\,^1J_{NH} - 6 \qquad (1)$$

Table II. ^1H NMR[a] and ^{13}C NMR[b] Shifts of Aminodiazonium Ions and Their Azide Precursors

	azide RN_3			aminodiazonium ion $RHNN_2^+$		
R	H	CH_2	CH_3	H	CH_2	CH_3
			^1H NMR Shifts			
H	5.41[c]			9.83		
CH_3			3.04	8.80		3.82
C_2H_5		2.38	1.34	8.84	4.22	1.76
			^{13}C NMR Shifts			
CH_3			35.41			36.77
C_2H_5		44.57	11.89		49.02	10.26

[a] ^1H NMR shifts are in ppm from external Me_4Si at −80 °C. [b] ^{13}C NMR shifts are in ppm from external Me_4Si at −80 °C. [c] The ^1H NMR shift of hydrazoic acid is strongly dependent on the solvent and concentration.[16] The value reported is for a 1:1 solution of HN_3 in SO_2ClF at −90 °C.

The calculated %s character according to eq 1 in the aminodiazonium ions has a range of 37.0–40.1% (theoretical for sp^2 = 33.3%).

These results are in contrast with the protonation of diazomethane,[5] which is considered to lead to a mixture of methyl diazonium ion and methylene diazenium ion.

^1H and ^{13}C NMR Spectroscopy. Further structural information of the aminodiazonium ions was obtained from their ^1H and ^{13}C NMR spectra. The chemical shifts of the ions and their precursors are reported in Table II.

The NH proton in the aminodiazonium ions appears in a range between δ 8.80 and 9.83, which is only slightly more deshielded than the NH resonance in protonated amides (δ 8.28–8.72)[17] and less than in protonated imines (δ 9.40–11.00).[18] The two latter cations show considerable double-bonded nitrogen character,[19] implying that the amino nitrogen of the aminodiazonium ions also have considerable double-bond character. This view is further supported by similar methyl and methylene chemical shift differences ($\Delta\delta(^1H)$ and $\Delta\delta(^{13}C)$) on protonation of the alkyl azides as compared to *N*-alkyl amides and *N*-alkyl imides. In the case of protonated hydrazoic acid the NH chemical shift depends on the temperature indicating a rapid exchange of the protonated form with FSO_3H.[20] Protonated methyl azide shows a doublet for the *N*-methyl group (J_{HNCH_3} = 3.4 Hz) at δ 3.82, again confirming the site of protonation in the aminodiazonium ions. In the ethylaminodiazonium ion the CH_2 group was observed as a multiplet due to the coupling with the NH proton and the methyl group, respectively; however, the methyl protons split to a triplet at δ 1.76 (J_{HH} = 6.8 Hz).

The ^{13}C NMR data are in accordance with the other NMR spectroscopic observations, supporting the established site of protonation of azides. The ^{13}C NMR chemical shift differences between the aminodiazonium ions and their precursors are, however, only small. The deshielding of the carbon attached to the amino nitrogen is 1.4 and 4.4 ppm for methyl and ethyl azide, respectively, upon protonation.

Theoretical Calculations. We also have addressed with ab initio[21] and MINDO/3[22] molecular orbital calculations the

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(14) See ref 13, p 38 and 54.

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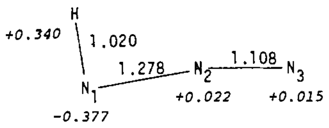
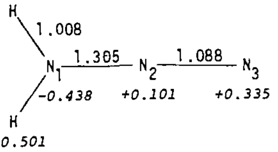
(20) At higher temperatures, e.g., −20 °C, only one signal is observed for FSO_3H and hydrazoic acid at $\delta(H)$ = 10.3 ppm.

thermodynamics of the protonation of hydrazoic acid. In accordance with the NMR interpretations the formation of the aminodiazonium ion is preferred. At the 3-21G level[23] of theory the energy difference over the experimentally ellusive diazenium ion is as large as 49.8 kcal/mol.[24] The theoretical calculations also show that the diazenium ion might indeed be a viable species as evidenced from the zero eigenvalues of the force constant matrix. In the related case of C- vs. N-protonation of diazomethane, where both ions were observed,[5] the methyldiazonium ion is the thermodynamically preferred species by 50 kcal/mol (3-21G). However, the 3-21G calculated proton affinity of diazomethane is significantly higher than that of hydrazoic acid, i.e., 233 vs. 210 kcal/mol, respectively.[25] Interestingly the semiempirical MINDO/3 method gives the proton affinities as 228 and 221, respectively.[26,27]

