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Trifluoromethanesulfinate Esters

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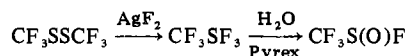
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An improved route to the synthesis of trifluoromethanesulfinyl chloride by oxidation of trifluoromethanesulfonyl chloride with *m*-chloroperbenzoic acid is reported. Additional study of the metathetical reactions of $\text{CF}_3\text{S}(\text{O})\text{X}$ ($\text{X} = \text{F}, \text{Cl}$) has resulted in the preparation of the new compounds $\text{CF}_3\text{S}(\text{O})\text{CN}$, $[\text{CF}_3\text{S}(\text{O})\text{OCH}_2]_2$, $[\text{CF}_3\text{S}(\text{O})\text{OCH}_2]_2\text{CHOH}$, $\text{CF}_3\text{S}(\text{O})\text{ON}(\text{CF}_3)_2$, and $\text{CF}_3\text{S}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$. With ethylene oxide, $\text{CF}_3\text{S}(\text{O})\text{Cl}$ gives $\text{CF}_3\text{S}(\text{O})\text{OCH}_2\text{CH}_2\text{Cl}$.

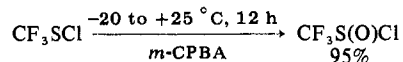
Introduction

Trifluoromethanesulfinyl chloride and trifluoromethanesulfinyl fluoride are useful reagents for introducing the trifluoromethanesulfinyl group into a variety of compounds by reaction with alcohols,¹ amines,¹ and lithium salts.² For use in these reactions, the trifluoromethanesulfinyl fluoride was obtained from a multistep process involving fluorination of bis(trifluoromethyl)disulfane with AgF_2 to form CF_3SF_3 which was hydrolyzed subsequently by catalytic amounts of water in a Pyrex glass vessel³.



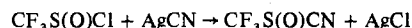
Further reaction of $\text{CF}_3\text{S}(\text{O})\text{F}$ with anhydrous hydrogen chloride produced $\text{CF}_3\text{S}(\text{O})\text{Cl}$ in nearly quantitative yields.⁴

We now find that $\text{CF}_3\text{S}(\text{O})\text{Cl}$ results from the oxidation of $\text{CF}_3\text{S}(\text{O})\text{Cl}$ which is a less expensive and more readily accessible precursor than the disulfane



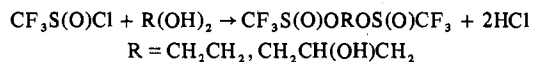
Fluorination of $\text{CF}_3\text{S}(\text{O})\text{Cl}$ with NaF gives $\text{CF}_3\text{S}(\text{O})\text{F}$ essentially quantitatively.⁴

A large number of compounds have resulted from the reactions of trifluoroacetyl chlorides or bromides with silver pseudohalides. It has been shown that a similar reaction occurs between trifluoromethanesulfinyl chloride and silver isocyanate to form $\text{CF}_3\text{S}(\text{O})\text{NCO}$.⁵ We now find that the analogous reaction occurs with silver cyanide⁶

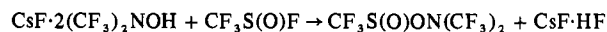
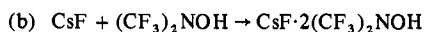
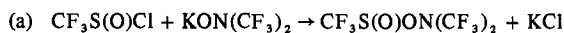


However, this reaction mode does not extend to the preparation of $\text{CF}_3\text{S}(\text{O})\text{SCN}$.

