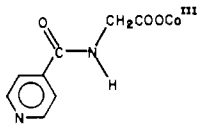
ring at N and C_γ and is presumed not to extend to the 4f orbital involved in electron transfer from Eu^{2+},[25,26] for the latter undergoes a sign inversion on passage through the same plane. On this basis, through-space interaction between the ring and metal center may be taken to assume a more significant role in the Eu(II) reactions, and the different attenuation patterns noted for the two reductants may thus be linked (albeit tentatively) to differences in the symmetry character of the donor orbitals.

Specific rates for reduction by V^{2+} (k_V values) do not appear to be enhanced by the ligands used in this study. This lack of response cannot be reasonably attributed to the limit on inner-sphere rates imposed by sluggish substitution at the V(II) center,[10,27] for a number of carboxylato derivatives of $(NH_3)_5Co^{III}$ have been found to exhibit k_V values several times those noted here.[14a,28] Instead, we suspect that the formal potential of V^{2+} ($E^\circ = -0.242$ V)[29] is not sufficiently negative to allow a significant degree of charge transfer to the pyridine ring, a condition presumably necessary for intervention of the proposed homoallylic intermediate.[30,31]

Registry No. II, 77482-19-0; III, 77482-22-5; IV, 77482-25-8; V, 77482-27-0; VI, 77482-30-5; pentaammine[4-carboxy-1-methylpyridiniumato(1−)-*O*]cobalt(3+) triperchlorate, 77482-31-6; Cr^{2+}, 22541-79-3; Eu^{2+}, 16910-54-6; V^{2+}, 15121-26-3.

(25) It is assumed here that the ligand environments about both Eu(II) and Eu(III) in our systems are approximately octahedral. The 4f orbital taken to be active in the electron transfer process is the antisymmetric f_{z^3} orbital.[26]
(26) See, for example: (a) H. G. Friedman, G. R. Choppin, and D. G. Feuerbacher, *J. Chem. Educ.*, **41**, 354 (1964); (b) M. K. Loar, M. A. Sens, G. W. Loar, and E. S. Gould, *Inorg. Chem.*, **17**, 330 (1978).
(27) N. Sutin, *Acc. Chem. Res.*, **1**, 225 (1968).
(28) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).
(29) (a) Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **16**, 2516 (1977); (b) G. Jones and J. H. Colvin, *J. Am. Chem. Soc.*, **66**, 1573 (1944).
(30) A reviewer has directed our attention to the very low k_{Eu} value for complex VII (Table II), the only oxidant in this series with an amide function in the side chain. We suspect that this reflects the circumstance that this complex, like a large number of known N-alkylated amides,[31] exists preferentially as the trans conformer



XI

in which interaction between the pyridine ring and the carboxyl-bound reducing center is ruled out. Such a conformational preference would be expected to erode the proposed homoallylic route.
(31) See, for example, M. B. Robin, F. A. Bovey, and B. Basch, in "The Chemistry of the Amides", J. Zabicky, Ed., Wiley-Interscience, New York, 1970, p 1934.

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Symmetrical Cleavage and Some New Derivatives of Pyrazabole[1]

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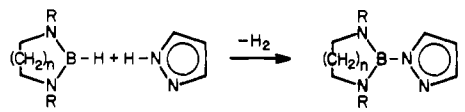
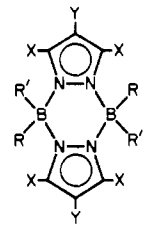
The B_2N_4 ring of pyrazabole as well as C-substituted pyrazaboles is symmetrically cleaved when boron-bonded hydrogen is replaced by strongly electron-donating amino substituents; monomeric pyrazol-1-ylboranes containing trigonal boron are obtained. However, hydrogen replacement by amino ligands of weak donor ability does not affect the pyrazabole structure. Similarly, boron-bonded organylthio groups lead to pyrazaboles in all cases.

Although a wide number of boron derivatives of pyrazole are known,[2] the first examples of monomeric pyrazol-1-ylboranes containing trigonal borons have only recently been prepared[3,4] by the condensation of 1,3-dimethyl-1,3,2-diazaboracycloalkanes with pyrazole according to the equation



I
$R = CH_3$; $n = 2, 3$

It was concluded that strong π interaction of the nitrogen atoms of the aliphatic diamine moiety in I, possibly enhanced by the virtual planarity of the BN_2C_n heterocycle,[5] results in electronic saturation of the boron and thus prevents the dimerization of I to form "pyrazabole" structures of type II, containing a B_2N_4 heterocycle.



