

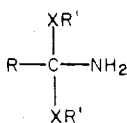
Reactions of 2-Amino-2-(trifluoromethyl)-1,3-dioxolane and -1,3-dithiolane with Some Electrophilic Agents

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2-Amino-2-(trifluoromethyl)-1,3-dioxolane and -1,3-dithiolane are perfluoroacetylated by perfluoroacetyl halides and trifluoroacetic anhydride to give the corresponding amides. Reaction of the 1,3-dioxolane with sulfur tetrafluoride in the presence of cesium fluoride affords (2-(trifluoromethyl)-1,3-dioxol-2-yl)iminosulfur difluoride and 2-(trifluoromethyl)- Δ^2 -oxazoline in an 83/17 ratio. The ratio is a function of the base used. With trimethylamine, the iminosulfur difluoride is obtained exclusively. Similarly, reaction of the 1,3-dithiolane with sulfur tetrafluoride in the presence of trimethylamine gives only (2-(trifluoromethyl)-1,3-dithiol-2-yl)iminosulfur difluoride.

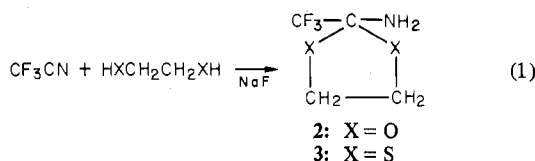
α,α -Bis(hetero)-substituted primary alkylamines (**1**) here-



1: X = O, S

before have not been explored.¹ Reactivities of the NH_2 group might be expected to vary with the nature of the hetero-function.

Our previous paper reported a route to 2-amino-2-(trifluoromethyl)-1,3-dioxolane (**2**) and 1,3-dithiolane (**3**) in which fluoride ion catalyzed the cyclization reactions of trifluoroacetonitrile with 1,2-ethanediol and 1,2-ethanedithiol (eq 1).²

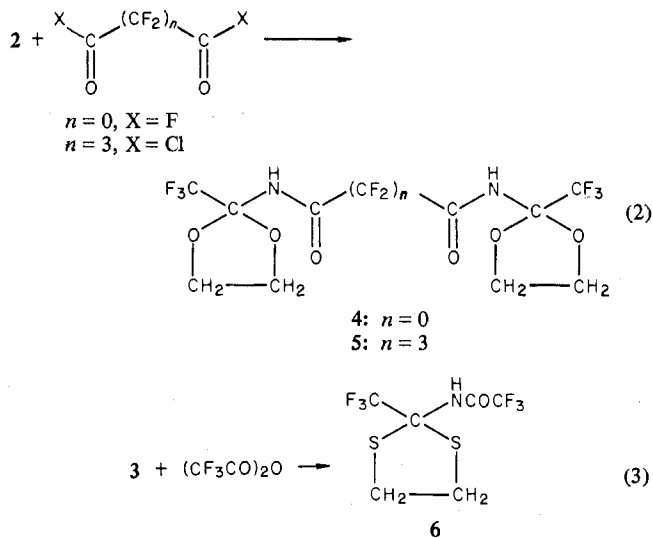


We now wish to report on the reactions of these amines **2** and **3** with some electrophiles such as acyl halides and sulfur tetrafluoride. Perfluoroacetylations of these amines **2** and **3** by perfluoroacetyl halides and trifluoroacetic anhydride easily proceeded to give the corresponding amides. Reaction of amine **2** with sulfur tetrafluoride afforded the ring opening and then closing product, 2-(trifluoromethyl)- Δ^2 -oxazoline (**8**), as well as the (2-(trifluoromethyl)-1,3-dioxol-2-yl)iminosulfur difluoride (**7**) expected. The ratio of these products depends on bases used. When trimethylamine was used, iminosulfur difluoride was obtained exclusively. Similarly, the reaction of amine **3** with sulfur tetrafluoride in the presence of trimethylamine gave only (2-(trifluoromethyl)-1,3-dithiol-2-yl)iminosulfur difluoride (**11**).