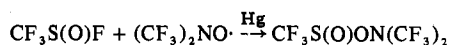
Reaction of trifluoromethanesulfinyl halides has also been found to occur with compounds containing labile hydrogens, such as alcohols, to form trifluoromethanesulfinate esters.¹ Such reactions have now been carried out with di- and triols to give bis(trifluoromethanesulfinyl) compounds which comprise the first members of a new class



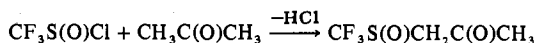
Previously, it was shown that trifluoromethanesulfinyl bis(trifluoromethyl)nitroxide, $\text{CF}_3\text{S}(\text{O})\text{ON}(\text{CF}_3)_2$, could be prepared by two routes⁷



In this work, another route to this sulfinyl ester was attempted in order to learn more about the fluorine atom abstracting ability of the stable radical $(\text{CF}_3)_2\text{NO}^\bullet$, in the presence of mercury.⁸ It was found that this reaction proceeds easily with $\text{CF}_3\text{S}(\text{O})\text{F}$ and trifluoromethanesulfinyl bis(trifluoromethyl)nitroxide results⁶

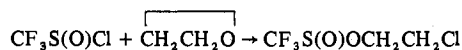


In a reaction reported earlier by others,⁹ trifluoromethanesulfonyl chloride was reacted with acetone to give $\text{CF}_3\text{SCH}_2\text{C}(\text{O})\text{CH}_3$. We find that the reaction with trifluoromethanesulfinyl chloride occurs similarly to yield $\text{CF}_3\text{S}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$



This new compound is similar to acetylacetone and preliminary work indicates that it may act as a bidentate ligand with appropriate metals.

In addition, we have found that trifluoromethanesulfinyl chloride reacts with ethylene oxide to yield the corresponding chloro ester in good yield



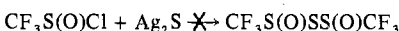
Results and Discussion

The improved synthesis of trifluoromethanesulfinyl chloride by oxidation of trifluoromethanesulfonyl chloride with *m*-chloroperbenzoic acid has several advantages in comparison with the previously reported method. In the earlier method, it is necessary to prepare AgF_2 by high-temperature fluorination of AgF with elemental fluorine. Also, the reaction sequence requires the use of bis(trifluoromethyl)disulfane

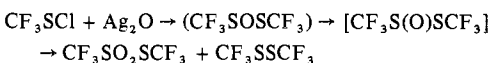
which, although available commercially, is expensive. In our synthesis of trifluoromethanesulfinyl chloride we require only *m*-chloroperbenzoic acid which is available commercially and trifluoromethanesulfonyl chloride, which is easily prepared in good yields.¹⁰

The new compounds derived from $\text{CF}_3\text{S}(\text{O})\text{X}$ ($\text{X} = \text{Cl}, \text{F}$) are colorless or light yellow liquids of low volatility and are often subject to rearrangement or decomposition. The infrared data for the new trifluoromethanesulfinyl derivatives show bands for the $\text{S}=\text{O}$ stretch which are shifted downward from that found in $\text{CF}_3\text{S}(\text{O})\text{Cl}$ and overlap with the bands due to the absorption by the CF_3 group(s) present. The ^{19}F NMR chemical shifts are typically in the region $\phi^* 75\text{--}79$ for the sulfinyl esters and slightly lower, $\phi^* 68\text{--}70$, for the others. The mass spectral data show small and, at times, only trace peaks for the parent ion and fragmentation is extensive at 17-eV ionization potential.

In metathetical reactions with silver pseudohalides, trifluoromethanesulfinyl chloride forms $\text{CF}_3\text{S}(\text{O})\text{CN}$ and $\text{CF}_3\text{S}(\text{O})\text{NCO}$ with AgCN and AgNCO ; however, it does not form $\text{CF}_3\text{S}(\text{O})\text{SCN}$ with AgSCN under the conditions tried. Other attempts in this laboratory to prepare compounds containing the $-\text{S}(\text{O})-$ grouping have met with similar results, e.g.

