**Acknowledgment.** The financial support of this work by the Natural Sciences and Engineering Research Council of Canada, in the form of operating and equipment grants, is gratefully acknowledged.

**Registry No.** $Os(CN)_6^{4-}$, 19356-45-7; $Na^+$, 17341-25-2; $Li^+$, 17341-24-1; $K^+$, 24203-36-9; $NH_4^+$, 14798-03-9.

**Supplementary Material Available:** Tables of observed $^{13}C$ NMR line widths as a function of $[Os(CN)_6^{3-}]$, temperature, pH, cation concentration, and ionic strength (3 pages). Ordering information is given on any current masthead page.

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# Quantitative Preparations of 1,3,2-Dithiazolium, 1,3,2,4-Dithiadiazolium, and 1-Halo-1,2,4,3,5-trithiadiazolium Cations by the General, Symmetry-Allowed Cycloadditions of $SNSAsF_6$ with Alkynes, Nitriles, and Thiazyl Halides. Kinetics of Cycloadditions of the 1,3-Dipolar-like $SNS^+$ with Aliphatic and Aromatic Nitriles and Alkynes

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The dithionitronium cation ($SNS^+$) undergoes general, quantitative, thermally allowed cycloaddition reactions with alkynes (giving 1,3,2-dithiazolium salts), nitriles (giving 1,3,2,4-dithiadiazolium salts), and thiazyl halides (generated in situ, to give 1-halo-1,2,4,3,5-trithiadiazolium salts). When carried out in $SO_2$ solvent with $SNS^+$ as the $AsF_6^-$ salt, these cycloadditions give analytically and spectroscopically pure products in one step, which have been characterized by chemical analysis, NMR ($^1H$, $^{19}F$, $^{13}C$, $^{14}N$) and vibrational spectroscopy, melting point, and X-ray crystallography (published previously). The wide generality of these reactions is unusual in the context of sulfur-nitrogen chemistry. The rates of cycloadditions of $SNS^+$ to various alkynes and nitriles were systematically investigated, and lg (relative rate) was shown to be approximately porportional to −IP(triple bond). This is consistent with the results of MO calculations, which predict that the dominant orbital interaction during these cycloadditions is between the LUMO($SNS^+$) and the HOMO(triple bond), even for electrophilic alkynes and nitriles. Our rate/IP correlation for nitrile cycloaddition rates is quantitative, but for alkynes it is only qualitative. This is interpreted in terms of an asynchronous transition state in which steric effects are significant for alkynes but not nitriles. Surprisingly long $^1H$ longitudinal NMR relaxation times ($T_1$) were also determined for $H\overline{CSNSC}H^+$ (47 ± 7 s) and $CF_3\overline{CSNSC}H^+$ (63 ± 3 s) in $SO_2$ solvent.

## Introduction

Despite significant recent progress,[1] much of the chemistry of sulfur-nitrogen compounds is nonquantitative and poorly understood.[2] In contrast, we have shown that the $SNS^+$ (cf. $ONO^+$) cation (as the $AsF_6^-$ salt) undergoes quantitative, symmetry-allowed cycloaddition reactions with some alkynes ($CF_3CCCF_3$, HCCH, MeCCH),[3,4] nitriles (RCN, R = Me, tBu, $CF_3$, I),[3,5] alkenes (*E*-MeCHCHMe, $H_2CCH_2$),[6] and $SN^+$.[1f,g] We now show that quantitative cycloaddition reactions in fact occur with a very wide range of alkynes, nitriles, and thiazyl halides to give analytically and spectroscopically (IR, multinuclear NMR) pure materials (see Table I and II).[7] Cycloaddition of $SNS^+$ to alkynes and nitriles thus appears to be completely general and potentially extendable to other triply bonded systems (e.g. phosphaalkynes[8]). This is in contrast to other cycloadditions involving sulfur-nitrogen compounds, which usually possess less generality. For example, cycloadditions of $S_4N_4$ are restricted to strained alkenes[9] (e.g. norbornene) and $ClSNSCl^+$ [10] and $RR'\overline{CSNSC}RR'^+$ (R,R' = H,H and H,Me)[6] will cycloadd to some alkynes (HCCH, MeCCH), but there is no reaction with $CF_3CCCF_3$ or nitriles.[11]

We show that the reactions of RCN (R = Me, 2,5-$Me_2C_6H_3$, $C_6H_5$, 3,5-$(O_2N)_2C_6H_3$, *p*-$O_2NC_6H_4$) and $CF_3CCCF_3$ with $SNS^+$ are first order in both reactants, consistent with the proposed cycloadditions. In addition, we show that the logarithm of the second-order rate constants for a wide variety of alkynes and nitriles is approximately proportional to −IP of the triple bond. Within the context of Sustmann's classification of 1,3-dipolar cycloadditions[12] the reactions of $SNS^+$ are of "type III", in which

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**Table I.** Reaction Data for the Reactions of $SNSAsF_6$ with Compounds Containing Triple Bonds

| substrate (g, mmol) | amount<br>$SNSAsF_6$, g, mmol | <br>$SO_2$, g | apparent reacn time[a] | recovered product (g, mmol, %)[b] |
|---|---|---|---|---|
| $HCCCF_3$ (0.46, 4.86) | 1.19, 4.46 | 4.58 | <5 min | $H\overline{CSNSC}CF_3AsF_6$[c] (1.62, 4.50, 100) |
| $CF_3CCCF_3$ (1.73, 10.68) | 1.19, 4.46 | 5.88 | ~7 days | $CF_3\overline{CSNSC}CF_3AsF_6$[d] (1.80, 4.21, 95) |
| $(CH_3)_3SiCCSi(CH_3)_3$ (0.17, 1.02) | 0.28, 1.06 | 3.36 | 20 h | $(CH_3)_3Si\overline{CSNSC}Si(CH_3)_3AsF_6$[e] (0.45, 1.04, 100) |
| $CH_3CO_2CCCO_2CH_3$ (0.32, 2.26) | 0.63, 2.34 | 3.21 | <5 min | $CH_3CO_2\overline{CSNSC}CO_2CH_3AsF_6$[f] (0.91, 2.33, 95) |
| HCN (0.22, 8.23) | 0.55, 2.05 | 3.73 | <1 h | $H\overline{CSNSN}AsF_6$[g] (0.53, 1.90, 93) |
| ICN (0.98, 6.40) | 1.70, 6.40 | 11.21 | <1 h | $I\overline{CSNSN}AsF_6$[h] (2.38, 6.57, 89) |
| $(CH_3)_3CCN$ (0.33, 4.02) | 1.04, 3.88 | 6.29 | <1 h | $(CH_3)_3C\overline{CSNSN}AsF_6$[i] (1.20, 3.43, 89) |
| $CF_3CN$ (2.61, 27.44) | 2.66, 9.96 | 9.41 | ~14 days | $CF_3\overline{CSNSN}AsF_6$[j] (3.61, 9.96, 97) |
| HCCCN (1.20, 19.03) | 2.70, 10.11 | 28.83 | 20 h | $H\overline{CSNSC}CNAsF_6$[k] (3.19, 9.66, 96) |
| NSF (0.20, 3.02) | 0.81, 3.02 | 3.73 | <30 min | $F\overline{SSNSN}AsF_6$[l] (0.91, 2.75, 91) |
| NSCl (0.25, 3.09) | 0.82, 3.09 | 7.17 | ~24 h | $Cl\overline{SSNSN}AsF_6$[m] (1.04, 2.99, 97) |

