(15.8), 91.1 (59.9), 78.1 (37.9), 77.1 (23.6), 68.1 (11.1).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.37; H, 9.59.

Heptacyclo[5.5.1.1^{4,10}.0^{2,6}.0^{3,11}.0^{5,9}.0^{8,12}]tetradecane-13,14-bis(spiro-1′-cyclopentane) (3). A mixture of **1** (28.0 g, 19.1 mmol) and iron pentacarbonyl (9.38 g, 47.9 mmol) was heated with stirring under nitrogen atmosphere at 140 °C for 72 h. The reaction mixture was then allowed to cool slowly to room temperature, whereupon a solution of ferric trichloride hexahydrate (13.5 g, 50 mmol) in acetone (50 mL) was added. The resulting mixture was stirred at room temperature for 1 week to decompose any unreacted iron pentacarbonyl and Fe(0) complexes that might be present.[3,13] The resulting black mixture was diluted with brine (100 mL) and extracted with pentane (3 × 50 mL). The combined organic layers were then washed with brine (3 × 30 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo, affording a dark yellow oil. Recrystallization of this oil from acetone afforded a light yellow solid; this material was further purified by careful chromatography on silica gel (pentane eluent) to afford **3** (1.15 g, 41%) as a colorless microcrystalline solid: mp 115–116 °C; ^{1}H NMR (CDCl$_3$) δ 2.53 (s, 8 H), 2.01 (s, 4 H), 1.53 (s, 16 H); ^{13}C NMR (CDCl$_3$) δ 25.53 (t), 33.23 (t), 52.51 (d), 58.58 (d), 67.09 (s); IR (KBr) 2940 (s), 2850 (s), 1450 (m), 1370 cm^{-1} (m); mass spectrum (70 eV), m/e (relative intensity) 294.2 (3.0), 293.2 (24.1), 292.3 (M$^+$, 100.0), 264.3 (10.8), 263.2 (30.3), 250.3 (7.3), 197.2 (4.0), 184.1 (3.1), 183.1 (3.1), 169.2 (3.1), 159.1 (4.8), 155.1 (3.4), 145.2 (3.5), 143.1 (4.9), 131.1 (6.1), 117.1 (8.9), 91.1 (19.0), 67.0 (9.0).

Anal. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.26; H, 9.74.

Registry No. 1, 6572-54-9; 3, 94111-39-4; 4, 766-29-0; 5, 94111-36-1; 6, 94111-37-2; 7, 94111-38-3; Br-(CH$_2$)$_4$-Br, 110-52-1; H$_2$C=C(Cl)CN, 920-37-6; 1,3-cyclopentadiene, 542-92-7.

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1,3-Dipole Cycloaddition of Azides with Nitroso Compounds: ESR Studies

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Attention in the chemistry of organic azides continues to be strong because of their utilities for heterocycle synthesis and interests in the reaction mechanisms.[1] 1,3-Dipole cycloaddition of azides to carbon–carbon double[2] or triple[3] bonds and thiocarbonyl[4] and sulfoxide[5] groups is well known. However, there has been no report on the reaction of azides with the nitroso group. We describe here

the ESR studies of the reactions of organic azides with some nitroso compounds.