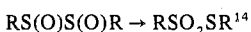
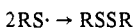
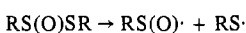


It is possible that the expected compounds are indeed formed and are stable only at low temperatures. At 20 °C only decomposition products, e.g., $\text{CF}_3\text{SO}_2\text{SCF}_3$, are found. Similar decomposition reactions have been reported¹¹



Although instability of the $-\text{S}(\text{O})-$ group is also encountered in nonfluorinated analogues, decomposition occurs more readily and at lower temperatures with the fluorinated species.

The mechanism by which the disproportionation occurs must involve homolytic cleavage of the sulfur-sulfur bond, which may be induced either thermally¹² or photolytically¹³

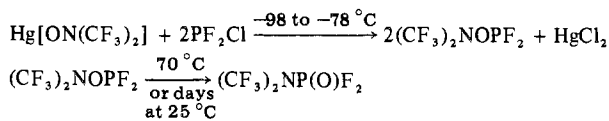


It has been shown that homolytic cleavage of the sulfur-sulfur bond is very dependent on the oxidation states of the sulfur atoms involved and occurs with increasing ease as follows:¹² $(\text{ArSSAr}, \text{ArSO}_2\text{SAr}, \text{ArSO}_2\text{SO}_2\text{Ar}) \ll \text{ArS}(\text{O})\text{SAr} \ll \text{ArS}(\text{O})\text{SO}_2\text{Ar} \ll \text{ArS}(\text{O})\text{S}(\text{O})\text{Ar}$.

One explanation for the observed order of stability is that in compounds containing a sulfinyl group, the sulfur-sulfur bond is longer and therefore weaker.¹² Considering the mechanism of disproportionation as discussed above, the instability of the compounds containing fluorinated end groups is due to the electron-withdrawing ability of these groups which causes a weakening in the sulfur-sulfur bond not present in the nonfluorinated analogues, thereby facilitating homolytic cleavage, both thermally and photolytically.

The reaction of $\text{CF}_3\text{S}(\text{O})\text{F}$ with $(\text{CF}_3)_2\text{NO}\cdot$ occurs to form $\text{CF}_3\text{S}(\text{O})\text{ON}(\text{CF}_3)_2$ which is unstable at 25 °C and undergoes rearrangement. The infrared spectrum for the new product contains a strong peak at 1470 cm^{-1} , indicating the presence of an SO_2 moiety, and the absence of a band in the 1020–1040- cm^{-1} region suggests that no $(\text{CF}_3)_2\text{NO}$ group is present. Also, the mass spectral data are such that a compound with the molecular formula $\text{C}_3\text{F}_9\text{NO}_2\text{S}$ is indicated. These data

strongly indicate that the compound formed is $\text{CF}_3\text{SO}_2\text{N}(\text{CF}_3)_2$. A similar isomerization involving a bis(trifluoromethyl)nitroxide derivative has been reported for $(\text{CF}_3)_2\text{N}\cdot\text{OPF}_2$.¹⁷



Reports of the rearrangement of sulfonates to sulfones are also found in the literature; e.g., trityl 2-methylbenzenesulfinate, when refluxed in chloroform, rearranges to trityl 2-methylphenyl sulfone.¹⁸

There are numerous examples reported of the rearrangement of sulfenates to sulfoxides¹⁹ where the reversal in direction of the rearrangement as compared with the formally analogous Meisenheimer rearrangement²⁰ is attributed to the formation of the strong sulfoxide bond.²¹ Thus it is feasible to argue that it is the formation of the energetically favored sulfone from the sulfinate which is the driving force in the rearrangement of $\text{CF}_3\text{S}(\text{O})\text{ON}(\text{CF}_3)_2$ to $\text{CF}_3\text{SO}_2\text{N}(\text{CF}_3)_2$.