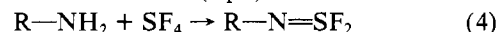
Results and Discussion

Perfluoroacetylations of amine **2** using oxalyl fluoride and hexafluoroglutaric chloride in the presence of trimethylamine were carried out. Both reactions proceeded exothermically to give *N,N'*-bis(2-(trifluoromethyl)-1,3-dioxol-2-yl)ethanediamide (**4**) and *N,N'*-bis(2-(trifluoromethyl)-1,3-dioxol-2-yl)hexafluoropentanediamide (**5**) in moderate yields, respectively (eq 2). Moreover, the similar reaction of amine **3** with trifluoroacetic anhydride afforded the stable *N*-(2-(trifluoromethyl)-1,3-dithiol-2-yl)trifluoroacetamide (**6**) in 75% yield (eq 3).

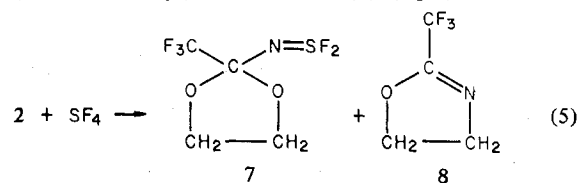
It is well-known that perfluoroisopropyl-,³ perfluorophenyl-,⁴



and methylamines⁵ react with sulfur tetrafluoride in the presence of bases such as metal fluorides and trialkylamines to give iminosulfur difluorides (eq 4).⁶



The reaction of amine **2** with excess sulfur tetrafluoride using cesium fluoride as base gave not only (2-(trifluoromethyl)-1,3-dioxol-2-yl)iminosulfur difluoride (**7**) expected but 2-(trifluoromethyl)- Δ^2 -oxazoline (**8**) (eq 5). The ¹⁹F



NMR spectrum indicated that the ratio of **7** and **8** is 83/17. Each component was separated successfully by a combination of trap-to-trap separation and gas chromatography. Iminosulfur difluoride **7** was identified by its spectral data and elemental analysis. The ¹⁹F NMR spectrum contains a peak at δ 59.1 due to the =SF₂ group.⁷ Similarly, the structure of oxazoline **8** was determined by its spectroscopic properties which are consistent with the literature values. Its IR spectrum shows a strong band at 1690 cm⁻¹ due to the carbon-nitrogen double bond,⁸ and its ¹H NMR spectrum indicates the very complex AA'BB' methylene peaks at δ 3.8-4.8.⁹ The similar reactions using less basic sodium fluoride and more basic trimethylamine were carried out. Table I gives the results of

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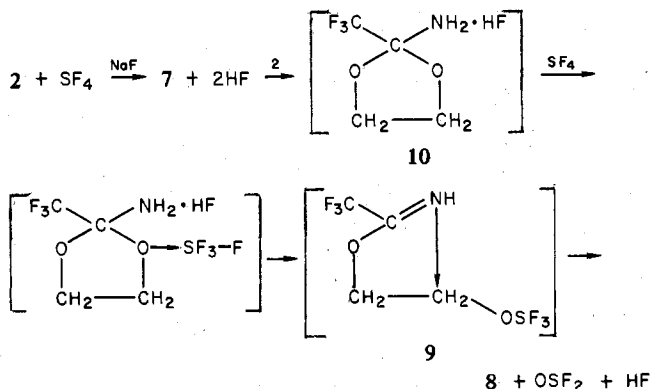
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Table I. Reactions of Amine 2 with Sulfur Tetrafluoride

base	yield, %		product ratio 7/8 ^a
	7	8	
NaF	36	31	54/46
CsF	67	14	83/17
(CH ₃) ₃ N	79	0	100/0

^a Determined by ¹⁹F NMR analysis of the reaction mixtures.