II

On this basis it should be possible to symmetrically cleave the pyrazabole skeleton of II, R = R′ = H, by appropriate hydrogen displacement at the exocyclic boron sites. In order to test this hypothesis and to develop a second route for the preparation of monomeric pyrazol-1-ylboranes, we have investigated the reaction of pyrazabole (II, R = R′ = X = Y = H) and C-substituted derivatives thereof with selected amines. In further documentation of the dependence of the monomeric structure of pyrazol-1-ylboranes on the electronic

(1) Boron–Nitrogen Compounds. 90. For part 89 of this series see ref 4.
(2) "Gmelin Handbuch der Anorganischen Chemie"; Springer-Verlag: West Berlin, 1975; Vol. 23, Supplement Boron Compounds 5, pp 1–18.
(3) Niedenzu, K.; Weber, W. *J. Organomet. Chem.* **1980**, *195*, 25.
(4) Weber, W.; Niedenzu, K. *J. Organomet. Chem.* **1981**, *205*, 147.
(5) Niedenzu, K.; Miller, C. D. *Top. Curr. Chem.* **1970**, *15*, 191.

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nature of the additional boron substituents, several *B*-(organylthio) boron–pyrazole derivatives have been prepared and were found to be pyrazaboles in all cases.

Results and Discussion

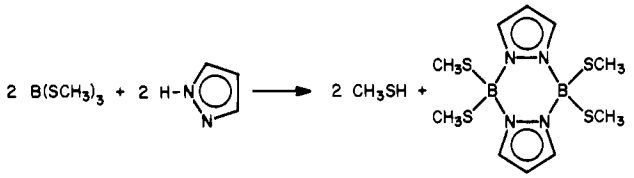
When pyrazabole is reacted with *N,N'*-dimethyl-1,2-diaminoethane or 1,3-diaminopropane, respectively, condensation occurs with simultaneous symmetrical cleavage of the pyrazabole skeleton to yield the monomeric pyrazol-1-ylboranes I. This result supports the assumption of strong π interaction between the nitrogen atoms of the aliphatic diamine moiety and the boron atom. The resultant electronic saturation of the latter is sufficient to promote symmetrical cleavage of the pyrazabole skeleton, and the monomeric species I containing trigonal boron are obtained.

If the preceding interpretation concerning the formation of monomeric pyrazol-1-ylboranes from pyrazabole is correct, one must assume that amines of lesser donor ability than that of the cited diamines should interact with pyrazabole to yield derivatives in which the B_2N_4 skeleton of pyrazabole is retained.

The N–B bond of pyrrol-1-ylboranes is considerably more reactive than that of other aminoboranes.[6,7] This is caused by the relatively high group electronegativity of the pyrrol-1-yl moiety, which results in a weak N–B bond. This weakness is exemplified by the shift of the N–B stretching mode of pyrrol-1-ylboranes to lower frequencies than normally encountered for aminoboranes.[6] Hence, the pyrrol-1-yl moiety may be considered as an amino group of relatively weak π-donor ability. Indeed, when pyrazabole is reacted with pyrrole, condensation occurs with the release of hydrogen. However, the pyrazabole skeleton is retained in the reaction product, and 4,4,8,8-tetrapyrrol-1-ylpyrazabole, II with R = R' = NC_4H_4 (X = Y = H), is obtained. This result tends to support the above hypothesis concerning the effect of boron substituents on the nature of the pyrazol-1-ylboranes and to confirm the weak π-donor ability of the pyrrol-1-yl group. Under these circumstances it is also not surprising that the only other previously known *B*-amino-substituted pyrazaboles, i.e., where the R and/or R' substituents in II constitute pyrazol-1-yl groups, exist only in the pyrazabole structure.[2]