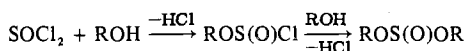
In preparing the compounds which contain two trifluoromethanesulfinyl groups from ethylene glycol and glycerol, it was hoped that stable, high-boiling compounds would be formed. However, decomposition was found to occur at relatively low temperatures (130–150 °C). The decomposition products typically included SO_2 and $\text{CF}_3\text{SO}_2\text{SCF}_3$, which forms from the rearrangement of $\text{CF}_3\text{S}(\text{O})\text{S}(\text{O})\text{CF}_3$. It is interesting to note that under the reaction conditions tried, only the terminal hydroxyl groups of glycerol underwent reaction. This would indicate that the remaining hydroxyl group has a less reactive proton. The relative reactivities of the protons may be related to their acidic nature which, in part, is a factor of polar inductive effects.²² Such a consideration does support a higher degree of acidity and therefore reactivity for the terminal protons.

The reaction of $\text{CF}_3\text{S}(\text{O})\text{Cl}$ with acetone to give $\text{CF}_3\text{S}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$ is of particular interest due to the close analogy of this compound to acetylacetone.

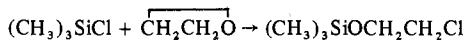


The apparent similarity of these compounds suggests that $\text{CF}_3\text{S}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$ too could be useful as a bidentate ligand. Although $\text{CF}_3\text{S}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$ decomposes slowly at 20 °C, we have found that it is possible to generate this compound in situ using acetone as both reactant and solvent in the presence of a metal ion, thereby making it possible for chelation to occur before decomposition. Investigation of the use of this compound as a bidentate ligand has begun and preliminary results tend to indicate that it does indeed chelate with the metal ions tried; however, further work is needed in this area.

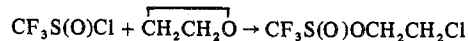
Compounds of the type $\text{RS}(\text{O})_x(\text{CH}_2)_2\text{Cl}$, where $x = 1\text{--}3$ and R is various organic groups, have long been of interest because of their use as pesticides and herbicides. Such compounds have been synthesized both by reaction of chlorides with various alcohols,²³ e.g.



and by using hydrocarbon epoxides,²⁴ e.g.

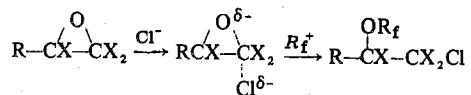


We now show that it is possible to prepare a trifluoromethanesulfinate ester with trifluoromethanesulfinyl chloride and ethylene oxide



It is interesting to note that under similar conditions the corresponding reaction of trifluoromethanesulfinyl chloride with hexafluoropropylene oxide (HFPO) does not occur.

It is generally accepted that the ring-opening reaction of epoxides takes place by ionic mechanism of the $\text{S}_{\text{N}}2$ type^{25,26}



In the case of HFPO where $\text{R} = \text{CF}_3$ and $\text{X} = \text{F}$, the substituents on the carbons bonded to the oxygen are highly electron withdrawing. It is this factor which affects the reactivity of HFPO in comparison with ethylene oxide. The electron-withdrawing substituents enhance the positive character of the carbons and thereby make them more susceptible to nucleophilic attack; however, these substituents also decrease the polar character of the carbon-oxygen bond and strengthen this bond therefore making the ionic splitting of the carbon-oxygen bond more difficult. Since we find that under similar conditions, trifluoromethanesulfinyl chloride will react with ethylene oxide and not with HFPO, the bond-breaking step in the reaction with HFPO is the more important step and governs the reactivity.

Experimental Section

Apparatus. All gases and volatile liquids were handled in a conventional glass vacuum apparatus using standard *PVT* techniques. Purification of products was by low-temperature, vacuum-distillation techniques. Infrared spectra were recorded with a Perkin-Elmer Model 457 infrared spectrometer by using a 10-cm gas cell fitted with KBr windows. Varian HA-100 and EM-360 nuclear magnetic resonance spectrometers were used for ^{19}F and ^1H spectra with CCl_3F and $(\text{CH}_3)_4\text{Si}$ (TMS), respectively, as internal standards. The mass spectra were determined on a Hitachi Perkin-Elmer RMU 6-E mass spectrometer. Vapor pressure studies were made by an isothermometric method. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany, and by D. Harsh at the University of Idaho.