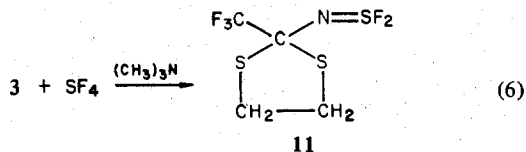
Scheme I



these reactions. It is particularly interesting in Table I that the reaction using trimethylamine gives exclusively 7, whereas the reaction using sodium fluoride affords a mixture of 7 and 8 in the ratio of ca. 1/1. Thus the formation of 8 is seen to be dependent on the basicity of the base used, increasing in the order of NaF > CsF > N(CH₃)₃.

The formation of oxazoline 8 can be explained in terms of cyclization of the ring-opening intermediate 9 formed via electrophilic attack of sulfur tetrafluoride at the dioxolane oxygen of the hydrogen fluoride salt 10 of 2. Salt 10 should be formed by hydrogen fluoride derived together with 7 (Scheme I). Thus the results that the formation of oxazoline 8 is observed when the weak bases like sodium fluoride are used can be reasonably rationalized by the fact that salt 10 is formed only when such weak bases are used.

The similar reaction of amine 3 with sulfur tetrafluoride in the presence of cesium fluoride afforded the tarry matter, the components of which showed six different trifluoromethyl groups. But the reaction in the presence of trimethylamine gave only (2-(trifluoromethyl)-1,3-dithiol-2-yl)iminosulfur difluoride (11) in 83% yield (eq 6). Difluoride 11 was similarly identified by its spectral data and elemental analysis.



Experimental Section

All gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus equipped with a Heise Bourdon tube gauge. All gaseous starting materials were measured quantitatively by PVT techniques. Amines 2 and 3 were prepared by following the procedures described in the previous paper.² Infrared spectra were recorded with either a Perkin-Elmer 599B or 457 spectrometer. ¹⁹F NMR spectra were obtained on a Varian HA-100 spectrometer by using CCl₃F as a standard. ¹H NMR spectra were measured on a Varian EM 360 with tetramethylsilane as an internal standard. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer operating at 17 eV. Elemental analyses were performed either in house or by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Reaction of Amine 2 with Oxalyl Fluoride. Into a Pyrex-glass vessel (50 mL) equipped with a Kontes stopcock which contained 590 mg (3.8 mmol) of 2 were condensed oxalyl fluoride (1.9 mmol) and

trimethylamine (20 mmol) at -196 °C. The reaction mixture was warmed at room temperature and stirred for 12 h. After the excess trimethylamine was pumped off, the mixture was washed several times by water to give 370 mg (53%) of amide 4. This crude solid was recrystallized from chloroform to give the pure amide 4, mp 186–188.5 °C. IR (KBr): 3400 (m), 2970 (w), 2925 (w), 1725 (s), 1498 (s), 1328 (s), 1182 (vs), 1155 (vs), 1052 (s), 1020 (m), 955 (m), 720 (vw), 600 (w), 540 (w), 495 (w), 440 (vw) cm⁻¹. Mass spectrum (*m/e*): M⁺, 368; M - CH₂O⁺, 338; M - CON⁺, 326; M - CF₃⁺, 299; M - (CONH)₂⁺, 282; C₂H₄O₂C(CF₃)NHCO⁺, 184; C₂H₄O₂C(CF₃)⁺, 141; C₂H₄O₂C(CF₂)⁺, 122; CF₃⁺, 69. ¹⁹F NMR (Me₂SO-*d*, external CCl₃F): ϕ -80.6 (s). ¹H NMR (Me₂SO-*d*): δ 3.3 (s, 2H); 4.2–4.5 (m, 8H). Anal. Calcd: C, 32.63; H, 2.74. Found: C, 32.50; H, 2.78.