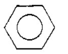
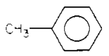
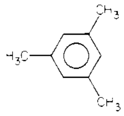
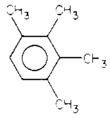
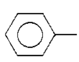
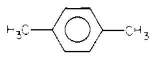
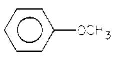
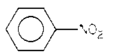
Consideration of the optimized geometrical parameters of the aminodiazonium ion also support the conclusions drawn from the NMR studies. The calculated $H_2N-N_2^+$ bond length of 1.305 Å indicates significant double-bond character[25] as well as the fact that the optimized structure has a planar conformation (C_{2v} symmetry). Actually as compared to hydrazoic acid this bond has lengthened by only 0.027 Å and the diazonium bond shortened by 0.020 Å to 1.088 Å. Employing the 3-21G calculated total atomic charges as a crude measure for the trend of the NMR chemical shifts, it is confirmed that N-3 and the protons carry most of the positive charge.





Electrophilic Amination of Aromatics. Aromatic amines serve as one of the most important class of synthetic intermediates and as entries into nitrogen heterocycles. Their most common synthetic preparation is by the reduction of the corresponding aromatic nitro compounds.[28] Continued studies were also carried out on the direct amination of aromatics with various reagents. These include hydroxylammonium salts,[29] hydroxylamine-*O*-sulfonic acid,[30] hydrazoic acid,[31] as well as several organic azides[32] mostly under Lewis-acid-catalyzed conditions and also with thermal initiation[33] or photolysis.[34] More recently Kovacic and his co-workers[35] reinvestigated many of the direct aminating reagents under more quantitative conditions. He furthermore found that haloamines[36] can be used as a new reagent for direct amination, giving preferential meta orientation. Large excess of aluminum chloride is needed for these reactions. They also restudied aromatic amination with hydrazoic acid catalyzed by $AlCl_3$ or H_2SO_4, but the reaction condition necessitated a 2:1 ratio of catalyst to azide at reflux temperature, giving modest to low yields.[37]

Table III. Yield and Isomer Distribution of Aromatic Amines Obtained by Amination of Aromatic Substrates with 1

		isomer distribution, %		
2	yield, %[a]	ortho	meta	para
	63.3			
	72.6 (65)[37] (37)[35a]	47.3 (49) (31)	13.8 (14) (14)	38.9 (37) (55)
	77.8			
	39.0			
	25.1 (60)[35c] (18)[37]	28.5 (47) (36)	15.3 (17) (19)	56.2 (36) (43)
	69.8			
	48.7	74.4	4	21.6
	1.5			

[a] Data in parentheses for electrophilic amination are given from literature for comparison.

Preparation and characterization of the aminodiazonium ion ($NH_2N_2^+$) discussed in our present work also allowed us to study its use as simple and effective reagent for electrophilic aromatic amination. As discussed the simplest way of preparing the aminodiazonium ion is the protonation of hydrazoic acid with a suitable superacid such as FSO_3H/SbF_5, HF/BF_3, or HF/SbF_5.

$$N_3H + FSO_3H/SbF_5 \text{ or } HF/SbF_5 \rightarrow NH_2N_2^+SbF_6^-$$

$$N_3H + HF/BF_3 \rightarrow NH_2N_2^+BF_4^-$$

However, to avoid difficulties in handling hydrazoic acid and side effects of using superacids, we directed our interest to a more convenient in situ preparation of the aminodiazonium ion allowing its use in the amination of aromatic compounds.

Schmidt during his studies on hydrazoic acid also reported that antimony(V) tetrachloroazide reacts with excess hydrogen chloride to give aminodiazonium hexachloroantimonate.[38] We have found

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(24) The 3-21G energies are for hydrazoic acid −162.87642 au for aminodiazonium ion−163.21068 au, and for iminodiazenium[25] ion−163.10967 au.