Reagents. Trifluoromethanesulfinyl chloride¹⁰ and bis(trifluoromethyl) nitroxide²⁶ were prepared by literature methods. All other materials were reagent grade and were used without further purification.

Preparation of $\text{CF}_3\text{S}(\text{O})\text{Cl}$. A 10-mmol sample of CF_3SCl was condensed into a 50-mL Pyrex reaction vessel which contained an excess of *m*-chloroperbenzoic acid. The vessel was allowed to warm immediately from -196 to $+20$ °C and then from -20 to $+25$ °C over a 12-h period. Volatile products were separated by fractional distillation; yield 95%; identified by IR.⁴

Preparation of $\text{CF}_3\text{S}(\text{O})\text{OCH}_2\text{CH}_2\text{OS}(\text{O})\text{CF}_3$ and $[\text{CF}_3\text{S}(\text{O})\text{OCH}_2]_2\text{CHOH}$. An excess of $\text{CF}_3\text{S}(\text{O})\text{Cl}$ was condensed into a 25-mL Pyrex reaction vessel which contained 2 mmol of either $\text{HOCH}_2\text{CH}_2\text{OH}$ or $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$. The vessel was allowed to warm slowly from -196 to $+25$ °C over an 8-h period. The volatile products were removed under vacuum leaving the low-volatile product. In the case of $[\text{CF}_3\text{S}(\text{O})\text{OCH}_2]_2\text{CHOH}$, vacuum distillation of the product was necessary to effect separation from unreacted glycerol.

Data for $\text{CF}_3\text{S}(\text{O})\text{OCH}_2\text{CH}_2\text{OS}(\text{O})\text{CF}_3$ are as follows: yield 90%; IR 2980 (w), 1415 (m), 1402 (w), 1368 (w), 1190 (s, br), 1122 (s), 1034 (m), 998 (m), 892 (s), 740 (m, br), 590 (m), 491 (w), 462 (w) cm^{-1} ; NMR ϕ^* 76.2 (s, CF_3), τ 5.58 (m, CH_2). The proton NMR spectrum consists of a complex multiplet due to the asymmetric centers at the sulfurs. The vapor pressure curve was determined over the range 58–130 °C and the boiling point is 112 °C (117 mm). The compound begins to decompose at approximately 130 °C. Anal. Calcd: C, 16.3; H, 1.4. Found: C, 16.1; H, 1.3.

Data for $\text{CF}_3\text{S}(\text{O})\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OS}(\text{O})\text{CF}_3$ are as follows: yield 90%; IR 3400 (m, br), 2975 (w), 1450 (w), 1200 (s, br), 1125 (s), 1050 (w), 960 (m, br), 928 (m), 875 (w), 775 (m, br), 490 (w)

cm^{-1} ; NMR ϕ^* 81.0 (s, CF_3), τ 5.48 (m, CH_2), 4.42 (m, OH). The proton NMR spectrum consists of complex multiplets due to the asymmetric centers at the sulfurs. The vapor pressure curve was determined over a range of 60–145 °C and is described by $\log P_{\text{mm}} = 6.2 - 1712/T$. The boiling point is 135 °C (78 mm). The compound begins to decompose at approximately 145 °C. Anal. Calcd: C, 18.52; H, 1.85. Found: C, 18.79; H, 1.90.

Preparation of $\text{CF}_3\text{S}(\text{O})\text{CN}$.⁶ A 3-mmol amount of $\text{CF}_3\text{S}(\text{O})\text{Cl}$ was condensed into a stainless steel reaction vessel containing an excess of AgCN . The vessel was allowed to warm to 25 °C and was agitated for 3 days. Separation was achieved via fractional distillation: yield 34%; IR 2185 (m), 1240 (sh), 1230 (vs), 1190 (sh), 1180 (w), 1114 (vs), 749 (w), 600 (w), 465 (w) cm^{-1} ; NMR ϕ^* 68.8 (s, CF_3). The equation $\log P_{\text{mm}} = 8.80 - 2090/T$ describes the vapor pressure curve from which ΔH_v (9.6 kcal/mol), ΔS_v (27.1 eu), and the boiling point (79 °C) are obtained. Anal. Calcd: C, 16.7; S, 22.4; F, 39.9; N, 9.8. Found: C, 16.0; S, 22.4; F, 39.9; N, 10.4.