Reaction of Amine 2 with Hexafluoroglutaric Chloride. A solution of amine 2 (1400 mg, 8.9 mmol) in dichloromethane (5 ml) was dropped into a solution of hexafluoroglutaric chloride (620 mg, 2.2 mmol) in dichloromethane (10 ml) at -10 °C. The reaction mixture was warmed to room temperature and stirred for 10 h. After the precipitated salt was filtered off, the solvent was evaporated under reduced pressure to leave a solid. This solid was washed with dilute aqueous hydrogen chloride solution and water to leave 790 mg (68%) of crude amide 5. The crude crystals were recrystallized from chloroform to give pure amide 5, mp 151.5–152.5 °C. IR (KBr): 3430 (s), 2980 (w), 2920 (w), 1750 (s), 1535 (s), 1520 (w), 1330 (s), 1300 (w), 1250–1110 (br, s), 1060 (s), 1015 (w), 990 (w), 948 (m), 890 (vw), 850 (vw), 830 (w), 790 (m), 746 (w), 720 (w), 705 (w), 660 (w), 620 (m), 555 (w), 530 (m), 500 (vw), 425 (m), 350 (w), 330 (vw) cm⁻¹. Mass spectrum (*m/e*): M⁺, 518; M - CONH⁺, 475; M - CF₃⁺, 449; M - CF₃C₂H₄O⁺, 405; M - CF₃C₃H₄O₂⁺, 377; M - CF₃C₃H₄O₂NCO⁺, 335; CF₃C₃H₄O₂⁺, 141; CF₃CO₂H, 114; CF₃⁺, 69. ¹⁹F NMR (Me₂SO-*d*, internal CCl₃F): ϕ -82.0 (s, 6F), -116.5 (s, 4F), -121.8 (s, 2F). ¹H NMR (Me₂SO-*d*): δ 3.8 (br s, 8H), 4.3 (s, 2H). Anal. Calcd: C, 30.14; H, 1.95. Found: C, 30.12; H, 2.03.

Trifluoroacetylation of Amine 3. A 1.56-g (8.3-mmol) sample of amine 3 was added to trifluoroacetic anhydride (10 mL) at -20 °C. The reaction mixture was warmed to room temperature and stirred for 5 h. To this mixture was added water, and the crystals which formed were collected. They were washed with water several times to give 1.76 g (75%) of the crude amide 6. This crude material was recrystallized from chloroform to afford the pure amide 6, mp 93.5–95.5 °C. IR (KBr): 3235 (m), 3060 (w), 2890 (vw), 1730 (s), 1545 (m), 1425 (vw), 1340 (vw), 1175 (vs), 950 (vw), 895 (m), 815 (w), 713 (w), 515 (w) cm⁻¹. Mass spectrum (*m/e*): M⁺, 285; M - CF₃⁺, 216; M - CF₃CONH⁺, 173; M - CF₃CONH₂, 172; CF₃CO-NH₂, 113; CF₃CO⁺, 97; CF₃⁺, 69. ¹⁹F NMR (CDCl₃, internal CCl₃F): ϕ -75.5 (s, 3F), -76.0 (s, 3F). ¹H NMR (CDCl₃): δ 3.1–4.0 (A₂B₂, 4H), 7.0 (br s, 1H). Anal. Calcd: C, 25.27; H, 1.77; N, 4.91. Found: C, 25.41; H, 1.69; N, 4.96.

Reaction of Amine 2 with Sulfur Tetrafluoride in the Presence of Cesium Fluoride. Sulfur tetrafluoride (7.8 mmol) was condensed into a 75-mL Hoke cylinder containing amine 2 (410 mg, 2.6 mmol) and anhydrous cesium fluoride (1520 mg, 10.0 mmol). The reaction mixture was warmed to room temperature and agitated for 10 h. A slightly volatile liquid (440 mg) was collected by removing the product under dynamic vacuum (10⁻² torr) at 20 °C after the excess sulfur tetrafluoride was pulled off at -78 °C. This liquid was a mixture of iminosulfur difluoride 7 (67%) and oxazoline 8 (14%) (¹⁹F NMR assay). Difluoride 7 was purified by pumping on the mixture at 0 °C to remove the oxazoline 8, and then collecting 7 by extended pumping at 20 °C. IR (film) of 7: 3000 (w), 2920 (w), 2020 (w), 1840 (w), 1478 (s), 1455 (s), 1375 (s), 1325 (vs), 1228 (vs), 1210 (vs), 1195 (vs), 1145 (vs), 1125 (s), 1072 (s), 1010 (m), 990 (s), 947 (m), 888 (w), 802 (w), 735 (m), 712 (s), 635 (m), 590 (w), 580 (w), 510 (w), 440 (w) cm⁻¹. Mass spectrum (*m/e*): M⁺, 225; M - HNSF⁺, 159; M - CF₃⁺, 156; M - NSF₂⁺, 141; M - NSFCH₂O⁺, 130; CONSF₂⁺, 112; C₂H₄O₂CF⁺, 91; CF₃⁺, 69; NSF⁺, 65. ¹⁹F NMR (neat, external CCl₃F): ϕ -85.3 (s, 3F), 59.1 (s, 2F). ¹H NMR (CDCl₃): δ 4.3 (br s). Anal. Calcd: C, 21.34; H, 1.79; N, 6.22. Found: C, 20.72; H, 2.04; N, 5.76.