[a] The apparent reaction times were inferred from the solution color changes and net mass changes in the reaction mixtures. [b] The recovered product was the combined yield of both the soluble crystals and the undissolved solid when the recrystallization solvent was $SO_2/SO_2ClF$. The % yields were calculated on the basis of $SNSAsF_6$ and eqs 1–3. [c] The product was recovered as a colorless crystalline solid by recrystallization from $SO_2/SO_2ClF$ (decomp pt 216 °C). Anal. Element (calcd, obsd): S (17.76, 17.68), N (3.88, 3.98), C (9.98, 10.04), H (0.12, 0.28). Infrared spectrum[n] [$cm^{-1}$ (relative intensity)]: 3067 (s), 1470 (s), 1382 (w), 1267 (vs), 1220 (vs), 1190 (vs), 1177 (vs), 1009 (s), 972 (w), 874 (m), 862 (m), 792 (s), 693 (vs), 574 (s), 394 (s). [d] The product was recovered as a colorless crystalline solid by recrystallization from $SO_2$ (decomp pt 230 °C). Anal. Element (calcd, obsd): S (14.95, 14.97), N (3.26, 2.79), C (11.40, 11.26). Infrared spectrum[n] [$cm^{-1}$ (relative intensity)]: 1504 (m), 1404 (w), 1371 (w), 1348 (w), 1299 (s), 1265 (s), 1195 (s), 993 (m), 963 (m), 779 (m), 694 (vs), 608 (w), 583 (w), 398 (s). [e] The product was recovered as a colorless crystalline solid by recrystallization from $SO_2/SO_2ClF$ (decomp pt 155 °C). Anal. Element (calcd, obsd): S (14.69, 15.39), N (3.20, 3.40), C (21.97, 22.31), H (4.15, 4.36). Infrared spectrum[n] [$cm^{-1}$ (relative intensity)]: 2970 (m), 1414 (m), 1375 (w), 1340 (m), 1258 (s), 1018 (m), 895 (s), 849 (vs), 790 (s), 759 (w), 696 (vs), 639 (m), 630 (m), 576 (m), 487 (m), 400 (vs). [f] The product was recovered as a colorless crystalline solid by recrystallization from $SO_2/SO_2ClF$ (mp 110 °C). Anal. Element (calcd, obsd): S (15.65, 15.61), N (3.42, 3.32), C (17.60, 18.35), H (1.49, 2.12). Infrared spectrum[n] [$cm^{-1}$ (relative intensity)]: 2955 (m), 1760 (vs), 1746 (vs), 1485 (s), 1450 (s), 1430 (s), 1260 (vs), 1130 (s), 1013 (m), 985 (m), 907 (s), 861 (s), 798 (s), 777 (m), 755 (m), 695 (vs), 579 (m), 397 (s). [g] The product was recovered as a colorless crystalline solid by recrystallization from $SO_2/SO_2ClF$ (decomp pt 223 °C). Anal. Element (calcd, obsd): S (21.80, 22.29), N (9.52, 9.95), C (4.08, 4.48), H (0.37, 0.35). Infrared spectrum[n] [$cm^{-1}$ (relative intensity)]: 3110 (m), 1405 (w), 1378 (w), 1350 (ms), 1219 (ms), 1010 (vw), 955 (w), 880 (w), 868 (w), 834 (m), 809 (m), 699 (vs), 580 (m), 510 (s), 394 (s). [h] The product was recovered as a yellow crystalline solid by recrystallization from $SO_2$ (mp 190 °C). Anal. Element (calcd, obsd): S (13.98, 15.27), N (6.71, 6.67). Infrared spectrum[n] [$cm^{-1}$ (relative intensity)]: 1328 (m), 1295 (sh), 1255 (sh), 1020 (w), 992 (w), 975 (ms), 885 (m), 875 (m), 845 (m), 783 (ms), 690 (vs), 649 (sh), 580 (m), 550 (w), 438 (ms), 390 (s). [i] The product was recovered as a colorless crystalline solid by recrystallization from $SO_2$ (decomp pt 100 °C). Anal. Element (calcd, obsd): S (18.07, 18.31), N (8.08, 8.00), C (17.08, 17.15), H (2.58, 2.59). Infrared spectrum[n] [$cm^{-1}$ (relative intensity)]: 2975 (s), 2865 (s), 1473 (s), 1458 (s), 1449 (m), 1415 (m), 1232 (w), 1058 (m), 1025 (m), 897 (m), 822 (w), 793 (ms), 700 (vs), 680 (sh), 602 (w), 597 (w), 583 (w), 527 (w), 459 (m), 401 (s). [j] The product was recovered as a noncrystalline white solid by recrystallization from $SO_2$ (mp 149 °C). Infrared spectrum[n] [$cm^{-1}$ (relative intensity)]: 1480 (s), 1437 (w), 1412 (w), 1356 (w), 1337 (w), 1286 (sh), 1278 (s), 1239 (sh), 1212 (s), 1051 (sh), 1033 (s), 1020 (sh), 985 (m), 933 (w), 872 (m), 803 (m), 787 (m), 695 (vs), 676 (sh), 597 (w), 583 (w), 463 (m), 396 (s), 368 (w). [k] The product was recovered as a colorless crystalline solid by recrystallization from $SO_2$. Anal. Element (calcd, obsd): S (20.16, 20.45), N (8.81, 8.76), C (11.33, 11.36), H (0.32, 0.37). Infrared spectrum [$cm^{-1}$ (relative intensity)]: 3084 (s), 1434 (s), 1274 (w), 1208 (ms), 1146 (w), 1095 (w), 984 (w), 985 (w), 882 (m), 845 (m), 835 (m), 780 (ms), 699 (vs), 576 (sh), 570 (ms), 483 (w), 456 (m), 429 (m), 394 (s). [l] The product was recovered as a red-black crystalline solid by recrystallization from $SO_2$. Infrared spectrum [$cm^{-1}$ (relative intensity)]: 1050 (w), 1018 (m), 983 (ms), 760 (sh), 693 (vs), 575 (ms), 496 (ms), 445 (w), 390 (s). An insoluble white solid was recovered from the bulb in which the NSF was generated. The white solid was shown to be $CsAsF_6$ (0.92 g, 2.87 mmol, 95%) by infrared spectroscopy. [m] The product was recovered as a partially crystalline yellow-brown solid by recrystallization from $SO_2$. Anal. Element (calcd, obsd): S (27.59, 26.89), N (8.04, 7.94), Cl (10.17, 9.97). Infrared spectrum [$cm^{-1}$ (relative intensity)]: 1018 (w), 946 (s), 893 (w), 758 (m), 698 (vs), 678 (sh), 572 (m), 536 (w), 526 (w), 481 (m), 450 (ms), 398 (s). [n] The original IR spectra of the products are included in the supplementary material (see Figure S1).