The symmetrical cleavage of the pyrazabole skeleton is also realized when C-substituted species are employed in reactions as described above. Thus, the reaction of 2,6-dichloropyrazabole with *N,N'*-dimethyl-1,3-diaminopropane yields 1,3-dimethyl-2-(4-chloropyrazol-1-yl)-1,3,2-diazaboracyclohexane. The mass spectrum of the compound features peaks in the parent ion region, M/z 215–205, with M/z 212 being the base peak of the spectrum; no ions of higher mass are observed. Furthermore, the ^{11}B chemical shift δ = 24.3 illustrates the presence of three-coordinate boron, and the expected three ^{13}C resonance signals are observed for the pyrazole carbon atoms. Similarly, 1,2,3,5,6,7-hexabromopyrazabole reacts with *N,N'*-dimethyl-1,3-diaminopropane to yield 1,3-dimethyl-2-(3,4,5-tribromopyrazol-1-yl)-1,3,2-diazaboracyclohexane. Again, a parent ion cluster with the calculated isotopic distribution is observed in the region M/z 418–411 as the highest peak in the mass spectrum of the compound. The ^{11}B chemical shift datum, δ = 25.6, further confirms the monomeric nature of this latter pyrazol-1-ylborane.

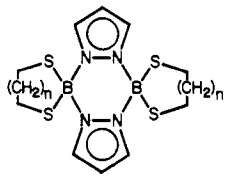
The electronic effect of the boron substituents on a Bpz moiety (pz = pyrazol-1-yl) is further documented by the synthesis of several *B*-(organylthio)pyrazaboles. The organylthio group is known to be a weak π donor and, therefore, $(RS)_2$Bpz species are expected to exist in a pyrazabole structure. Boron-bonded organylthio groups are readily displaced by a pyrazolyl group. For example, when equimolar quantities of $B(SCH_3)_3$, $B(SC_2H_5)_3$, or $C_6H_5B(SC_2H_5)_2$ are reacted with pyrazole at elevated temperatures and in inert solvents, the expected pyrazol-1-ylboranes are readily obtained in the dimeric pyrazabole form, e.g.



III

The resultant species of type II (X = Y = H) with R = R' = SCH_3, with R = R' = SC_2H_5, and with R = SC_2H_5 and R' = C_6H_5 are crystalline materials that are chemically quite stable. For example, they can be heated with methanol or ethanol without apparent decomposition. Also, when 4,4,8,8-tetrakis(methylthio)pyrazabole (III) is heated to reflux with excess pyrazole in toluene solution, no additional methylthio group displacement is observed. This is unusual inasmuch as the formation of a B–N bond by reaction of an (organylthio)borane with amine is a facile preparative procedure,[8] although some more recent studies illustrate the somewhat limited value of this method.[9] In any case, the four-coordination of the boron in a pyrazabole structure seems to reduce the reactivity of alkylthio groups bonded at the exocyclic boron sites.

Alternatively, *B*-(organylthio)pyrazaboles can be obtained by originating from a preformed pyrazabole skeleton. For example, reaction of $HS(CH_2)_nSH$ (n = 2, 3) with pyrazabole (I, R = R' = X = Y = H) provides for the desired species of type IV in which the boron is simultaneously incorporated into a CSB heterocyclic system.



IV
n = 2, 3

This event illustrates that incorporation of the boron into a second ring system does not prevent the existence of a pyrazabole skeleton. The structures of the *B*-(organylthio)-pyrazaboles are readily confirmed by the NMR data. Characteristic is the observation of only one ^1H and one ^{13}C resonance signal for the C^3 and C^5 atoms and their hydrogen atoms of the pyrazole rings and of the ^{11}B signal in the range of four-coordinate boron in all cases. Noteworthy is the accidental overlap of the resonance signals of the methylene carbon atoms of IV, n = 3, which was confirmed by signal integration. The mass spectral fragmentations of the various compounds are also in complete consonance with a pyrazabole structure.[10]

Although several *B*-(aryloxy)pyrazaboles are known,[2] the electronic effect of an organyloxy group bonded to a Bpz moiety has not yet been rigorously established. Condensations

(6) Szarvas, P.; Emri, J.; Győri, B. *Magy. Khem. Foly.* **1968**, *74*, 142.
(7) Köster, R.; Bellut, H.; Hattorie, S. *Liebigs Ann. Chem.* **1969**, *720*, 1.
(8) Niedenzu, K.; Dawson, J. W. "Boron-Nitrogen Compounds"; Springer-Verlag: West Berlin, 1965.
(9) Niedenzu, K.; Read, R. B.; Seelig, S. S. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 373.
(10) May, C. E.; Niedenzu, K.; Trofimenko, S. *Z. Naturforsch. B.: Anorg. Chem., Org. Chem.* **1976**, *31B*, 1662.

