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SOME FIVE OR SEVEN-MEMBERED SULFUR-CONTAINING HETEROCYCLES

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SUMMARY

Five membered heterocycles are formed when F-ethylaminosulfur difluoride is reacted with catechol or 2,3-dihydroxynaphthalene. With o,o'-biphenol, a seven membered ring is obtained.

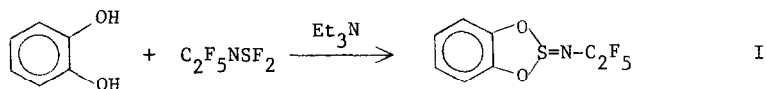
INTRODUCTION

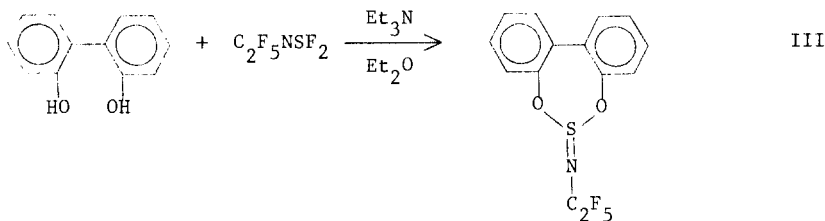
Iminosulfur difluorides have been demonstrated to be useful precursors of a very large number of acyclic and cyclic compounds [1,2]. Of particular interest are the five-membered sulfur-containing heterocycles which result when F-ethylaminosulfur difluoride, $C_2F_5N=SF_2$, is reacted with amines [3,4], ethylene glycol [5] and $((R_f)_2CO)_2Li_2$ [6]. There are very few such derivatives that are comprised of aromatic systems and none of these contains fluorine [1,5].

We now wish to report the successful syntheses of new five and seven-membered heterocycles via the reactions of F-ethylaminosulfur difluoride with catechol, 2,3-dihydroxynaphthalene, and o,o'-biphenol.

RESULTS AND DISCUSSION

When F-ethylaminosulfur difluoride is reacted with catechol, 2,3-dihydroxynaphthalene, and o,o'-biphenol, the heterocycles I, II, and III are obtained. Each of the three compounds is sufficiently stable to be charac-





terized at 25°C, but I decomposes after a few hours and III somewhat more slowly at that temperature.

Spectral data and elemental analysis are very useful in assigning the correct structure to these new heterocycles (details are found in the Experimental section). In the infrared spectra, there is no activity in the ν_{O-H} region and the characteristic medium to strong band at 1388–1392 cm^{-1} is assigned to $\nu_{S=N}$. Molecular ions were obtained in the mass spectra for I, II, and III with appropriate P+1 and P+2 accounting for one sulfur atom. ^{19}F and 1H NMR spectra support the cyclic structures.

In earlier studies of S(IV) compounds with catechols, we observed that reaction with $(CF_3)_2SF_2$ occurred only when the silylated catechol derivatives were used [8]. However, in the present case, reactions were observed to proceed under mildly basic conditions demonstrating the much greater reactivity of the sulfur-fluorine bond in the three-coordinate imino-sulfur(IV) difluoride compared to $(CF_3)_2SF_2$.

One of the purposes for synthesizing this set of compounds was to prepare precursors of tetracoordinated sulfur(IV) compounds which could be reacted with suitable small molecules. We have demonstrated that 2-F-isopropylbenzo-2-thioxazole reacts readily with HCl or HBr to give the 2-halogeno-2-F-isopropylbenzo-2-thioxazolines and their ion pairs [9]. These thioxazolines contain sulfur(IV) in a chelate ring bonded through N and O with two additional monodentate ligands, C_3F_7 and Cl or Br. Our study of reactivity of the N-S bond in these new molecules is just commencing and the results will be reported at a later time.

EXPERIMENTAL

General procedures. Volatile liquids and gaseous materials were handled in a standard Pyrex vacuum line equipped with a Heise-Bourdon tube gauge. Pentafluoroethyliminosulfur difluoride was prepared via literature methods [3]. The other reagents were standard shelf items and were used after crystallization or drying over molecular sieves in the case of liquids. Infrared spectra were obtained by using a liquid film between KBr plates or solids as KBr disks. The ^{19}F and ^1H nuclear magnetic resonance spectra were obtained on a Jeol FX-90 Q Fourier-transform nmr spectrometer with CCl_3F and $(\text{CH}_3)_4\text{Si}$ as internal references. CDCl_3 was used as solvent. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 17 eV or with Hewlett-Packard 5990A GC/MS system at 70 eV. Elemental analyses were completed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Preparation of $\text{C}_6\text{H}_4\text{O}_2\text{SNC}_2\text{F}_5$ (I) nc.