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(26) Niemeyer, H. M. *Helv. Chim. Acta* **1976**, *59*, 1133.

(27) The energy difference for the differently substituted ions is only 12.9 kcal/mol with MINDO/3 still favoring the aminodiazonium ion. A similar energy variation between ab initio 4-31G and MINDO/3 has been calculated for the C- vs. N-protonation of diazomethane.[26]

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it now extremely convenient to react NaN_3 (or trimethylsilyl azide)[39] with anhydrous $AlCl_3$ and subsequently with dry HCl to form in situ aminodiazonium tetrachloroaluminate (**1**).[40]

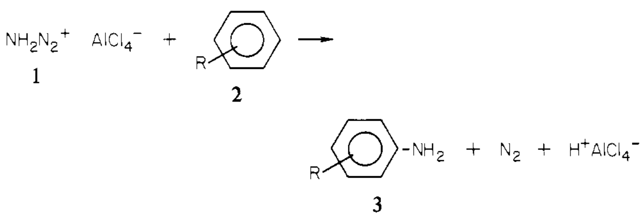
$$NaN_3 + AlCl_3 \rightarrow AlCl_2N_3 + NaCl$$

$$AlCl_2N_3 + 2HCl \rightarrow \underset{\mathbf{1}}{N_3H_2{}^+AlCl_4{}^-}$$

The formation of aminodiazonium tetrachloroaluminate from sodium azide or trimethylsilyl azide with $AlCl_3$/HCl was confirmed by NMR spectroscopy. The spectra in SO_2ClF were identical (except some medium effect) with those of the direct protonation of HN_3 in $FSO_3H/SbF_5/SO_2ClF$. Similar NMR spectra were also observed for azidotrimethylsilane/HF/BF_3 in SO_2ClF.

The preferred conditions for the preparation of the aminodiazonium ion is a 1:1.1 molar ratio of $NaN_3/AlCl_3$ and an excess of hydrogen chloride. An increased amount of $AlCl_3$ did not improve yields.

Aminodiazonium tetrachloroaluminate when reacted with aromatic hydrocarbons gives amino arenes in good yield. Best results for aromatic amination were obtained when an excess of the aromatic substrate itself is also used as the reaction medium.



The yield of arylamines was 39–78% for benzene and alkylbenzenes. Less reactive aromatics with heteroatom-containing electron-withdrawing groups gave substantially lower yields (Table III).

Attempts to replace the excess of the aromatic with hexane as solvent led to an increasingly heterogeneous system and decreased the yields of amination. 1,2-Dichloroethane and nitromethane are unsuitable as solvents because of strong complexation with the catalyst system.

The isomer distribution of toluidines shown in Table III (46–48% ortho, 13–14% meta, and 38–39% para) is characteristic of electrophilic substitution with a strongly electron-deficient reagent. Meta substitution is comparable to that in Friedel–Crafts methylation and ethylation and higher than in nitration, sulfonation, or halogenation,[41] which could be affected by some intramolecular isomerization in the benzenium ion intermediate of the reaction. The amination of anisole gave only 4% meta isomer, with 74% ortho and 22% para. The relative $k_{\text{toluene}}/k_{\text{benzene}}$ rate as determined from competition experiments was 4:1. Even if fast encounter-controlled reaction conditions cannot be excluded, and the lack of complete homogeneity of the system makes rate determination of little value. However, it seems that the amination of benzene/toluene and anisole display low substrate but high positional selectivity.

Conclusion. It is clear from the present ^1H, ^{13}C, and ^{15}N NMR studies and related molecular orbital calculations that azides are protonated in superacids exclusively on N-1 forming aminodiazonium ions. Our investigation also indicates the charge delocalization through all three nitrogens represented by the resonance structures C $\rightleftarrows$ D $\rightleftarrows$ E.

It was also shown that the aminodiazonium ion, easily prepared in situ from $NaN_3/AlCl_3/HCl$, serves as an efficient direct electrophilic aminating agent for aromatics. Generally high regioselectivity and low substrate selectivity are indicative of a highly reactive and less selective electrophilic aminating agent.