the rate of reaction is determined by the energy separation between the LUMO(1,3-dipole) and HOMO(dipolarophile). This regime corresponds closely to the reverse electron demand situations encounterd in Diels–Alder chemistry.[13] These observations are in accord with predictions made from molecular orbital calculations: the high electronegativity of S and N and the positive charge on $SNS^+$ result in its frontier molecular orbitals being of such low energy that type III cycloadditions are predicted for even the most electrophilic alkynes and nitriles. Similar behavior has been described for ozone, although studies on its reactions have been hampered by experimental difficulties.[14] In contrast, the kinetics of the clean, quantitative cycloadditions of $SNS^+$ were readily investigated and shown to be among the simplest of any 1,3-dipole-type species. A preliminary account of this work has been published.[15]

## Experimental Section

**Reagents and General Procedures.** Apparatus, techniques, and chemicals, unless specified, have been described.[16] Chemical analyses were determined by Bellor Mikroanalytisches Laboratorium or by the Analytical Services of the Department of Chemistry, Durham University, Durham, England.

$HCCCF_3$, $CF_3CCCF_3$, $(CH_3)_3SiCCSi(CH_3)_3$ (PCR Inc.), $CH_3CO_2CCCO_2CH_3$, $H_3CCCCH_3$, $(CH_3)_3CCN$ (Aldrich), and $CF_3CN$ (Fluorochem Ltd.) were used as received. $SNSAsF_6$,[17] HCN,[18] ICN,[19]

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**Table II.** NMR Spectral Data[a] for R$\overline{\text{CSNSC}}$R$'^{+}$ (**1**), R$\overline{\text{CSNSN}}^{+}$ (**2**), and X$\overline{\text{SSNSN}}^{+}$ (**3**)

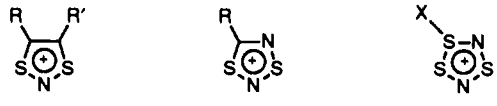
| compd | $^1$H NMR | $^{13}$C NMR[b] | $^{19}$F NMR[c] | $^{14}$N NMR[d] |
|---|---|---|---|---|
| **1a**[e] (R = R′ = H) | 10.6 | 170 ($C_r$) | | −5 (350) |
| **1b**[e] (R = H, R′ = $CH_3$) | 10.4 (H)[f]<br>3.1 ($CH_3$)[g] | 187 ($C_r'$)<br>167 ($C_r$)<br>13 ($CH_3$) | | −14 (350) |
| **1c** (R = H, R′ = $CF_3$) | 11.1[h] | 175 ($J_{C\text{-}F}$ = 43, $C_r$)<br>170 ($C_r$)<br>119 ($J_{C\text{-}F}$ = 277, $CF_3$) | −53 ($CF_3$)<br>−60 ($AsF_6^-$) | 0 (300) |
| **1d** (R = R′ = $CF_3$) | | 176 ($J_{C\text{-}F}$ = 46, $C_r$)<br>119 ($J_{C\text{-}F}$ = 280, $CF_3$) | −55 ($CF_3$)<br>−62 ($AsF_6^-$) | 3 (400) |
| **1e** (R = R′ = $(CH_3)_3Si$) | 0.7 | 194 ($C_r$)<br>0 ($CH_3$) | | −2 (400) |
| **1f** (R = R′ = $CO_2CH_3$) | 3.7 | 175 ($C_r$)<br>154 ($CO_2$)<br>56 ($CH_3$) | | 16 (1600)[i] |
| **1g** (R = H, R′ = CN) | 10.8 | 175 ($C_r$)<br>154 ($C_r'$)<br>105 (CN) | | 2 (500, SNS)<br>−79 (800, CN) |
| **1h** (R = R′ = $CH_3$) | 3.3 | 185 ($C_r$)<br>12 ($CH_3$) | | −31 (400) |
| **2a** (R = H) | 10.6 | 144 ($C_r$) | | −16 (350, N′)<br>25 (380, N″) |
| **2b** (R = I) | | 146 ($C_r$) | | −9 (550, N′)<br>37 (900, N″) |
| **2c**[e] (R = $CH_3$) | 1.9 | 208 ($C_r$)<br>18 ($CH_3$) | | −27 (500, N′)<br>126 (550, N″) |
| **2d** (R = $C(CH_3)_3$) | 1.9 | 223 ($C_r$)<br>42 ($C(CH_3)_3$)<br>30 ($CH_3$) | | −28 (580, N′)<br>28 (870, N″) |
| **2e** (R = $CF_3$) | | 193 ($J_{C\text{-}F}$ = 48, $C_r$)<br>118 ($J_{C\text{-}F}$ = 280, $CF_3$) | −58 ($CF_3$)<br>−57 ($AsF_6^-$) | −11 (290, N′)<br>32 (460, N″) |
| **2f** (R = $N(CH_3)_2$) | 3.5<br>3.6 | | | −17 (236, N′)<br>−101 (131, N″)<br>−266 (211, N‴) |
| **3a** (X = F) | | | 38.5 ($S_3N_2F^+$)<br>−58 ($AsF_6^-$) | −27 (350, N′)<br>−173 (370, N″) |
| **3b** (X = Cl) | | | | −40 (260, N′)<br>−176 (470, N″) |

[a] The NMR spectra (ppm) were acquired from $SO_2$ solutions in 5-mm ($^1$H, $^{13}$C, and $^{19}$F NMR) or 10-mm ($^{13}$C, $^{14}$N NMR) o.d. NMR tubes. All the observed resonances were singlets unless stated otherwise. The assignments were made on the basis of chemical shift, integration, and spin-coupling comparison with other compounds. [b] Proton-decoupled spectra, assignments based on chemical shift and signal intensity analysis. The coupling constants are given in Hz. [c] In all spectra the signal assigned to the $AsF_6^-$ anion was observed as a 1:1:1:1 quartet ($J_{As\text{-}F}$ = 950 Hz). [d] The assignments of the observed resonances were based on chemical shift, line width, and symmetry arguments given in ref 26. Some of these data were previously published in ref 1f. [e] The partial characterization of this compound by $^1$H NMR spectroscopy was initially reported in ref 3. However, the spectra were referenced with respect to TMS in $CDCl_3$ (not $SO_2$ as in this report), which accounts for differences in the reported chemical shift. [f] Quintet, $^4J_{HH}$ = 0.8 Hz. [g] Doublet, $^4J_{HH}$ = 0.8 Hz. [h] Quintet, $^4J_{HF}$ = 0.8 Hz. [i] The spectrum was recorded on a 360-MHz Nicolet spectrometer by Dr. D. Hooper of the Atlantic Magnetic Resonance Center, Dalhousie University.