When a solution of trifluoromethanesulfonyl azide and 2-nitroso-2-methylpropane in benzene was degassed and placed in an ESR spectrometer at room temperature, a stable triplet and a stable triplet of quartet ESR signals were observed. The former signal was assigned as di-*tert*-butyl nitroxide radical (**1**) by its hyperfine splitting
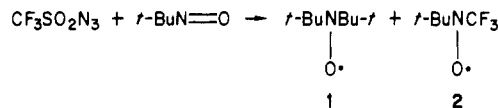
constants and g value (A_N = 15.6 G, g = 2.0060).[6] The latter one was assigned as *tert*-butyl trifluoromethyl nitroxide (**2**) based on the hyperfine splitting constants and g value (A_N = 12.1 G, A_F = 12.7 G, g = 2.0065). This observation shows that trifluoromethanesulfonyl azide reacts with 2-nitroso-2-methylpropane at room temperature and that the product formed by the reaction decomposes homolytically, giving trifluoromethyl and *tert*-butyl radicals, both of which are spin trapped by 2-nitroso-2-methylpropane. The 1,3-dipole reaction of trifluoromethanesulfonyl azide with 2-nitroso-2-methylpropane may form oxatetrazolidine **3** similar to the 1,3-dipole reactions of azide with the sulfoxide[5] or thiocarbonyl[4] group (Scheme I). The cycloadduct **3** will easily lose nitrous oxide at room temperature, affording *tert*-butylazo trifluoromethyl sulfone (**4**). Since azo sulfones homolytically cleave at the S–N bond,[7] **4** will cleave homolytically giving *tert*-butyldiazenyl radical **5** and trifluoromethanesulfonyl radical (**6**). The radicals **5** and **6** will easily release nitrogen and sulfur dioxide, affording *tert*-butyl radical and trifluoromethyl radicals, respectively. These two radicals are spin trapped by 2-nitroso-2-methylpropane to give nitroxide radicals **1** and **2**, both of which are detected by ESR. GC–mass spectral analysis of the gasous products of this reaction supported the reaction mechanism proposed in Scheme I. Two peaks observed by GC were determined
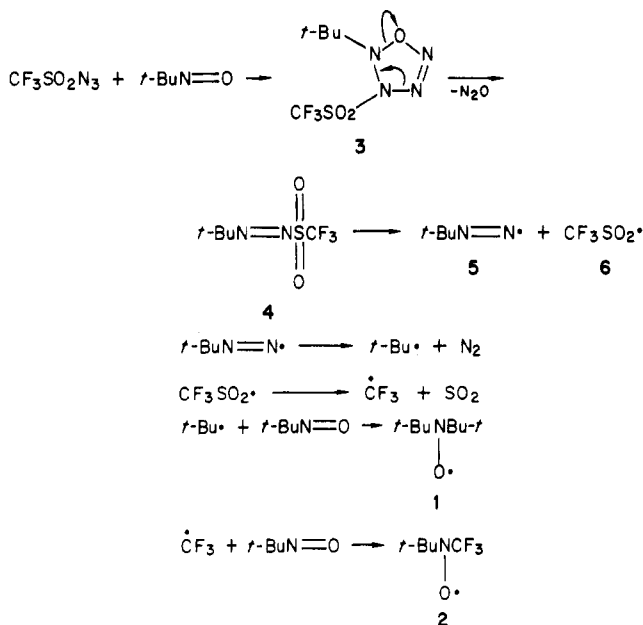
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Scheme I

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Table I. Hyperfine Splitting Constants^a and g Values of Nitroxide Radicals in the Reaction of Azide with 2-Nitroso-2-methylpropane and Nitrosobenzene in Benzene^b

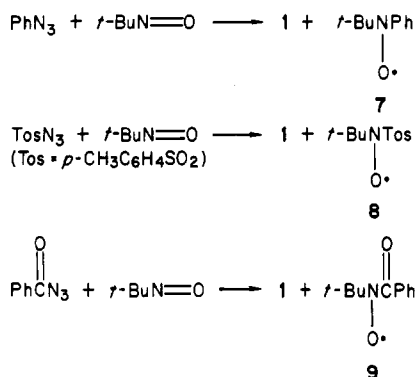| nitroxide radical	A_N	A_F	A_{H-N}	$A_{o,p\text{-}H}$	$A_{m\text{-}H}$	g
1	15.6					2.0060
1^c	15.3					2.0060
2	12.1	12.7				2.0065
7	12.3			2.0	0.9	2.0060
7^d	12.4			2.0	0.9	2.0060
8	12.4					2.0060
8^e	12.5					
9	7.67					
9^f	7.53			1.55	0.70	
10	9.7			1.9	0.9	2.0069
10^g	9.73			1.91	0.82	
11	11.4			1.8	0.9	2.0069
12	9.2		12.1	2.9	0.98	2.0058
12^h	9.13		12.12	3.07	0.98	
				2.74		
16	9.1			2.9	0.98	2.0058

^{a} In gauss at room temperature. ^{b} The solutions were degassed. ^{c} Reference 7. ^{d} Reference 8. ^{e} Reference 9. ^{f} Reference 10. ^{g} Reference 11. ^{h} Reference 12.

as nitrous oxide (M$^+$ = 44) and sulfur dioxide (M$^+$ = 64).