Oxazoline 8 was purified by gas chromatography (OV 17, 90 °C). IR (film): 2980 (w), 2965 (w), 1690 (s), 1410 (s), 1340 (m), 1280 (m), 1200 (vs), 1160 (vs), 1125 (vs), 970 (w), 940 (w), 905 (m), 745 (w), 720 (w), 584 (w), 530 (w) cm⁻¹. Mass spectrum (*m/e*): M⁺, 139; M - CH⁺, 126; M - CH₂O⁺, 109; CF₃⁺, 69. ¹⁹F NMR (CCl₄,

external CCl_3F): ϕ -69.3 (s). ^1H NMR (CCl_4): δ 3.8-4.3 (AA', 2 H), 4.4-4.8 (BB', 2 H).

The similar reaction in the presence of sodium fluoride gave a mixture of **7** (36%) and **8** (31%) (^{19}F NMR assay).

The similar reaction in the presence of trimethylamine afforded only **7** in 79% yield.

Reaction of Amine 3 with Sulfur Tetrafluoride. Sulfur tetrafluoride (9.7 mmol) and trimethylamine (12.9 mmol) were condensed into the 75-mL Hoke cylinder containing amine **3** (610 mg, 3.2 mmol). The reaction mixture was warmed to room temperature and agitated for 10 h. The slightly volatile liquid was collected by removing the product under dynamic vacuum (10^{-2} torr) at 40 °C after the excess sulfur tetrafluoride and trimethylamine was pulled off at -78 °C. Trap-to-trap separation of this liquid at 33 °C gave the pure difluoride **11** (690 mg, 83%). IR (film): 2940 (w), 2030 (w), 1835 (w), 1422 (s), 1386 (s), 1281 (s), 1242 (s), 1227 (vs), 1197 (vs), 963 (m), 912 (m), 870 (w), 840 (m), 720 (m), 700 (s), 618 (m), 584 (w) cm^{-1} . Mass

spectrum (m/e): M^+ , 257; $\text{M} - \text{NSF}^+$, 192; $\text{M} - \text{NSF}_2^+$, 173; $\text{M} - \text{C}_3\text{H}_4\text{S}_2\text{F}^+$, 134; $\text{C}_3\text{H}_4\text{S}_2\text{F}^+$, 123; $\text{C}_2\text{H}_4\text{S}^+$, 60. ^{19}F NMR (neat, external CCl_3F): ϕ -75.5 (s, 3 F), 59.4 (s, 2 F). ^1H NMR (CDCl_3): δ 3.2-3.9 (A_2B_2). Anal. Calcd: C, 18.68; H, 1.57; N, 5.45. Found: C, 18.51; H, 1.49; N, 5.25

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Registry No. **2**, 70247-62-0; **3**, 70247-65-3; **4**, 74007-42-4; **5**, 74036-85-4; **6**, 74007-43-5; **7**, 74007-44-6; **8**, 4368-72-3; **11**, 74007-45-7; SF_4 , 7783-60-0; FCOCOF , 359-40-0; $\text{ClCO}(\text{CF}_2)_2\text{COCl}$, 678-77-3; $(\text{CF}_3\text{CO})_2\text{O}$, 407-25-0.

