Adams, R. D.; Cotton, F. A.; Cullen, W. R.; Hunter, D. L.; Mihichuk, L. *Inorg. Chem.* **1975**, *14*, 1395–1399. Flood, T. C.; Di Santi, F. J.; Campbell, K. D. *Ibid.* **1978**, *17*, 1643–1646.
(28) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933–938.
(29) Maisonnat, A.; Poilblanc, R. *J. Organomet. Chem.* **1978**, *160*, 307–317.
(30) Corrigan, A.; Dickson, R. S.; Fallon, G. G.; Michel, K. J.; Mok, C. *Aust. J. Chem.* **1978**, *31*, 1937–1951.
(31) Bonnet, J. J.; Maisonnat, A.; Poilblanc, R., to be published.
(32) Curtis, M. D.; Butler, W. M.; Greene, J. *Inorg. Chem.* **1978**, *17*, 2928–2931.

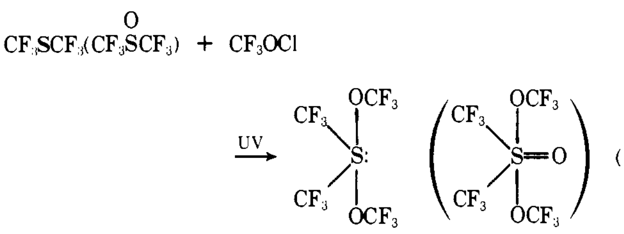
A Comparative Study of the Reactions of *F*-(*tert*-Butyl) Hypochlorite and *F*-Methyl Hypochlorite with Simple Sulfur Compounds

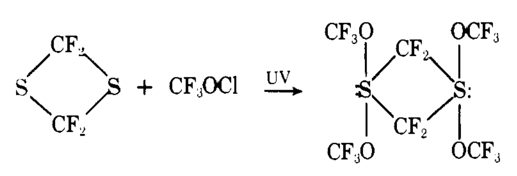
Qui-Chee Mir, Kirk A. Laurence,[1] Robert W. Shreeve, Daniel P. Babb,[2] and Jean'ne M. Shreeve*

Contribution from the Department of Chemistry, University of Idaho, Moscow, Idaho 83843. *Received March 19, 1979*

Abstract: While CF_3SCF_3, $CF_3S(O)CF_3$, and SF_4 readily undergo oxidative addition with CF_3OCl to form $(CF_3)_2S(OCF_3)_2$, $(CF_3)_2S(O)(OCF_3)_2$, and $SF_4(OCF_3)_2$, no reaction is observed with $(CF_3)_3COCl$. On the other hand, CF_3SCl and $\overline{SCF_2SC}F_2$ are reacted with $(CF_3)_3COCl$ to yield $CF_3S(OC(CF_3)_3)_2Cl$ (A) and $\overline{CF_2SCF_2S}(OC(CF_3)_3)_2$ (E). *F*-Methyl hypochlorite adds two CF_3O groups to each sulfur in $\overline{SCF_2SC}F_2$. With $CF_3S(O)Cl$, oxidative displacement of chlorine with $(CF_3)_3COCl$ forms $CF_3S(O)OC(CF_3)_3$ (B). In reaction with SCl_2 or CCl_3SCl, both oxidative displacement and oxidative addition occur with $(CF_3)_3COCl$ to give the tetrakis derivative, $S(OC(CF_3)_3)_4$ (D). Unsymmetric oxidative addition to a single sulfur in CF_3SSCF_3 occurs with $(CF_3)_3COCl$ to prepare $CF_3S(OC(CF_3)_3)_2SCF_3$ (C). With CF_3SCl, $CF_3S(O)Cl$, SCl_2, and CF_3SSCF_3, CF_3OCl assumes the role of fluorinating reagent. Neither hypochlorite was found to react with $(CF_3)_2SF_2$.

In recent papers, we have demonstrated that *F*-methyl hypochlorite is an excellent F-methoxylating reagent with acyclic and cyclic sulfur(II)- and -(IV)-containing compounds,[3,4] viz., eq 1 and 2. Earlier, others had studied the insertion of olefins[5-7] into the O–Cl bond of a variety of R_FOCl compounds (R_F = CF_3, *i*-C_3F_7, $(CF_3)_3C$–, SF_5–) to form fluorocarbon ethers with excellent thermal stability, especially in the case of perhalofluorinated materials. Small molecules or atoms, such as SO_2,[8,9] CO,[9] and Hg,[10] also insert into the O–Cl bond to form chlorosulfates, chloroformates, and a reactive mercurial. This type of insertion reaction is in contrast to the oxidative addition in reactions 1 and 2 where, if insertion does occur, a subsequent reaction must take place to replace the chlorine by a second *F*-methoxy group.


(1)


(2)

In another reaction mode, Fox and co-workers have shown that *F*-(*tert*-butoxy)phosphoranes and *F*-(*tert*-butoxy)boranes result from oxidative displacement of chlorine from $PClF_4$ and PCl_2F_3,[11] and from BCl_3[12] by $(CF_3)_3COCl$. While exploring the versatility of *F*-(*tert*-butyl) hypochlorite as a synthetic reagent, we were impressed by the marked difference in chemical behavior and concomitant products obtained when compared with our observations for *F*-methyl hypochlorite in analogous reactions.