NCCCH,[20] $(NSCl)_3$,[21] and NSF[22a] were prepared according to literature procedures. Infrared spectra were recorded as Nujol mulls (CsI or KBr windows) on a Perkin-Elmer Model 683 spectrometer. Raman spectra were recorded at the Department of Chemistry, Technical University of Berlin, Berlin, Germany, on a Jobin-Yvon U1000 spectrometer with a Spectra Physics Krypton laser (6471-Å exciting line) and slit width 10 cm$^{-1}$. NMR spectra were recorded at room temperature on a Varian Associates XL-200 instrument operating at 200 MHz ($^1$H), 188.15 MHz ($^{19}$F), 50.29 MHz ($^{13}$C), and 14.45 MHz ($^{14}$N). Chemical shifts were externally referenced to $Si(CH_3)_4$ ($^1$H and $^{13}$C), $CCl_3F$ ($^{19}$F) (in $SO_2$), or neat $CH_3NO_2$ ($^{14}$N), high-frequency direction positive. Unless otherwise specified NMR acquisition parameters were the same as described in ref 10. Melting points were uncorrected.

**Reactions of $SNSAsF_6$ with Triply Bonded Molecules.** Dithionitronium hexafluoroarsenate, $SNSAsF_6$, was reacted with alkynes $HCCCF_3$, $CF_3CCCF_3$, $(CH_3)_3SiCCSi(CH_3)_3$, and $CH_3CO_2CCCO_2CH_3$, nitriles (HCN, ICN, $(CH_3)_3CCN$, $CF_3CN$, $(CH_3)_2NCN$), and thiazyl halides (XSN, X = F, Cl). The reactions were carried out in $SO_2$ in Pyrex, two-bulbed vessels fitted with J. Young Teflon in glass valves. The experimental details, color changes and results of the reactions are given in Table I.

**Chart I**



| 1 | 2 | 3 |
|---|---|---|
| R/R′ | R | X |
| **a**, H/H | **a**, H | **a**, F |
| **b**, H/$CH_3$ | **b**, I | **b**, Cl |
| **c**, H/$CF_3$ | **c**, $CH_3$ | |
| **d**, $CF_3$/$CF_3$ | **d**, tBu | |
| **e**, $SiMe_3$/$SiMe_3$ | **e**, $CF_3$ | |
| **f**, $CO_2CH_3$/$CO_2CH_3$ | **f**, $N(CH_3)_2$ | |
| **g**, H/CN | | |
| **h**, $CH_3$/$CH_3$ | | |

In a typical reaction an excess of the compound containing the triple bond was condensed onto a frozen solution of $SNSAsF_6$ completely dissolved in $SO_2$ (see eqs 1–3; structures are given in Chart I). For

$$SNSAsF_6 + RCCR' \rightarrow \mathbf{1}AsF_6 \qquad (1)$$

$$SNSAsF_6 + RCN \rightarrow \mathbf{2}AsF_6 \qquad (2)$$

$$SNSAsF_6 + \text{“XSN”} \rightarrow \mathbf{3}AsF_6 \qquad (3)$$

nonvolatile compounds ($(CH_3)_3SiCCSi(CH_3)_3$, $CH_3CO_2CCCO_2CH_3$, ICN) a stoichiometric amount of the triply bonded substrate was placed into the second bulb of the reaction vessel and dissolved in $SO_2$, and then the solution washed at room temperature onto the solution of $SNSAsF_6$.

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Solutions of the thiazyl halides were generated in the second bulb of the reaction vessel by dissolving $(NSCl)_3$ in $SO_2$ (NSCl) or by the reaction of $SNAsF_6$ with CsF (NSF)[1f,22] (eq 4). The volatile materials (solvent

$$SNAsF_6 + CsF \rightarrow FSN + CsAsF_6 \qquad (4)$$

and excess substrate) were then removed by evacuation, and the solid product was recrystallized from $SO_2/SO_2ClF$ (1:3 w/w). The residue (if present) generally had IR and NMR spectra identical with those of the highly crystalline product. Products were characterized by melting point, elemental analysis, infrared spectroscopy and Raman spectroscopy in some cases (given in Table I), and NMR spectroscopy (given in Table II). In all cases when a ground sample of the product was exposed to moist air for 1 h, decomposition was observed (N–H, 3300 $cm^{-1}$, and S–O, 1200–1350 $cm^{-1}$, bands in the IR spectra).

**Reactions of $SNSAsF_6$ with Excess Alkyne and Nitrile Followed in Situ by $^1H$ and/or $^{19}F$ NMR Spectroscopy.** $SNSAsF_6$ (ca. 0.2 mmol) was reacted with $HCCCF_3$ (0.56 mmol), $CF_3CCCF_3$ (0.84 mmol), $CH_3CO_2CCCO_2CH_3$ (1.93 mmol), $CF_3CN$ (0.95 mmol), and $(CH_3)_3CCN$ (2.02 mmol) in $SO_2$ (ca. 0.56 g) in 5-mm o.d. NMR tubes fitted with J. Young Teflon in glass valves. $^1H$ and/or $^{19}F$ NMR spectra were acquired immediately, after 1 week, and then after 30 days. The $CF_3CCCF_3$ and $CF_3CN$ samples were heated to 70 °C for 24 h. The spectra showed only $^1H$ and $^{19}F$ peaks attributable to the cycloaddition products and starting materials.

**Determination of the Orders and Absolute Rate Constants of the Reactions of $SNSAsF_6$ with MeCN and $CF_3CCCF_3$.**[23] An aliquot of MeCN was condensed onto a frozen mixture of $SNSAsF_6$ (0.063 g, 0.23 mmol) and $CH_2Cl_2$ (0.018 g, 0.21 mmol) in $SO_2$ (0.923 g) in a 5-mm NMR tube, which was then flame-sealed. The mixture was warmed quickly to room temperature, and $^1H$ NMR spectra were recorded as a function of time. In a similar experiment the $^{19}F$ NMR spectra of a reaction mixture containing $CF_3CCCF_3$, $SNSAsF_6$ (0.035 g, 0.13 mmol), and $CFCl_3$ (0.072 g, 0.52 mmol) in $SO_2$ (0.899 g) were similarly recorded. A slight modification was necessary in the case of the nonvolatile phenyl-substituted nitriles. A preweighed quantity of $SO_2$ (0.866 g) was condensed onto a mixture of $SNSAsF_6$ (0.016 g, 0.16 mmol) and PhCN (0.028 g, 0.11 mmol) in a 5-mm NMR tube at −196 °C. The tube was then flame-sealed, and NMR spectra were acquired as detailed above. Similar experiments were performed for the reactions 2,5-$Me_2C_6H_3CN$ (0.024 g, 0.19 mmol), *p*-$NO_2C_6H_4CN$ (0.022 g, 0.15 mmol), and 3,5-$(NO_2)_2C_6H_3CN$ (0.024 g, 0.12 mmol) with $SNSAsF_6$ (0.033 g (0.12 mmol), 0.033 g (0.12 mmol), and 0.038 g (0.14 mmol), respectively) in $SO_2$ (0.869 g, 0.823 g, and 0.840 g, respectively).