Similarly, phenyl, *p*-toluenesulfonyl, and benzoyl azide were reacted with 2-nitroso-2-methylpropane, and the ESR signals of *tert*-butyl phenyl nitroxide radical **7**, *tert*-butyl

$$PhN_3 + \text{\textit{t}-BuN}=O \longrightarrow 1 + \text{\textit{t}-BuNPh}$$

7

$$TosN_3 + \text{\textit{t}-BuN}=O \longrightarrow 1 + \text{\textit{t}-BuNTos}$$
$$(Tos = \text{\textit{p}-CH}_3C_6H_4SO_2)$$

8

$$PhCN_3 + \text{\textit{t}-BuN}=O \longrightarrow 1 + \text{\textit{t}-BuNCPh}$$

9

p-toluenesulfonyl nitroxide radical (**8**), and benzoyl *tert*-butyl nitroxide radical (**9**) were observed, respectively, in addition to the di-*tert*-butyl nitroxide radical (**1**). The hyperfine splitting constants and g values are summarized in Table I. The reaction seems to proceed by a similar mechanism as proposed in Scheme I.
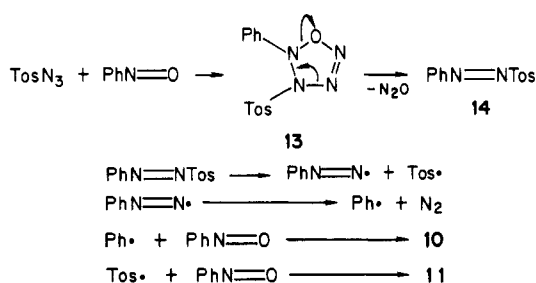
ESR studies of the reaction of azides with nitrosobenzene were also carried out. When a solution of tosyl azide and nitrosobenzene in benzene was degassed and placed in an ESR spectrometer at room temperature, ESR signals of diphenyl nitroxide radical (**10**), phenyl tosyl
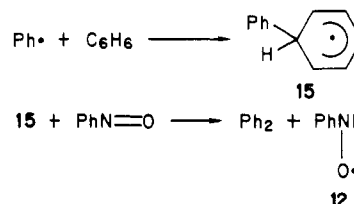
$$TosN_3 + PhN=O \longrightarrow PhNPh + PhNTos + PhNH$$

10   **11**   **12**
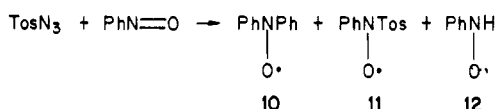
nitroxide radical (**11**), and phenyl nitroxide radical (**12**) were observed. The mechanism of the formation of radicals **10** and **11** will be similar to the reactions of azides with 2-nitroso-2-methylpropane (Scheme II). The cycloadduct **13**, formed by the 1,3-dipole reaction of tosyl azide with nitrosobenzene, loses nitrous oxide, giving phenylazo tolyl sulfone (**14**). Homolytic cleavage of **14** will afford phenyl radical and tosyl radical, both of which are trapped by nitrosobenzene to give **10** and **11**, respectively.

The formation of phenyl nitroxide radical (**12**) is quite interesting and may be accounted for by the following mechanism: Phenyl radical, formed according to the
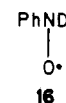
Scheme II

$$TosN_3 + PhN=O \longrightarrow 13 \xrightarrow[-N_2O]{} PhN=NTos$$
14

$$PhN=NTos \longrightarrow PhN=N\cdot + Tos\cdot$$
$$PhN=N\cdot \longrightarrow Ph\cdot + N_2$$
$$Ph\cdot + PhN=O \longrightarrow 10$$
$$Tos\cdot + PhN=O \longrightarrow 11$$

Scheme III

$$Ph\cdot + C_6H_6 \longrightarrow 15$$

$$15 + PhN=O \longrightarrow Ph_2 + PhNH\text{-}O\cdot$$
12

mechanism shown in Scheme II, attacks the solvent benzene, affording phenyl cyclohexadienyl radical (**15**). Nitrosobenzene oxidizes **15** to give biphenyl and phenyl nitroxide radical (**12**) as shown in Scheme III.