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

New Seven-Coordinate Mixed Phosphine-Alkyl Isocyanide Complexes of Molybdenum(II) Obtained from the Reactions of Phosphine Dimers of the Type $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ and the $[\text{Mo}(\text{CNR})_7]^{2+}$ Cations

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The reactions of the tertiary phosphine complexes $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$, $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$, and $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$, where dppm = bis(diphenylphosphino)methane and dppe = 1,2-bis(diphenylphosphino)ethane, with alkyl isocyanides RNC , where R = CH_3 , $\text{C}(\text{CH}_3)_3$, or C_6H_{11} , lead to the cleavage of the Mo-Mo quadruple bonds and the formation of the following cations: $[\text{Mo}(\text{CNR})_5(\text{dppm})]^{2+}$, $[\text{Mo}(\text{CNR})_5(\text{dppe})]^{2+}$, $[\text{Mo}(\text{CNR})_5(\text{PR}_3)_2]^{2+}$, and $[\text{Mo}(\text{CNR})_6(\text{PR}_3)]^{2+}$. These can all be isolated as their PF_6^- salts. These same products are formed upon reaction of the homoleptic seven-coordinate complexes $[\text{Mo}(\text{CNR})_7](\text{PF}_6)_2$ with the appropriate phosphines, thereby demonstrating the existence of a potentially extensive substitution chemistry for the 18-electron $[\text{Mo}(\text{CNR})_7]^{2+}$ ions. The spectroscopic characterization of these complexes has included measurement of their ^1H NMR, IR, electronic absorption, and X-ray photoelectron spectra. These data support the mixed-ligand complexes possessing seven-coordinate geometries since there is no evidence for unbound phosphine donor atoms (an obvious possibility in the case of the dppm and dppe ligands). These new complexes exhibit one-electron quasi-reversible electrochemical oxidations between +0.9 and +1.2 V.

Introduction

Reactions of compounds containing metal-metal quadruple bonds ($(\sigma)^2(\pi)^4(\delta)^2$ configuration) lead to products in which the quadruple bond is retained, decreased in order, or completely disrupted. The last of these three reaction pathways is important since it can provide a good synthetic route to either new or previously known compounds. Thus, it is one of the classes of reactions which are currently of interest to us in our investigations into the reaction chemistry of metal-metal multiple bonds.

Following our recent discovery that the phosphine complexes $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ ($\text{X} = \text{Cl}$, Br , or NCS) react with NO to produce the monomeric species $\text{Mo}(\text{NO})_2\text{X}_2(\text{PR}_3)_2$,¹ a reaction which proves to be an excellent general synthetic route to complexes of this type, we have sought to establish the factors which determine whether the metal-metal quadruple bond is cleaved. The possibility that this is the usual reaction course when π -acceptor ligands are used is supported by our recent studies on the reactions of the dimers $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{K}_4\text{Mo}_2\text{Cl}_8$ with alkyl isocyanides.² The seven-coordinate homoleptic cations $[\text{Mo}(\text{CNR})_7]^{2+}$ which are formed² turn out to be the

same class of molybdenum(II) isocyanide complexes which had first been reported by Lippard and co-workers.^{3,4}

An important question which emerges from our previous work^{1,2} concerns the generality of this reaction path when π -acceptor ligands are used since it could be maintained (by a "devil's advocate") that the two systems we have so far studied^{1,2} are in fact atypical. Accordingly we are, at the present time, focusing our attention on other such reactions and in the present report describe the reactions of the phosphine dimers $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ with alkyl isocyanides. This work has led to (1) the isolation of a new class of seven-coordinate mixed phosphine-alkyl isocyanide complexes of molybdenum(II) and (2) the discovery that the $[\text{Mo}(\text{CNR})_7]^{2+}$ cations exhibit an interesting substitution chemistry with neutral donors.

Experimental Section

Starting Materials: The following compounds were prepared by standard literature procedures: CH_3NC ,⁵ $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$,⁶ α -

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