A 9.1 mmol sample of $\text{C}_2\text{F}_5\text{NSF}_2$ was condensed at -196°C into a glass vessel equipped with a Teflon stopcock which contained 9.0 mmol catechol dissolved in 30 ml Et_3N . The mixture was stirred overnight at 0°C . The solid formed was separated from the solution and dissolved in CCl_4 . The solvent and most of the Et_3N were evaporated under dynamic vacuum. The product was purified by column chromatography on silica through the use of n-hexane-benzene (1:1) and gave 1.53 g (5.6 mmol) of a yellow liquid. Distillation with a rotatory sublimation apparatus at $50^\circ\text{C}/1$ Torr gave 1.5 g (5.5 mmol) of a pale yellow liquid. The yield was 62%. The ^{19}F nmr spectrum consists of two singlets at δ -86.70 and -87.22 for CF_2 and CF_3 respectively. The ^1H nmr spectrum had one singlet of δ 7.06. A molecular ion at m/e 273 was observed in the mass spectrum with appropriate $M+1$ and $M+2$ which account for one sulfur atom. Other major peaks m/e 204 ($\text{M}-\text{CF}_3$) $^+$; 165 ($\text{S}=\text{N}-\text{C}_2\text{F}_5$) $^+$; 154 ($\text{M}-\text{C}_2\text{F}_5$) $^+$; 108 [$\text{M}-(\text{S}=\text{N}-\text{C}_2\text{F}_5)$] $^+$; 80 (base peak at 70 eV); 69 (CF_3) $^+$. The infrared spectrum (neat) had bands at 3070 (w), 3040 (vw), 1620 (m), 1480 (s), 1386 (s), 1328 (m), 1290 (s), 1215 (vs), 1150 (shoulder), 1110 (s), 1030 (s), 1010 (m), 925 (w), 855 (w), 838 (w), 810 (s), 770 (w), 742 (m), 730 (m), 690 (m), and 635 (m) cm^{-1} .

Preparation of $\text{C}_{10}\text{H}_6\text{O}_2\text{SNC}_2\text{F}_5$ (II) nc.

A 3.8 mmol sample of $\text{C}_2\text{F}_5\text{NSF}_2$ was condensed at -196°C into a 100 ml Pyrex glass vessel equipped with a Teflon stopcock which contained 3.7 mmol

of 2,3-dihydroxynaphthalene dissolved in 30 ml of dimethylformamide. The mixture was stirred overnight at 25°C. Removal of solvent under dynamic vacuum gave 1.2 g (3.4 mmol, 91% yield) of a dark white solid. TLC in CHCl_3 showed two spots. After crystallization from CHCl_3 and sublimation (50°C/1 Torr) 0.91 g (2.8 mmol, 76% yield) of white crystalline solid was obtained, m.p. 89–91°C. The ^{19}F nmr spectrum consisted of two singlets at ϕ -86.41 and -86.07 for CF_2 and CF_3 respectively. The ^1H nmr spectrum had two multiplets centered at δ 7.73 and 7.46 (ratio of 2:4, respectively). A molecular ion at m/e 323 was observed in the mass spectrum and other appropriate fragment peaks, such as m/e 304 (M-F) $^+$; 267 ($\text{M-C}_2\text{O}_2$); 254 (M-CF_3) $^+$; 165 ($\text{C}_2\text{F}_5\text{NS}$) $^+$; 158 [$\text{M-(SNC}_2\text{F}_5)$] $^+$; 148 ($267\text{-CF}_3\text{CF}_2$); 130 ($\text{C}_4\text{O}_2\text{S}$) $^+$; 102 (148-NS) $^+$ and 69 (CF_3) $^+$. The infrared spectrum (KBr pellet) had bands at 3060 (w), 1520 (m), 1455 (s), 1408 (shoulder), 1388 (m), 1295 (s), 1215 (vs), 1155 (m), 1140 (w), 1090 (s), 1025 (s), 955 (m), 855 (vs), 755 (s), 725 (s), 673 (s), 640 (m), 600 (m), 539 (m), 485 (m), 455 (m), 405 (w), 375 (w), and 360 (w) cm^{-1} . Anal. Calcd: C, 44.59; H, 1.87; F, 29.38. Found: C, 44.62; H, 1.31; F, 29.1.

Preparation of $(\text{C}_6\text{H}_4)_2\text{O}_2\text{SNC}_2\text{F}_5$ (III) nc.

A 5.4 mmol sample of $\text{C}_2\text{F}_5\text{NSF}_2$ was condensed at -196°C into a 100 ml Pyrex glass vessel equipped with a Teflon stopcock which contained 5.3 mmol *o,o'*-biphenol dissolved in 30 ml of Et_2O and 1.3 mmol of Et_3N . The mixture was stirred for 4 hrs. Removal of volatile compounds gave 1.58 g of a crude pale brown oil. The product was purified by sublimation at 103°C/0.2 Torr to give 1.47 g (4.2 mmol) of a colorless oil. The yield was 79%. The oil changed color to yellow then brown overnight. The ^{19}F nmr spectrum consisted of two singlets at ϕ -79.29 and -86.74 for CF_2 and CF_3 respectively. The ^1H nmr spectrum had one multiplet at δ 7.22–7.38. A molecular ion at m/e 349 was observed in the mass spectrum and other appropriate fragment peaks, such as m/e 330 (M-F) $^+$; 301 (M-SO) $^+$; 285 (M-SO_2) $^+$; 184 [$\text{M-(SNC}_2\text{F}_5)$] $^+$; 168 [$\text{M-(C}_2\text{F}_5\text{NSO)}$] $^+$; 64 (SO_2) $^+$ were found. The infrared spectrum (neat) had bands at 3065 (m), 3025 (shoulder), 1605 (m), 1500 (s), 1474 (s), 1435 (s), 1392 (s), 1280 (vs), 1215 (vs), 1175 (vs), 1100 (vs), 1025 (s), 946 (m), 855 (s), 830 (m), 795 (w), 770 (s), 750 (w), 730–720 (m) (doublet), 680 (m), 660 (m), 618 (vw), 605 (vw), 585 (vw) cm^{-1} . Anal. Calcd: C, 48.14; H, 2.31; N, 4.01; F, 27.20. Found: C, 48.13; H, 2.45; N, 4.09; F, 27.5.

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