To confirm this mechanism, the reaction of tosyl azide with nitrosobenzene was carried out in hexadeuteriobenzene. The ESR signal of *N*-deuterio phenyl nitroxide radical (**16**) was observed with tht of **10** and **11**. This shows

$$PhND\text{-}O\cdot$$
16

that the N hydrogen of phenyl nitroxide raadical (**16**) comes from solvent benzene, and the mechanism shown in Scheme III is plausible. Biphenyl, the only stable product in the reaction of tosyl azide with nitrosobenzene, was detected by GC–MS; *m/z* 154 (M$^+$). The reaction of phenyl azide with nitrosobenzene in benzene solution afforded radicals **10** and **12**.

The sole issue of the mechanism shown in Schemes I and II is why azo sulfones **4** and **14** decompose so easily at room temperature in the present cases since they are known as fairly stable compounds (for example, according to our earlier work the half-life of **14** at room temperature is ~20 days[6]). We speculate that azo sulfones **4** and **14**, formed from the adduct **3** and **13**, respectively, are possessing the structure of the more labile cis form which decompose easily at room temperature.

Experimental Section

Materials. Trifluoromethanesulfonyl azide was prepared by adding dropwise 8.4 g of trifluoromethanesulfonyl chloride into a slurry of 4.2 g of sodium azide in 60 mL of acetonitrile with stirring at 0 °C. The mixture was stirred for additional 3 h. The oragnic layer was extracted with Decalin and the extract was washed with water and dried over with anhydrous magnesium sulfate. Careful distillation of the extract gave 6.8 g (78%) of trifluoromethanesulfonyl azide: bp 45 °C (350 mmHg) [lit.[13] 52.2

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°C (444 mmHg)]; IR (neat) 2150, 1420, 1220, 1160, 1130 cm⁻¹; MS, m/z 175 (M⁺). Phenyl azide,[14] *p*-toluenesulfonyl azide,[15] and benzoyl azide,[16] were prepared by the methods reported in the literature. 2-Nitroso-2-methylpropane[17] and nitrosobenzene[18] were also synthesized according to literature methods.

ESR Measurements. A solution of 20 mg of azide and 5 mg of 2-nitroso-2-methylpropane (or nitrosobenzene), in 2.0 mL of benzene in an ESR tube, was degassed and then placed in a JEOL JES-PE-3X ESR spectrometer. Strong ESR signals were observed at room temperature.

Identification of Gaseous Products by GC–Mass Spectrometry. To a degassed solution of 18 mg of 2-nitroso-2-methylpropane in 2.0 mL of benzene was added 18 mg of trifluoromethanesulfonyl azide by a microsyringe, and the solution was allowed to stand for 3 h at room temperature. The gasous product evolved was collected by a microsyringe and analyzed by GC–mass spectrometry using a JEOL JMS-DX 300 mass spectrometer. Two major peaks were observed by GLC (1-m column packed with silicone OV-1 on Chromosorb W); one product with shorter retention time peak (2 min) and m/z 44 (M⁺) was determined to be nitrous oxide and the other product with longer retention time peak (3 min) and m/z 64 (M⁺) was determined to be sulfur dioxide.

Registry No. 1, 2406-25-9; 2, 27695-72-3; 7, 3229-61-6; 8, 52168-44-2; 9, 35822-90-3; 10, 712-51-6; 11, 42467-30-1; 12, 3229-38-7; 16, 94042-44-1; CF₃SO₂N₃, 3855-45-6; PhN₃, 622-37-7; TosN₃, 941-55-9; PhCON₃, 582-61-6; *t*-BuNO, 917-95-3; PhNO, 586-96-9.