The raw results (tables of NMR integrations) from these experiments have been deposited as supplementary material. The variation of lg $([X]/[SNS^+])$ (X is the alkene or nitrile) against time (in seconds) was linear in all cases,[23] with gradients (in $s^{-1}$) of $(1.32 \pm 0.07) \times 10^{-3}$ (MeCN), $(4.49 \pm 0.01) \times 10^{-4}$ ($CF_3CCCF_3$), $(1.61 \pm 0.04) \times 10^{-4}$ (2,5-$Me_2C_6H_3CN$), $5.9 \pm 0.2) \times 10^{-3}$ (PhCN), $(2.26 \pm 0.04) \times 10^{-4}$ (*p*-$O_2NC_6H_4CN$), and $(1.84 \pm 0.06) \times 10^{-3}$ (3,5-$(NO_2)_2C_6H_3CN$).

**Determination of Relative Rate Constants for the Cycloadditions of $SNSAsF_6$ with Various Alkynes and Nitriles.** A solution of MeCN (0.016 g, 0.40 mmol) and tBuCN (0.036 g, 0.44 mmol) in $SO_2$ (1.509 g) was poured into a 5-mm NMR tube containing $SNSAsF_6$ (0.089 g, 0.34 mmol) held at −196 °C. The solution froze on contact, and the NMR tube was flame-sealed. The solution was allowed to stand at room temperature for 2 days, after which the $^1H$ NMR spectrum was recorded. The NMR integrations were then used to determine the relative rates of the MeCN (*k*(MeCN)) and tBuCN (*k*(tBuCN)) cycloadditions with $SNS^+$ by using the formula[24]

$$\frac{k(\text{MeCN})}{k(\text{tBuCN})} = \frac{\ln [I(\text{MeCN})/(I(\text{MeCN}) + I(\text{MeCNSNS}^+))]}{\ln [I(\text{tBuCN})/(I(\text{tBuCN}) + I(\text{tBuCNSNS}^+))]}$$

where *I*(MeCN) is the integration of the MeCN resonance, etc. Experiments for other pairs of nitriles or alkynes were performed according to a similar procedure, and the results are shown in Table III. (A table of the raw NMR integrations has been deposited as supplementary material.) N.B.: In samples containing species with protons directly bonded to $CSNSC^+$ rings, spectra were acquired by using a single 90° (13 μs) pulse, after allowing the sample to equilibrate with the $B_0$ field for at least 10 min.[25] This was in order to accommodate the long longitudinal relaxation times for protons in this environment (see below).

**Table III.** Results of Competitive Cycloaddition Rate Experiments

| reagent A | reagent B | $k_A/k_B$ |
|---|---|---|
| MeCN | tBuCN | 0.5 |
| $Me_2NCN$ | $MeO_2CCCCO_2Me$ | 3 |
| tBuCN | $Me_2NCN$ | 0.02 |
| $CF_3CCCF_3$ | $CF_3CN$ | 10 |
| $CF_3CCH$ | HCCH | 0.05 |
| $MeO_2CCCCO_2Me$ | HCCH | 0.3 |
| $Me_2NCN$ | HCCH | 1 |
| MeCCMe | HCCH | 0.3 |
| MeCCH | HCCH | 1 |
| HCCMe | $HCCCF_3$ | 20 |
| PhCCPh | HCCH | 20 |

**Determination of the Longitudinal Proton Relaxation Times for $HCSNSCH^+$ and $CF_3CSNSCH^+$ in $SO_2$ at Room Temperature.** Solutions of $HCSNSCHAsF_6$ and $CF_3CSNSCHAsF_6$ (both 0.19 M) in $SO_2$ were prepared in 5-mm NMR tubes. The longitudinal ($T_1$) relaxation times of the protons were then determined by using the inversion recovery method[26] with a calibrated 180° pulse (26 μs). All manipulations were performed by using Varian Associates software.[27]

**Molecular Orbital Calculations.** The electronic structures of $SNS^+$, HCCH, $HO_2CCCCO_2H$ (as a model for $MeO_2CCCCO_2Me$), $CF_3CCH$, $CF_3CCCF_3$, HCN, $CF_3CN$, and $H_2NCN$ (as a model for $Me_2NCN$) were calculated at the ab initio RHF/STO-3G level with the GAUSSIAN-86 suite of programs.[28] Experimental geometries were used throughout.[29]

## Results and Discussion

**Preparation and Characterization of the Cycloadducts 1 and 2.** We previously reported[3] the quantitative syntheses of **1a**,**b** and **2c**. We have given preliminary accounts of the preparations of **1d**,[4] **2c**, and **2d**.[30] In this paper we give a full account of the quantitative preparations of **1c–h** and **2a**,**b**,**d–f** and show that $SNS^+$ quantitatively cycloadds to alkynes and nitriles according to eqs 1 and 2. We will report the preparation and characterization of the products from the related $SNS^+$ reactions with simple aryl-containing nitriles and alkynes in a separate publication.[7] Reactions were followed in situ by $^1H$ and/or $^{19}F$ NMR spectroscopy (**1a–h**, **2c–f**), in some cases with an excess of organic reagent (**1d**,**f**, **2d**,**e**), or heated to 80 °C for 7 days (**1d**, **2e**). In all cases the only observed product was the 1:1 cycloadduct. The distinct color changes, weight changes (see Table I), clean multinuclear NMR spectra, infrared (and in some cases Raman) spectra, good elemental analyses, and sharp melting or decomposition points (see Table I) of reactions carried out in situ and of isolated products all show that the reactions are clean and quantitative. If side reactions do occur (e.g. competing hydrolysis of $SNSAsF_6$), they are of minimal importance. Thus, although alternative syntheses of certain derivatives of these cations have been described,[6,10,31] eqs 1 and 2 constitute the only general and quantitative routes available.

The NMR spectra of the cycloadducts showed substituent resonances at higher frequency than in the related reactant. The

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[24] Williamson, D. G.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 3668.

[25] Field–sample equilibrium occurs in a time $5T_1$. See ref 27.

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[29] Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, England, 1984 ($H_2NCN$, HCN, NCCN, $CF_3CN$, and HCCH). Shechan, W. F.; Schomaker, V. *J. Am. Chem. Soc.* **1952**, *74*, 4668 ($HCCCF_3$). Kveseth, K.; Siep, H. M.; Stolevick, R. *Acta Chem. Scand.* **1971**, *25*, 13 ($CF_3CCCF_3$). Dunitz, J. D.; Robertson, J. M. *J. Chem. Soc.* **1946**, 148 ($HO_2CCCCO_2H$). Reference 46 ($SNS^+$).