Table I. ^{13}C Chemical Shifts (δ) of Skeletal Carbon Atoms of the Pyrazole Groups in Pyrazaboles of Type II (X = Y = H)

R and R′	$\delta(C^{3,5})$	$\delta(C^4)$	$\Delta\delta$
$R = R' = C_3H_7$	133.4	105.7	27.7
$R = R' = C_4H_9$	133.5	106.1	27.4
R = R′ = H	134.9	105.4	29.5
$R = R' = C_6H_5$	137.5	105.5	32.0
$R = R' = OC_6H_5$	136.8	106.7	30.1
$R = C_6H_5$, $R' = SC_2H_5$	138.6	107.4	31.2
$R = C_6H_5$, $R' = C_3H_3N_2$	138.7	107.2	31.5
$R = R' = SCH_3$	138.7	108.2	30.5
$R + R' = S(CH_2)_2S$	138.5	106.9	31.6
$R = R' = SC_2H_5$	138.9	107.9	31.0
$R + R' = S(CH_2)_3S$	138.2	107.0	31.2
$R = R' = C_3H_3N_2$	139.0	107.8	31.2
$R = R' = NC_4H_4$	139.1	108.5	30.6

of pyrazabole with alcohols require sufficiently high reaction temperatures for additional processes to occur, and other preparative routes have to be developed.

It is of interest to note that the chemical shift difference $\Delta\delta = \delta(C^{3,5}) - \delta(C^4)$ of the pyrazole carbon atoms of pyrazaboles of type II where X = Y = H remains fairly constant with a value of approximately 30 ± 2 ppm, independent of the nature of the exocyclic boron substituents (see Table I). The $\Delta\delta$ values are, however, greatly affected by substitution at the carbon sites of the pyrazabole skeleton.[11]

Experimental Section

All reactions and transfers were carried out under an argon atmosphere. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY; all compounds gave satisfactory data. Melting points (uncorrected) were determined in sealed capillaries on a Mel-Temp block. Tris(methylthio)borane,[12] tris(ethylthio)borane,[9] bis(ethylthio)phenylborane,[9] and pyrazabole[13] were prepared by the indicated literature procedures; the last compound was recrystallized from anhydrous methanol. A variety of B-substituted pyrazaboles were made available by Dr. S. Trofimenko, E. I. Du Pont de Nemours & Co., Wilmington, DE. All other reagents were commercial products.

Mass spectral data were obtained from the University of Kentucky Mass Spectrometry Center. Unless otherwise noted, the spectra were recorded with the use of a Perkin-Elmer Hitachi RMU-7 mass spectrometer, operating at 70 eV and an inlet temperature of 180 °C. NMR spectra of the compounds were obtained on solutions in $CDCl_3$ or CD_2Cl_2 with the use of internal tetramethylsilane (^1H, recorded on a Varian T-60 and/or CFT-20 instrument), external $(C_2H_5)_2OBF_3$ (^{11}B, Varian FT80-A spectrometer), and internal Me_4Si (^{13}C, Varian CFT-20) as references. All chemical shift data are given in ppm with positive values indicating positions downfield from the reference; s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, and m = unresolved multiplet; an asterisk denotes a broad signal.

1,3-Dimethyl-2-(pyrazol-1-yl)-1,3,2-diazaboracyclopentane. A mixture of 80 g (50 mmol) of pyrazabole and 8.8 g (100 mmol) of *N,N′*-dimethyl-1,2-diaminoethane is heated to gentle reflux. Hydrogen is slowly released, and the reaction is stopped when the calculated amount has been given off (ca. 2 days). The material is purified by vacuum distillation to give 13.8 g (82%) of the desired compound: bp 108 °C (9 torr); mp 24–25 °C. NMR spectra were identical with those of the previously described[4] material.

1,3-Dimethyl-2-(pyrazol-1-yl)-1,3,2-diazaboracyclohexane. This compound is prepared in a fashion analogous to that described in the preceding experiment by reacting 8 g (50 mmol) of pyrazabole with 10.2 g (100 mmol) of *N,N′*-dimethyl-1,3-diaminopropane (reaction time ca. 2 days): yield 14.4 g (79%); bp 90 °C (2 torr). NMR spectra were identical with those of the previously described[3,4] material.