Preparation of $\text{CF}_3\text{S}(\text{O})\text{ON}(\text{CF}_3)_2$.⁶ A 3-mmol amount of $\text{CF}_3\text{S}(\text{O})\text{F}$ and 3.0 mmol of $(\text{CF}_3)_2\text{NO}$ were condensed into a 500-mL Pyrex reaction vessel which contained a small amount of mercury. The vessel was agitated violently at 25 °C until the yellow color of the radical could not be detected when the reaction mixture was frozen. The products were separated by fractional distillation: IR 1325 (s), 1275 (vs), 1238 (vs), 1144 (s), 1030 (m), 979 (m), 806 (w), 764 (m), 716 (m), 634 (w), 568 (w), 453 (m) cm^{-1} ; NMR ϕ^* 66.8 (s, CF_3S), 75.8 [s, $\text{N}(\text{CF}_3)_2$]. Slow decomposition of the compound occurs at 25 °C upon standing.

Preparation of $\text{CF}_3\text{S}(\text{O})\text{OCH}_2\text{CH}_2\text{Cl}$. A 3-mmol amount of ethylene oxide was condensed into a 25-mL Pyrex reaction vessel which contained 3 mmol of $\text{CF}_3\text{S}(\text{O})\text{Cl}$. The vessel was allowed to warm slowly from -196 to 25 °C over an 8-h period. The volatile products were removed under vacuum leaving the nonvolatile product: yield 95%; IR 2960 (w), 2880 (w), 1452 (m), 1432 (m), 1385 (w), 1305 (s), 1196 (vs), 1158 (m), 1128 (vs), 1064 (s), 1000 (vs), 945 (vs), 876 (vs), 800 (w), 750 (m), 730 (s), 670 (s), 588 (m) cm^{-1} ; NMR ϕ^* 78.8 (s, CF_3), τ 5.64 (m, OCH_2), 6.3 (m, CH_2Cl). The vapor pressure curve was determined over a range of 47–130 °C and is described by $\log P_{\text{mm}} = 7.8 - 2117/T$. The boiling point is 130 °C (402 mm). The compound begins to decompose at approximately 130 °C. Anal. Calcd: C, 18.36; H, 2.04. Found: C, 18.13; H, 2.28.

Preparation of $\text{CF}_3\text{S}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$. A 3-mmol amount of $\text{CF}_3\text{S}(\text{O})\text{Cl}$ and 3 mmol of $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ were frozen together in a 25-mL Pyrex reaction vessel and allowed to warm from -196 to $+25$ °C. Reaction occurs over a period of 1–2 h and a brown color begins to appear due to decomposition. A colorless product, $\text{CF}_3\text{S}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$, may be obtained by fractional distillation; however, it begins to slowly decompose as evidenced by the development of a brown color upon warming to ambient temperature: IR 2983 (w), 2919 (w), 1423 (w), 1363 (s), 1283 (m), 1190 (vs, br), 1135 (vs), 1078 (s), 1040 (m, sh), 1000 (w), 975 (w, sh), 825 (m), 750 (m) cm^{-1} ; NMR ϕ^* 74.2 (s, CF_3), τ 5.82 (CH_2), 6.67 (CH_3).