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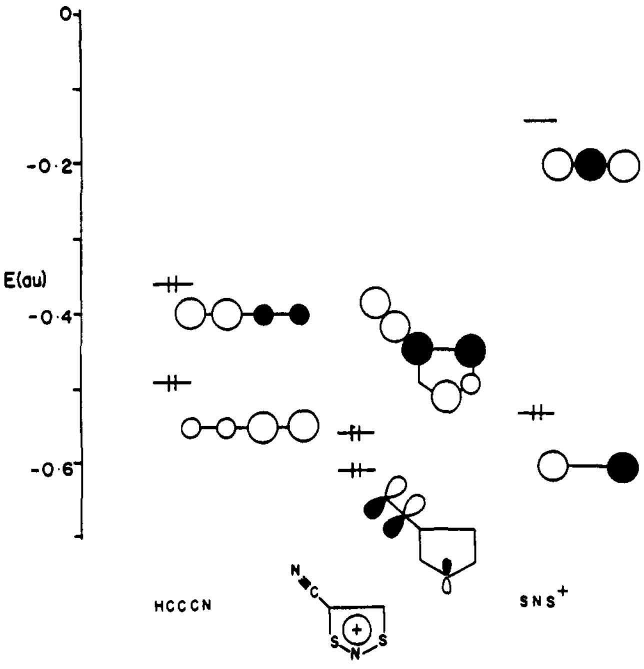

**Figure 1.** Comparison of the frontier molecular orbitals of HCCCN, **1g**, and $SNS^+$. Experimental geometries were used throughout.[15,30]

$^{19}F$ NMR[32] and vibrational spectra[33] showed the presence of the spectator ion $AsF_6^-$ and vibrations assignable to C–S stretches[3] and therefore rule out some alternative isomers of **1** and **2**. However, the nature of the rings is best established by a comparison of the $^{13}C$ and $^{14}N$ NMR chemical shifts of the ring atoms with those of cations for which the structure has been determined by X-ray crystallography, i.e. **1b**,[3] **1g**,[15] and **2c**.[3]

$^{13}C$ ring resonances in both **1** and **2** lie in the range 154–194 ppm (**1**) or 144–223 ppm (**2**), respectively, and all are in 90 ± 10 ppm to high frequency of the corresponding resonances in the alkyne and nitrile starting material. The $^{14}N$ chemical shift ranges of **1** (−31 to −16 ppm) and N′ in **2** ($\overline{RCN''SN'S}^+$) (−28 to −16 ppm) are also similar. Thus, both $^{13}C$ and $^{14}N$ chemical shifts reflect the similarity of the CSNS portion of the structures of both **1** and **2** cations. The $^{14}N'$ resonances in **2** are broader and occur over a wider chemical shift range than $^{14}N''$, reflecting a more pronounced substituent effect at this nucleus. The structures of the cationic rings are therefore reasonably established from the $^{13}C$ and $^{14}N$ data.[34]

**Preparation of 3 by the Reaction of $SNS^+$ with XSN (X = F, Cl) Prepared in Situ.** In order to explore the generality of cycloaddition reactions of $SNS^+$ with triple bonds, $SNSAsF_6$ was reacted with XSN [X = F, Cl] prepared in situ in liquid $SO_2$ (eq 3). The identity of the salts was established by elemental analyses (Table I), NMR spectroscopy (Table II), and comparison of their infrared spectra with those reported previously.[35]

NSF[1f,22a] was generated in situ according to eq 4, and NSCl was formed by dissolving impure $(NSCl)_3$ (mp = 75 °C) in $SO_2$. We have shown by $^{14}N$ NMR spectroscopy that solutions of impure $(NSCl)_3$ in $SO_2$ give >80% NSCl monomer.[1f] The generation of NSF via eq 4 has been shown to proceed in $SO_2$[22a] and tetramethylene sulfoxide.[22b] While this work was in progress, the reaction of NSF with $SNSAsF_6$ was reported independently by Mews,[35] confirming our results.

**Table IV.** Vertical Ionization Potentials and Rates of Cycloaddition to $SNS^+$ (Relative to MeCN) for Alkynes and Nitriles

| 1,3-dipolarophile | $k_{rel}$ | IP, eV | ref |
|---|---|---|---|
| $CF_3CN$ | 0.01 | 14.3 | 50 |
| $3,5\text{-}(O_2N)_2C_6H_3CN$ | 0.03 | 13.4 | 51 |
| $CF_3CCCF_3$ | 0.1 | 12.83 | 52 |
| $p\text{-}O_2NC_6H_4CN$ | 0.1 | 12.63 | 51 |
| MeCN | 1 | 12.2 | 53 |
| $C_6H_5CN$ | 2 | 12.09 | 51 |
| tBuCN | 2 | 12.11[a] | 52, 53 |
| $2,5\text{-}Me_2PhCN$ | 5 | 11.62 | 54 |
| $CF_3CCH$ | 5 | 12.12 | 52 |
| MeCCMe | 30 | 9.59 | 55 |
| $MeO_2CCCCO_2Me$ | 30 | 10.9 | 56 |
| MeCCH | 100 | 10.37 | 55 |
| $Me_2NCN$ | 100 | 9.44[b] | 37 |
| HCCH | 100 | 11.43 | 37, 57 |
| PhCCPh | 2000 | 7.91 | 58 |

[a] This is the IP of EtCN; that of tBuCN appears not to have been determined. [b] Ionization occurs principally from the amino lone pair. Ionization from the CN group occurs at 11.87 eV.

**Theoretical Aspects of the Cycloadditions of $SNS^+$ with Alkynes and Nitriles.** Frontier molecular orbital theory has been successfully employed in the analysis of cycloaddition reactions involving sulfur–nitrogen compounds,[1b,e] and this approach affords a simple explanation of the observed reactions between $SNS^+$ and alkynes and nitriles.

With the aim of rationalizing the cycloaddition reactions described in this paper, molecular orbital calculations were carried out on $SNS^+$ and some representative alkynes and nitriles (see above). The $\pi$ bonding in $SNS^+$ consists of two mutually perpendicular three-center/four-electron manifolds (see Figure 1) and is related to that found in the related 1,3-dipoles (e.g. nitrile oxides, ozone, etc).[12] In common with 1,3-dipoles the $\pi_n$ HOMO and $\pi^*$ LUMO of $SNS^+$ are of the correct symmetry to interact with the $\pi^*$ LUMO's and $\pi$ HOMO's of simple alkynes and nitriles.[12] Sustmann has classified 1,3-dipolar cycloadditions according to which interaction (HOMO(1,3-dipole)–LUMO(dipolarophile) or LUMO(1,3-dipole)–HOMO(dipolarophile)) dominates the reaction.[12] 1,3-Dipolar cycloadditions following the regime implied by our MO calculations are described as being "type III".

Most 1,3-dipolar reagents exhibit varying electron demand behavior over a range of substrates,[12] but the $\pi$ MO's of $SNS^+$ are of such low energy that type III cycloadditions are predicted even for the most electrophilic alkynes and nitriles. Such exclusive behavior is extremely unusual, and although similar effects have been described for ozone, studies on its reactions have been hampered by experimental difficulties.[14]

**Kinetic Aspects of $SNS^+$ Cycloadditions.** A characteristic of type III cycloadditions is that reaction rates are accelerated by electron-donating substituents on the dipolarophile,[12] which increase the energy of its HOMO. Decreasing the energy difference between HOMO(dipolarophile) and LUMO($SNS^+$) strengthens the interaction between these two orbitals, so that triply bonded species should cycloadd faster the lower their ionization potential. The kinetics of $SNS^+$ cycloadditions were investigated in order to test this hypothesis.