1,3-Dimethyl-2-(4-chloropyrazol-1-yl)-1,3,2-diazaboracyclohexane. This compound is prepared in a fashion analogous to that described above by reacting 9.2 g (40 mmol) of 2,6-dichloropyrazabole[14] with 8.2 g (80 mmol) of *N,N′*-dimethyl-1,3-diaminopropane for 20 h under gentle reflux. A yield of 14.1 g (83%) of the desired compound, bp 120–122 °C (7 torr) is obtained.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 8.00* (s, 1 H), 7.88* (s, 1 H), 3.43 (t, 4 H), 2.92 (s, 6 H), 2.38 (q, 2 H); $\delta(^{11}B)$ = 24.3; $\delta(^{13}C)$(proton decoupled) = 138.9, 130.1, 109.4, 47.7, 36.3, 25.3.

1,3-Dimethyl-2-(3,4,5-tribromopyrazol-1-yl)-1,3,2-diazaboracyclohexane. This compound is prepared in a fashion analogous to that described above by reacting 6.33 g (10 mmol) of 1,2,3,5,6,7-hexabromopyrazabole[14] with 2.24 g (22 mmol) of *N,N′*-dimethyl-1,3-diaminopropane for 2 days under gentle reflux. The resultant viscous material is purified by distillation at 10^{-4} torr and a bath temperature of 150 °C; yield 3.6 g (44%).

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 3.73 (t, 4 H), 3.02 (s, 6 H), 2.68 (q, 2 H); $\delta(^{11}B)$ = 25.6.

4,4,8,8-Tetrakis(pyrrol-1-yl)pyrazabole. In a procedure analogous to that described above a mixture of 16 g (100 mmol) of pyrazabole and 26.8 g (400 mmol) of pyrrole is refluxed for approximately 1 week. The resultant crude solid, melting near 250 °C, is obtained in essentially quantitative yield. A small amount was recrystallized from 1,1,2,2-tetrachloroethane to give colorless crystals, mp 261–262 °C dec, for analysis.

NMR data (solution in CD_2Cl_2): $\delta(^1H)$ = 7.69 (d, 2 H), $C^{3,5}$-bonded H of pyrazole), 6.68 (t, 1 H, C^4-bonded H of pyrazole), 6.22 (m, 4 H, NCH of pyrrole), 6.07 (m, 4 H, CCHC of pyrrole); $\delta(^{11}B)$ = 0.6; $\delta(^{13}C)$(proton decoupled) = 139.1 ($C^{3,5}$ of pyrazole), 123.0 ($C^{2,5}$ of pyrrole), 110.3 ($C^{3,4}$ of pyrrole), 108.5 (C^4 of pyrazole).

4,4,8,8-Tetrakis(methylthio)pyrazabole. A mixture of 36.60 g (240.6 mmol) of tris(methylthio)borane, 16.38 g (240.7 mmol) of pyrazole, and 150 mL of dry toluene is refluxed for approximately 15 h. The resultant clear liquid is cooled to room temperature, and a colorless precipitate is collected, washed with cold toluene, and dried under vacuum to yield 28.7 g (69.3%) of the desired compound, mp 184–188 °C. On concentration of the combined filtrate and washings, a second crop of material can be obtained for a total yield of 73%. The material can be recrystallized from benzene to yield colorless crystals, mp 191–192 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 8.42 (d, 2 H), 6.68 (t, 1 H), 1.63 (s, 6 H); $\delta(^{11}B)$ = 4.6; $\delta(^{13}C)$(proton-decoupled) = 138.7, 108.2, 10.5.

4,4,8,8-Tetrakis(ethylthio)pyrazabole. The compound is prepared in a fashion analogous to that described in the preceding experiment by reacting 20.40 g (105.1 mmol) of tris(ethylthio)borane with 7.15 g (105.1 mmol) of pyrazole. A total yield of 70% of the material, mp 106–107 °C, is obtained; the compound can be recrystallized from cyclohexane to yield colorless crystals, mp 116 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 8.39 (d, 2 H), 6.60 (t, 1 H), 2.07 (q, 4 H), 1.02 (t, 6 H); $\delta(^{11}B)$ = 4.3; $\delta(^{13}C)$(proton decoupled) = 138.9, 107.9, 22.1, 16.4.