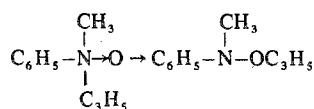
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Registry No. $\text{CF}_3\text{S}(\text{O})\text{Cl}$, 20621-29-8; $\text{CF}_3\text{S}(\text{O})\text{OCH}_2\text{CH}_2\text{OS}(\text{O})\text{CF}_3$, 61915-96-6; $[\text{CF}_3\text{S}(\text{O})\text{OCH}_2]_2\text{CHOH}$, 61915-97-7; $\text{CF}_3\text{S}(\text{O})\text{CN}$, 61951-27-7; $\text{CF}_3\text{S}(\text{O})\text{ON}(\text{CF}_3)_2$, 61915-98-8; $\text{CF}_3\text{S}(\text{O})\text{OCH}_2\text{CH}_2\text{Cl}$, 61915-99-9; $\text{CF}_3\text{S}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$, 61916-00-5; $\text{HOCH}_2\text{CH}_2\text{OH}$, 107-21-1; $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$, 56-81-5; $\text{CF}_3\text{S}(\text{O})\text{F}$, 812-12-4; $(\text{CF}_3)_2\text{NO}$, 2154-71-4; ethylene oxide, 75-21-8; $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, 67-64-1; CF_3SCl , 421-17-0.

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Contribution from the Laboratorio di Chimica e Tecnologia dei Radioelementi del CNR, Università di Padova, Padua, Italy

Technetium-Phosphonite Complexes. Synthesis of Hexacoordinate Technetium(II) and Technetium(III) Complexes of Diethyl Phenylphosphonite and the Crystal Structure of Dichlorotetrakis(diethyl phenylphosphonite)technetium(II)

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The preparation of the dichlorotetrakis(diethyl phenylphosphonite)technetium(III) complexes $[\text{TcCl}_2(\text{C}_6\text{H}_5\text{P}(\text{OC}_2\text{H}_5)_2)_4]\text{Y}$, where $\text{Y}^- = \text{Cl}^-, \text{ClO}_4^-, \text{B}(\text{C}_6\text{H}_5)_4^-$, and dichlorotetrakis(diethyl phenylphosphonite)technetium(II) $[\text{TcCl}_2(\text{C}_6\text{H}_5\text{P}(\text{OC}_2\text{H}_5)_2)_4]$, obtained by the reaction of $(\text{NH}_4)_2\text{TcCl}_6$ with $\text{C}_6\text{H}_5\text{P}(\text{OC}_2\text{H}_5)_2$, is described. The complexes have been characterized by elemental analysis, magnetic and conductivity measurements, and IR and electronic spectra. The crystal and molecular structure of the technetium(II) derivative has been determined by three-dimensional x-ray data collected by counter techniques. The compound crystallizes in a monoclinic cell with dimensions $a = 21.740$ (19), $b = 11.750$ (10), $c = 18.312$ (12) Å, and $\beta = 92.92$ (9)°. The space group is $P2_1/c$ (C_{2h}^5) and $Z = 4$. The final R factor for the least-squares refinement is 0.051 (Mo $K\alpha$; 5495 observed reflections). The crystal structure consists of discrete molecules each of which has a trans-octahedral configuration as anticipated from IR and proton NMR spectra. The molecule has the following metal-ligand bond lengths and angles: $\text{Tc}-\text{P} = 2.41$ (1), $\text{Tc}-\text{Cl} = 2.41$ (1) Å; $\text{P}-\text{Tc}-\text{P}(\text{trans}) = 164.2$ (1), $\text{P}-\text{Tc}-\text{P}(\text{cis}) = 91.9$ (1), $\text{Cl}-\text{Tc}-\text{Cl} = 178.8$ (1)°.