Initial experiments were carried out in which the reactions of $CF_3CCCF_3$ and RCN (R = Me, $2,5\text{-}Me_2C_6H_3$, $C_6H_5$, $p\text{-}(O_2N)C_6H_4$, $3,5\text{-}(O_2N)_2C_6H_3$) with $SNSAsF_6$ were monitored by $^{19}F$ or $^1H$ NMR spectroscopy as a function of time. The linear variation of $\lg \{[X]/[SNS^+]\}$ (X = triply bonded species) with time implied that all reactions were overall second order[23] (first order in X and $SNS^+$), consistent with the proposed cycloaddition. The second-order rate constants (in L $mol^{-1}$ $s^{-1}$) were $(3.8 \pm 0.1) \times 10^{-5}$ ($3,5\text{-}(O_2N)_2C_6H_3CN$), $(1.97 \pm 0.08) \times 10^{-4}$ ($CF_3CCCF_3$), $1.73 \pm 0.03) \times 10^{-4}$ ($p\text{-}(O_2N)C_6H_4CN$), $(1.49 \pm 0.01) \times 10^{-3}$ (MeCN), $(2.6 \pm 0.1) \times 10^{-3}$ ($C_6H_5CN$), and $(7.3 \pm 0.2) \times 10^{-3}$ ($2,5\text{-}Me_2C_6H_3CN$) and are seen to follow the trend predicted on

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(33) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley: New York, 1986.

(34) Corresponding neutral 7$\pi$ radicals are given on reduction of **1** and **2** in dilute solution, and the ESR spectra and parameters of these provide further evidence for the structures of the parent cations. (a) Reference 3 (**1•a,b, 2•c**). (b) Reference 4 (**1•e**). (c) Reference 5 (**2•b,c,e**). (d) Reference 11 (**1•c,e, 2•a**). (e) Reference 30 (**2•d**). (f) Preston, K. F.; Sutcliffe, L. H. *Magn. Reson. Chem.* **1990**, *28*, 189 (**1f**). (g) Passmore, J.; Schriver, M. J. To be published (**1g**).

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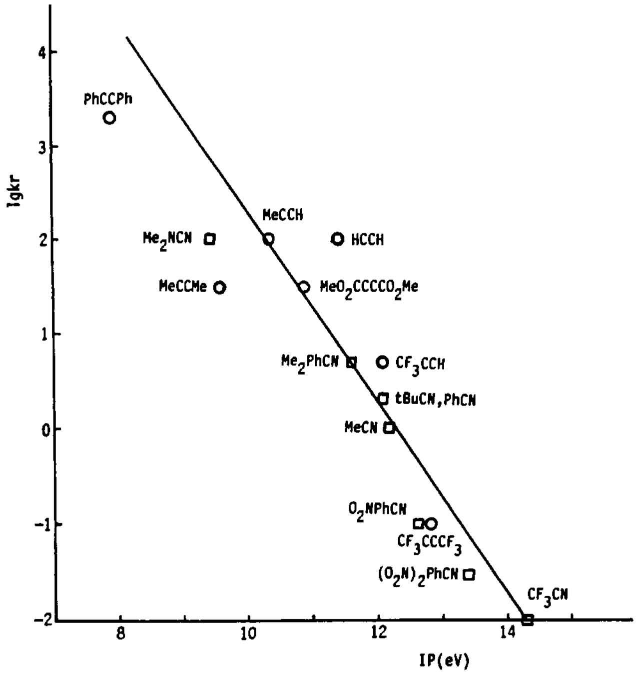

**Figure 2.** Plot of the common logarithm (base 10) of relative rates of the cycloadditions of nitriles (□) and alkynes (○) against ionization potential (eV).

the basis of type III behavior from the ionization potentials (see Table IV).

Relative rate constants ($k_{rel}$) were also obtained for a variety of pairs of nitriles and/or alkynes. Table IV shows the relative rates of cycloaddition of $SNS^+$ to alkynes and nitriles of differing ionization potential, and Figure 2 shows these data plotted as lg $k_{rel}$ versus IP (eV).[12] It should be noted that since NMR integrations are only reliable to ±5%,[26a] our relative rates are quoted to only one significant figure.

The plot of lg $k_{rel}$ against IP is almost linear, confirming the trend in cycloaddition rates anticipated on the basis of type III behavior. Apparent inconsistencies could arise from factors such as electrostatic effects, steric effects, in plane MO's, or the inductive effect on the orbital coefficients in the HOMO.[14] None of these are included in the simple frontier molecular orbital picture,[12,14] although they do appear in more rigorous (e.g. perturbational or ab initio)[14,36] models.

Separate analysis of the nitrile and alkyne data in Table IV can be used to probe the possible role of steric effects in these reactions. The correlation coefficient for the nitrile data alone is −0.97 and shows that steric effects have little or no effect in determining the rates of cycloaddition of nitriles to $SNS^+$ (note that even tBuCN adds faster than MeCN, implying pure electronic control). The most significant deviation from linearity is for $Me_2NCN$, which has an anomolously slow cycloaddition rate, which is likely due to the HOMO being comprised principally of the amino lone pair, with the main CN $\pi$ MO being at lower energy (11.87 eV).[37]

Although the rates of alkyne cycloadditions follow the trend anticipated from type III behavior, steric effects appear to be more significant, and the data no longer fall on a straight line. In particular the cycloaddition of $Me_3SiCCSiMe_3$ with $SNS^+$ yields **1e** quantitatively in a moderately fast reaction (apparent reaction time 20 h; see Table I), but which is much slower than would be anticipated from its IP (9.63 eV[38]). PhCCPh has the lowest IP (7.91 eV)[58] of the alkynes and nitriles studied in this work, and its cycloaddition with $SNS^+$ is by far the fastest that we have observed, with a rate 2000 times that of MeCN. This cycloaddition is nonetheless slightly slower than anticipated from the other data, which may be due to the steric effects of freely rotating phenyl groups and/or a reduced contribution from the acetylenic carbon AO's in the HOMO (resulting from delocalization effects). The differences between the alkyne and nitrile cycloadditions may be traced to nitriles being substituted on only one side of the triple bond, whereas alkynes are substituted on both sides. Thus, a nitrile can approach $SNS^+$ with its substituent pointing away from the center of reaction, whereas there will always be a steric interaction with the substituent of an alkyne, whatever the direction of its approach.

The exact nature of the transition state in 1,3-dipolar cycloadditions is one of the most controversial aspects of these reactions.[36] However, in the case of the nitrile cycloadditions at least, the unimportance of steric factors (see above) and their thermodynamic allowedness[39,40] imply a highly asynchronous, early transition state (the Hammond postulate).[41]

**Reaction of $SNS^+$ with HCCCN.** We illustrate the use of the FMO approach with the cycloadditions of $SNS^+$ with HCCCN. $SNS^+$ reacts with HCCCN at room temperature to give H-$CSNSCCN^+$ (**1g**) quantitatively. Reaction weights, multinuclear NMR, ESR (on the reduced product), and a crystal structure[15] all indicate that neither the alternative 1:1 cycloadduct, HCC-$CNSNS^+$, nor the dication $HCSNSCCNSNS^{2+}$ were formed. UV photoelectron spectroscopy shows that the ionizations from the CC and CN triple bonds in HCCCN occur at 11.60 and 14.03 eV, respectively.[42] The facile cycloaddition of $SNS^+$ to the CC triple bond in HCCCN is therefore completely in accord with the type III behavior described above. Since the HOMOs of **1g** are considerably lower in energy than those in HCCCN (see Figure 1), a further cycloaddition of $SNS^+$ to the cyano group in **1g** was predicted to be much less favorable. Accordingly, complete conversion of **1g**$AsF_6$ to $(SNSNC-CSNSCH)(AsF_6)_2$ by reaction with $SNSAsF_6$ in $SO_2$ was only observed after heating to 50 °C for 10 weeks (monitoring by $^{13}C$ NMR, $\delta$ 168.5, 172.8, 187.7 ppm).[15]