4,8-Bis(ethylthio)-4,8-diphenylpyrazabole. The compound is prepared in a fashion analogous to that described above by reacting 43.20 g (205.6 mmol) of bis(ethylthio)phenylborane and 13.99 g (205.6 mmol) of pyrazole. A total yield of 72% of the material, mp 183–185 °C, is obtained; the compound can be recrystallized from cyclohexane/benzene (2:1 by volume) to give colorless crystals, mp 186 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 8.17 (d, 2 H), 7.11 (s, 5 H), 6.51 (t, 1 H), 1.91 (q, 2 H), 0.92 (t, 3 H); $\delta(^{11}B)$ = 4.1; $\delta(^{13}C)$(proton decoupled) = 138.6, 130.9, 127.5, 127.3, 107.4, 21.4, 16.6.

4,4,8,8-Bis(1,2-ethylenedithio)pyrazabole. A mixture of 15.98 g (100 mmol) of pyrazabole and 18.82 (200 mmol) of 1,2-ethanedithiol is heated (reflux condenser) in a bath of approximately 160 °C for 4 days, after which time the calculated quantity of hydrogen has been released. The reaction mixture solidifies on cooling to room temperature. After recrystallization from toluene, 21.8 g (64%) of the desired product, mp 211–214 °C, is obtained.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 8.48 (d, 2 H), 6.53 (t, 1 H), 3.20 (s, 4 H); $\delta(^{11}B)$ = 8.4; $\delta(^{13}C)$(proton decoupled) = 138.5, 106.9, 38.4.

4,4,8,8-Bis(1,3-propylenedithio)pyrazabole. The compound is prepared in a fashion analogous to that described in the preceding

(11) Seelig, S. S. M.S. Thesis, University of Kentucky, 1979.
(12) Mikhailov, B. M.; Bubnov, Y. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1964**, 1294.
(13) Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99.
(14) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3165.

experiment by reacting 15.98 g (100 mmol) of pyrazabole with 21.65 g (200 mmol) of 1,3-propanedithiol (bath temperature 180 °C; reaction time 8 days). The material is recrystallized from toluene to yield 19.2 g (52%) of the desired product, mp 202–207 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 8.45 (d, 2 H), 6.55 (t, 1 H), 2.77 (unresolved t, 4 H), 1.97 (p, 2 H); $\delta(^{11}B)$ = 4.5; $\delta(^{13}C)$(proton decoupled) = 138.2, 107.0, 24.7.

Registry No. I (R = CH_3; n = 2), 77172-65-7; I (R = CH_3; n = 3), 76356-55-3; II (R = R′ = C_3H_7; X = Y = H), 77189-78-7; II (R = R′ = C_4H_9; X = Y = H), 14695-77-3; II (R = R′ = X = Y = H), 16998-91-7; II (R = R′ = C_6H_5; X = Y = H), 6431-90-9; II (R = R′ = OC_6H_5; X = Y = H), 16243-64-4; II (R = C_6H_5; R′ = SC_2H_5; X = Y = H), 77210-78-7; II (R = C_6H_5; R′ = $C_3H_3N_2$; X = Y = H), 77255-14-2; II (R = R′ = SC_2H_5; X = Y = H), 77189-77-6; II (R = R′ = $C_3H_3N_2$; X = Y = H), 16243-58-6; II (R = R′ = NC_4H_4; X = Y = H), 77210-77-6; II (R = R′ = X = H; Y = Cl), 18601-55-3; II (R = R′ = H; X = Y = Br), 18601-63-3; III, 77189-81-2; IV (n = 2), 77189-80-1; IV (n = 3), 77189-79-8; 1,3-dimethyl-2-(4-chloropyrazol-1-yl)-1,3,2-diazaboracyclohexane, 77172-66-8; 1,3-dimethyl-2-(3,4,5-tribromopyrazol-1-yl)-1,3,2-diazaboracyclohexane, 77172-67-9; pyrazole, 288-13-1; $B(SCH_3)_3$, 997-49-9; $B(SC_2H_5)_3$, 998-26-5; $C_6H_5B(SC_2H_5)_2$, 1870-68-4; *N*,*N*′-dimethyl-1,2-diaminoethane, 110-70-3; *N*,*N*′-dimethyl-1,3-diaminopropane, 111-33-1; pyrrole, 109-97-7; 1,2-ethanedithiol, 540-63-6; 1,3-propanedithiol, 109-80-8.