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Mechanistic Studies in the Deoxygenation of Pyridine *N*-Oxide: A New 1,2 Elimination

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Hexamethyldisilane, an isologue of hydrogen, possesses unique capabilities as a reagent for functional group transformations. It has been used extensively not only to prepare the trimethylsilyl anion[1] but also as a reducing agent[2] and as a source of halotrimethylsilanes.[3] Very recently, hexamethyldisilane was employed as a "counterattacking" reagent in a disproportionation reaction.[4]

We are interested in the mechanism of the reduction of pyridine *N*-oxides to pyridines with hexamethyldisilane. Although hexamethyldisilane does not react with pyridine *N*-oxide under pyrolytic conditions,[5] a successful conver-

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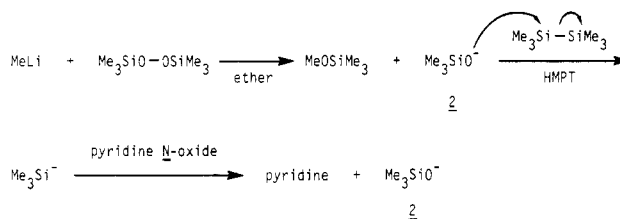
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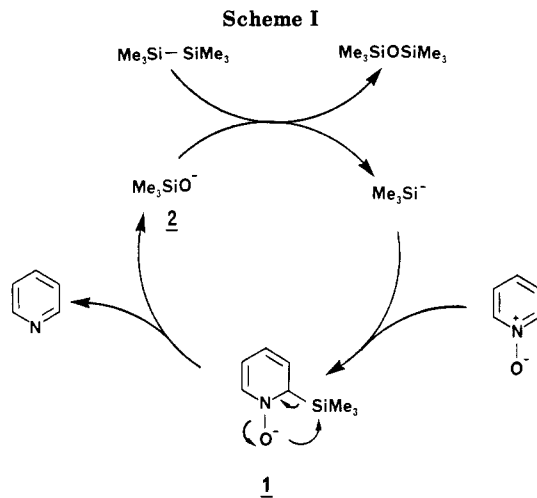
Scheme I

Scheme II

sion of the latter compound to pyridine in the presence of a catalytic amount of tetra-*n*-butylammonium fluoride (TBAF) in tetrahydrofuran (THF) has been reported by Vorbrüggen and Krolikiewicz.[6] We have also achieved this reduction, under different conditions ((trimethylsilyl)-lithium in hexamethylphosphoric triamide (HMPT)). Our data suggest a mechanism for the reaction in HMPT that is different from that proposed by the above authors for their reaction in THF. Our mechanism involves 1,2 elimination in a substrate containing an α-(trimethylsilyl) *N*-oxide moiety. Our findings are as follows.

Addition of pyridine *N*-oxide (1.0 equiv) to hexamethyldisilane (1.1 equiv) plus a catalytic amount (0.05 equiv) of (trimethylsilyl)lithium[1b] in HMPT at 0 °C, followed by warming to room temperature and stirring for 24 h gave a dark purple solution. After aqueous workup and purification, pyridine was obtained in 82% yield along with hexamethyldisiloxane. In a second experiment, pyridine *N*-oxide was added to excess (trimethylsilyl)-lithium in HMPT at 0 °C and the mixture was stirred at room temperature for 8 h. Pyridine was isolated in 86% yield. These results provide two pieces of mechanistic information: (1) The first reaction can only occur through a catalytic cycle. (2) The second reaction apparently involves spontaneous decomposition of α-trimethylsilyl *N*-oxide 1, formed by addition of trimethylsilyl anion (Me₃Si⁻) to pyridine *N*-oxide, to give pyridine and trimethylsiloxide ion (2). This can be inferred because no electrophilic silylating reagent was left in the reaction mixture when pyridine *N*-oxide was added. A mechanism that accounts for these findings is shown in Scheme I.

Completion of the cycle in Scheme I requires regeneration of trimethylsilyl anion from hexamethyldisilane and trimethylsiloxide ion (2). The feasibility of this step was proven by the following experiment. Reaction of MeLi (1.2 equiv) with bis(trimethylsilyl) peroxide[7] (1.2 equiv) in ether

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