**Cycloaddition Reactions of $SNS^+$ with Thiazyl Halides.** The salts $XSNSNSAsF_6$ (X = F, Cl) can be prepared by the reaction of $SNSAsF_6$ with a mixture of CsF and $SNAsF_6$ in $SO_2$ (X = F) or $(NSCl)_3$ (X = Cl), which may be viewed as the cycloaddition of $SNS^+$ with XSN generated in situ. However, these reactions do not conform to the thermally allowed, type III cycloaddition regime discussed above, since both calculations and photoelectron

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(39) We estimate the enthalpies of reaction for the nitrile, alkyne and thiazyl halide cycloadditions to be −170, −260, and −340 kJ $mol^{-1}$, respectively. These data, which were estimated in a manner similar to that described in ref 40 for the hypothetical cycloaddition of $N_2$ and $SNS^+$, are minimum estimates and are therefore rounded off at −200 and −300 kJ $mol^{-1}$ for the nitrile and alkynes in the text. The reactions of $SNS^+$ with HCCH and HCN become hot on mixing, qualitatively confirming our estimations.

(40) Thermochemical effects are clearly very important because reactions will not proceed if endothermic. For example, the enthalpy change for the cycloaddition of $SNS^+$ to $N_2$ (which, though symmetry allowed, does not occur) can be estimated to be +200 kJ $mol^{-1}$ as follows: $\Delta H = U(SNSAsF_6) - U(NSNSNAsF_6) - BET(N{=}N) - 2BET(N{-}S) - 2BET(N{=}S) + BET(N{\equiv}N) + 2BET[(SN)_{S_2N^+}]$, with $U(SNSAsF_6)$ = lattice energy of $SNSAsF_6$ (576 kJ $mol^{-1}$, estimated[45] from the molar volume of $SNSAsF_6$[46]) and $U(NSNSNAsF_6)$ = 543 kJ $mol^{-1}$ (estimated). BET(N=N) = N=N bond enthalpy term (418 kJ $mol^{-1}$ [47]). BET(N≡N) = 942 kJ $mol^{-1}$. $BET(SN)_{S_2N^+}$ = bond enthalpy term of the SN bond in $SNS^+$ (441 kJ $mol^{-1}$ [48,49]). BET(S—N) and BET(S=N) are estimated to be 273 and 328 kJ $mol^{-1}$, respectively, from assumed S—N bond lengths in $NSNSN^+$ of 1.65 and 1.60 Å, and calculated on the basis of the linear dependence of BET(SN) with SN bond length.[49] We note that $\Delta H$ is likely to be slightly lower than estimated here because a resonance and charge delocalization term has not been included. We also note that reactions are carried out in solution rather than in the solid state.

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spectroscopy indicate that the HOMOs of XSN are lone pairs located on X (IPs 11.82 (X = F), 10.96 (X = Cl)), with the MOs responsible for SN $\pi$ bonding at much lower energy (PES data: HOMO-3 (13.50 eV, X = F), HOMO-4 (13.77 eV, X = Cl)).[43] Moreover, in spite of the high IPs of thiazyl halides, these reactions are relatively fast, with FSN > ClSN, contrary to the ordering expected on the basis of type III behavior.[12] This arguably implies type I (or normal electron demand) behavior in which the principal orbital interaction would be between $\pi^*(SNS^+)$ and $\pi(XSN)$. We have not investigated the kinetics of these reactions, and in light of the electronic structure of thiazyl halides it seems probable that they are more complicated than the simple picture presented here.

**Longitudinal Relaxation Times of the Ring Protons in H$\overline{\text{CSNSC}}$H$^+$ and CF$_3\overline{\text{CSNSC}}$H$^+$.** The longitudinal (spin–lattice or $T_1$) relaxation times were measured for the ring protons in H$\overline{\text{CSNSC}}$H$^+$ and CF$_3\overline{\text{CSNSC}}$H$^+$ in SO$_2$ at room temperature by the inversion recovery method.[26] Relaxation was found to be unusually slow, with $T_1$'s of 47 ± 7 s for H$\overline{\text{CSNSC}}$H$^+$ and 63 ± 3 s for CF$_3\overline{\text{CSNSC}}$H$^+$; 1–10 s is much more common, although values of up to 100 s have been recorded.[44]

The dipolar relaxation mechanism is usually thought to be dominant for protons in solution,[26] and the surprisingly long relaxation times in these two cations can be traced to their small size, which leads to a short correlation time, and the relatively large distances between the interacting nuclei.[26] The $T_1$ in H$\overline{\text{CSNSC}}$CF$_3^+$ is longer than in H$\overline{\text{CSNSC}}$H$^+$ because $\gamma(F) < \gamma(H)$, and $r(HH) < r(HF)$. Since $T_1^{-1}$ is a function of $r^{-6}$, the second of these is especially potent.[26]

## Conclusion

The generality and high yields of the cycloaddition reactions described in this paper make SNS$^+$ a very powerful reagent in the synthesis of S–N-containing heterocycles. Few other S–N reagents possess comparable generality in their reactions, and the chemistry described in this paper is almost certainly extendable to other unsaturated systems (e.g. phosphaalkynes[8]) and multiply unsaturated species (e.g. as in ref 15).

In addition, reduction of **1** and **2** leads to the corresponding 7$\pi$ radicals **1**$^\bullet$ and **2**$^\bullet$,[3-5] some of which (e.g. **1**$^\bullet$ (R = CF$_3$) and **2**$^\bullet$ (R = tBu)) can be isolated as pure paramagnetic liquids. Derivatives of **2**$^\bullet$ undergo rearrangement to the more thermodynamically more stable isomer R$\overline{\text{CNSSN}}^\bullet$. The systematic, quantitative syntheses of C–N–S ring systems and their reduction products potentially provide a powerful and general synthetic strategy to a wide range of novel materials (e.g. synthetic metals).

The experimentally measured rates of the reactions of SNS$^+$ with alkynes and (especially) nitriles conform closely to simple theoretical predictions and constitute a textbook example of the importance of orbital interactions in cycloaddition chemistry, as well as furnishing the simplest known reverse electron demand cycloadditions. As such, our results clearly have predictive value, both in determining the likely site of reaction in a multifunctional species and in assessing the suitability of potential substrates for SNS$^+$ cycloadditions.

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**Supplementary Material Available:** Tables S1–S7, listing NMR integrations for the kinetic analyses of the cycloadditions of SNS$^+$ with alkynes and nitriles, and Figure S1, showing IR spectra (13 pages). Ordering information is given on any current masthead page.

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