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N-Substituted (*F*-Tetramethylene)sulfimides from Reactions of Lithium (*F*-Tetramethylene)sulfimide

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Lithium (*F*-tetramethylene)sulfimide, $\overline{CF_2CF_2CF_2CF_2S}$=NLi, is a moderately stable precursor to several new (*F*-tetramethylene)sulfimides. With $ClSi(CH_3)_3$, $ClC(O)CF_3$, ClCN, FSO_2CF_3, and FSO_2Cl, $\overline{CF_2CF_2CF_2CF_2S}$=$NSi(CH_3)_3$, $\overline{CF_2CF_2CF_2S}$=NC(=O)CF_3, $\overline{CF_2CF_2CF_2CF_2S}$=NCN, $\overline{CF_2CF_2CF_2CF_2S}$=$NSO_2CF_3$, and $\overline{CF_2CF_2CF_2CF_2S}$=$NSO_2Cl$ form. The bis[(*F*-tetramethylene)sulfimide], $\overline{CF_2CF_2CF_2CF_2S}$=NC(=O)N=$\overline{SCF_2CF_2CF_2CF_2}$, is formed with $COCl_2$. The reaction of FC(=O)C(=O)F with $\overline{CF_2CF_2CF_2CF_2S}$=NLi and $(CF_3)_2S$=NLi results in the formation of $\overline{CF_2CF_2CF_2S}$=NC(=O)C(=O)N=$\overline{SCF_2CF_2CF_2CF_2}$ and $(CF_3)_2S$=NC(=O)C(=O)N=$S(CF_3)_2$, respectively. While $\overline{CF_2CF_2CF_2CF_2S}$=$NSi(CH_3)_3$, $\overline{CF_2CF_2CF_2CF_2S}$=NC(=O)$CF_3$, and $\overline{CF_2CF_2CF_2CF_2S}$=$NSO_2Cl$ are nonvolatile liquids at 25 °C, the remainder of the N-substituted (*F*-tetramethylene)sulfimides are solids. With $(CF_3)_2C$=NF, $\overline{CF_2CF_2CF_2CF_2S}$=NLi gives the diazirine $(CF_3)_2C$—N=N.

Introduction

SF_4 reacts with NH_3 even at low temperature (−95 °C), giving rise to the formation of tetrasulfur tetrafluoride as the principal product.[2] By raising the reaction temperature to 25 °C, the formation of tetrasulfur tetranitride decreases with the concomitant increase in the formation of thiazyl fluoride. However, the isolation of the sulfimide, SF_2=NH, has been unsuccessful because of its instability with respect to NSF and HF at room temperature. However, its *N*-halogeno derivatives like SF_2=NCl[3] and SF_2=NBr[4] are well characterized.

Recently, it has been reported that bis(trifluoromethyl)-sulfimide, $(CF_3)_2S$=NH, forms when $(CF_3)_2SF_2$ is treated with NH_3 in the presence of benzylamine.[5] Furthermore, the lithium salt $(CF_3)_2S$=NLi, which is formed by the reaction of $(CF_3)_2S$=NH and *n*-BuLi, has been shown to be a valuable precursor to a large number of new compounds and interesting reactions.[6]

In an earlier paper, we demonstrated that $\overline{CF_2CF_2CF_2CF_2S}$=NH, in good yields when treated with $LiNH_2$ in the presence of NH_3.[7]

Now we will describe a modified method for the preparation of $(CF_3)_2S$=NLi, the first preparation of $\overline{CF_2CF_2CF_2CF_2S}$=NLi, and the reactions of $\overline{CF_2CF_2CF_2CF_2S}$=NLi to produce several new derivatives which contain the $\overline{CF_2CF_2CF_2CF_2S}$=N moiety.

Results and Discussion

It is known that the preparation of LiN=$S(CF_3)_2$ from the metalation of HN=$S(CF_3)_2$ is very difficult compared with that of LiN=$C(CF_3)_2$ because of the occurrence of side reactions.[6] A reddish black solid forms invariably unless $(CF_3)_2S$=NH is added in very small aliquots to the *n*-BuLi–hexane solution. (*F*-Tetramethylene)sulfimide, $\overline{CF_2CF_2CF_2CF_2S}$=NH, is converted to its lithium salt by reaction with *n*-BuLi–hexane solution in a similar manner. However, we have found that, if anhydrous ether is used as the solvent, when the sulfimide is added to *n*-BuLi–hexane solution, the metalation reaction proceeds very smoothly and the lithium salt is stabilized.

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