Experimental Section

Materials. The preparation of a solution of hydrazoic acid in SO_2ClF and of methyl azide and ethyl azide were performed by known methods.[8,9] Trimethylsilyl azide is commercially available. $NaNN^{15}N$ (99%) was obtained from Stohler Isotope Chemicals, Waltham, MA. FSO_3H, SbF_5, all the solvents, and aromatic compounds were anhydrous and distilled before use. Sodium azide (99%) and aluminum chloride (anhydrous powder) were used without further purification.

Preparation of Aminodiazonium Ions. A cool solution of the azide in SO_2ClF (−78 °C) was slowly added to a cool mixture of FSO_3H/SbF_5 (1:1) in SO_2ClF (−78 °C). Instead of a hydrazoic acid/SO_2ClF solution trimethylsilyl azide in SO_2ClF can be used, where the molar ratio of FSO_3H/SbF_5 was 6:1. The spectra were taken at −90 (HN_3) and −80 °C (alkyl azides). The concentration of the solutions was 10–15%.

^{15}N NMR Spectroscopy. The nitrogen-15 spectra were obtained on the Varian FT80 spectrometer equipped with a variable-temperature broad-band probe. The chemical shifts are referenced from anhydrous, external ammonia at 25 °C.

^{13}C NMR Spectroscopy. ^{13}C NMR spectra were obtained on the Varian FT80 spectrometer as described above. External Me_4Si (capillary tube) was used as the reference.

^1H NMR Spectroscopy. Proton magnetic resonance spectra were obtained with a Varian Associates Model A56/60A NMR spectrometer equipped with a variable-temperature probe. External Me_4Si (capillary tube) was used as the reference.

Calculational Methods. The restricted Hartree–Fock ab initio calculations with the 3-21G basis set[23] were performed with the GAUSSIAN80 series of programs.[21] The structures were completely optimized within C_s symmetry constraints. The eigenvalues of the harmonic force constant matrix were evaluated by numerical second-derivatives techniques. For the semiempirical MINDO/3 method[22] full geometry optimizations were employed.

General Procedure of Amination of Aromatics. NaN_3 (0.1 mol) and powdered anhydrous $AlCl_3$ (0.11 mol) were stirred in 200 mL of the corresponding aromatic overnight at 25 °C. Dry HCl gas was then introduced resulting in evolution of nitrogen indicating the start of the reaction. The introduction of HCl was continued until no more nitrogen evolution was observed. The reaction mixture was then poured into ice, neutralized with excess sodium hydroxide until precipitated aluminum hydroxide was dissolved, extracted with (3 × 200 mL) ether, dried over magnesium sulfate, and distilled. Alternatively steam distillation followed by extraction with ether then fractional distillation gave the aromatic amine. Products were characterized by their boiling points and ^1H NMR data as well as their GLC analysis in comparison with authentic samples.

GLC Analysis. Aromatic amines, including isomeric mixture, were determined by GC analysis using a Varian 3700 gas chromatograph equipped with a OV 101 coated-glass capillary column (50 m).

Acknowledgment. A. Mertens is thankful for financial support by a NATO grant. Support of our work by the National Institutes of Health and contribution to the theoretical calculations by Dr. M. Barzaghi are also gratefully acknowledged.

Registry No. 1, 86324-72-3; **2** (R = H), 71-43-2; **2** (R = CH_3), 108-88-3; **2** (R = 1,3,5-CH_3), 108-67-8; **2** (R = 1,2,3,4-CH_3), 488-23-3; **2** (R = Cl), 108-90-7; **2** (R = 1,4-CH_3), 106-42-3; **2** (R = OCH_3), 100-66-3; **2** (R = NO_2), 98-95-3; HN_3, 7782-79-8; CH_3N_3, 624-90-8; $C_2H_5N_3$, 871-31-8; $H_2NN_2{}^+$, 85990-23-4; $CH_3NHN_2{}^+$, 86324-71-2; $C_2H_5NHN_2{}^+$, 86324-73-4; NaN_3, 26628-22-8; $TMSN_3$, 4648-54-8; $AlCl_3$, 7446-70-0.

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