Introduction

Little is known about the coordination chemistry of technetium compared to that of manganese and rhenium, the principal reason being that only recently has the element become available in sufficiently large amounts to be used on a preparative scale. Only a few low-valent technetium complexes have been reported. These are $[\text{TcX}_2\text{D}_2]\text{Y}$ and $[\text{TcX}_2\text{D}_2]$ ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$; $\text{D} = o$ -phenylenebis(dimethylarsine), 1,2-bis(diphenylphosphino)ethane; $\text{Y}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{I}_3^-, \text{ClO}_4^-$),^{2,3} carbonyl complexes of the types $\text{Tc}_2(\text{CO})_{10}$, $\text{Tc}(\text{CO})_4$, $\text{Tc}(\text{CO})_5^+$, $\text{Tc}(\text{CO})_5^{4-7}$, $(\text{CO})_3\text{TcMPRe}(\text{CO})_3$,⁸ and $\text{MP}(\text{Tc}(\text{CO})_3)_2$ ⁹ ($\text{MP} = \text{meso-porphyrin IX dimethyl ester}$), and the compound $(\text{NH}_4)_3\text{Tc}_2\text{Cl}_8 \cdot n\text{H}_2\text{O}$.¹⁰⁻¹² No published data, other than our own,¹³ exist on technetium(II) and technetium(III) complexes with monodentate phosphine or phosphonite ligands. This lack of information prompted us to synthesize the complexes $[\text{TcCl}_2(\text{C}_6\text{H}_5\text{P}(\text{OC}_2\text{H}_5)_2)_4]\text{Y}$ ($\text{Y}^- = \text{Cl}^-, \text{ClO}_4^-, \text{B}(\text{C}_6\text{H}_5)_4^-$) and $[\text{TcCl}_2(\text{C}_6\text{H}_5\text{P}(\text{OC}_2\text{H}_5)_2)_4]$. The diethyl phenylphosphonite ligand was used because of its reducing properties and of its well established¹⁴⁻¹⁷ ability to stabilize low oxidation states of transition metals.

A preliminary account of the structure of the complex $[\text{TcCl}_2(\text{C}_6\text{H}_5\text{P}(\text{OC}_2\text{H}_5)_2)_4]$ has been reported,¹⁸ and the full structure, included in this paper, confirms the structural information obtained from spectroscopic studies.

Experimental Section

Materials. Solid NH_4TcO_4 was obtained by concentration and filtration of its ammonia solution (available from Radiochemical Centre Ltd., Amersham, England). $(\text{NH}_4)_2\text{TcCl}_6$ was prepared by the electrochemical method,¹⁹ which yields large amounts of product by a simple reduction of NH_4TcO_4 in HCl (6 N) on a platinum electrode. Diethyl phenylphosphonite was synthesized by the method of Rabinowitz and Pellon.²⁰ All solvents were purified and dried by standard methods.

Apparatus. Magnetic susceptibilities of nitromethane or benzene solutions were measured by the Evans method²¹ and corrected for diamagnetism of the ligands from tables given by Figgis and Lewis.²² ¹H NMR spectra were recorded using a Hitachi Perkin-Elmer R20A instrument with TMS as the internal standard. Conductivities (10^{-3} M solutions in nitromethane at 25 °C) were measured with an LKB conductivity bridge, Model 3116B. Electronic spectra were recorded using a CF4 Optica spectrophotometer. The absorptions of $[\text{TcCl}_2\text{L}_4]$ complex were measured in the presence of 1 M free phosphonite. Infrared spectra of Nujol samples, using CsI windows, were recorded using Perkin-Elmer 621 (4000–400 cm^{-1}) and Beckman IR-11 spectrophotometers (400–50 cm^{-1}).

Analytical Methods. The technetium was determined by treating a concentrated ethanol solution of the complex with H_2O_2 (30%) and then titrating the TcO_4^- formed with standard $\text{P}(\text{C}_6\text{H}_5)_4\text{Cl}$. The equivalent point was determined by measuring the radioactivity of microsamples (0.02 ml) of the solution.²³ Chlorine was determined by potentiometric titration (standard AgNO_3) of the ethanol solutions of the complexes after oxidation with H_2O_2 (30%). Only the coordinated chlorine was determined with this method.