Results and Discussion

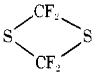
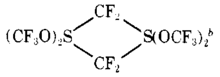
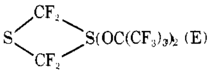
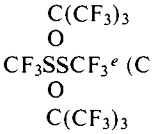
In Table I are listed the reaction products obtained when CF_3OCl or $(CF_3)_3COCl$ is reacted with a variety of simple sulfur compounds and with mercury. Insertion of mercury into the OCl bond of $(CF_3)_3COCl$ and the concomitant formation of a stable mercurial[10] are in keeping with the behavior exhibited by other small molecules cited above. Also, the lability of the fluorine on the α carbon is a well-known phenomenon, and it is therefore not surprising that CF_3OCl undergoes slow decomposition in the presence of mercury to form COF_2 and HgClF.

However, it is surprising that, when $(CF_3)_3COCl$ is reacted with CF_3SCl, a new stable chloro-*F*-methylbis(*F*-butoxy)sulfurane results, but with $CF_3S(O)Cl$ chlorine displacement occurs. The compounds CF_3SCl[13] and $CF_3S(O)Cl$[14a-d] undergo hundreds of reactions which support the polarity $CF_3S^{\delta+}Cl^{\delta-}$ and $CF_3S(O)^{\delta+}Cl^{\delta-}$ and which lead us to expect permanent loss of the sulfur–chlorine bond in each case. The new sulfurane is stable indefinitely at 0 °C and for limited periods at 25 °C. It is the first example of such an acyclic compound which is isolable at 25 °C. We had reported[15] earlier the chlorosulfurane and chlorosulfurane oxide, $CF_3S(NR_2)_2Cl$ and $CF_3S(O)(NR_2)_2Cl$, which are stable at 25 °C and above. The former was slowly hydrolyzed to $CF_3S(O)NR_2$, but $CF_3S(O)(NR_2)_2Cl$ was stable to hydrolysis in H_2O at 25 °C.

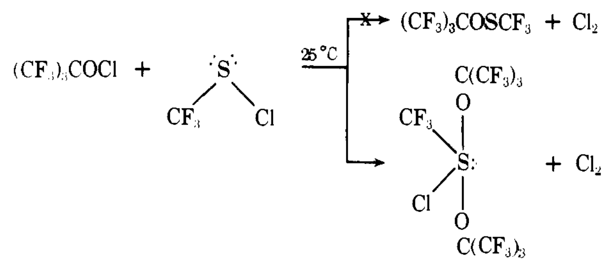
Chlorosulfuranes are in general much less stable than fluorosulfuranes. Several have been suggested as reaction intermediates without isolation,[16a-e] while those which have been isolated are unstable toward hydrolysis[17a-d] and thermolysis at 25 °C. By taking advantage of the enhanced stability of monocyclic and spirosulfuranes compared to acyclic sulfuranes, Martin and co-workers[17a,18] isolated a monocyclic

0002-7863/79/1501-5949$01.00/0

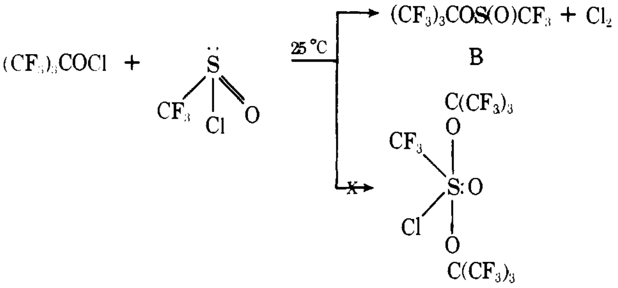
Table I

	$\mathrm{CF_3OCl}$	$\mathrm{(CF_3)_3COCl}$
Hg	$\mathrm{COF_2 + HgClF}$	$\mathrm{>COHgCl}$[a]
$\mathrm{CF_3SCF_3}$	$\mathrm{(CF_3)_2S(OCF_3)_2}$[b]	n.r.
$\mathrm{CF_3S(O)CF_3}$	$\mathrm{(CF_3)_2SO(OCF_3)_2}$[b]	n.r.
$\mathrm{CF_3SCl}$	$\mathrm{CF_3Cl, COF_2, SF_4, Cl_2, CF_3SF_3}$	$\mathrm{CF_3SCl(OC(CF_3)_3)_2}$[c] (A)
$\mathrm{CF_3S(O)Cl}$	$\mathrm{COF_2, Cl_2, SOClF, SOCl_2, CF_3SO_2Cl, CF_4, CF_3Cl}$	$\mathrm{CF_3S(O)OC(CF_3)_3}$[c] (B)
$\mathrm{SF_4}$	$\mathrm{SF_4(OCF_3)_2}$[d]	n.r.
		
$\mathrm{CF_3SF_2CF_3}$	n.r.	n.r.
$\mathrm{SCl_2}$	$\mathrm{COF_2, Cl_2, SF_4(OCF_3)_2}$	$\mathrm{S(OC(CF_3)_3)_4}$ (D)
$\mathrm{CF_3SSCF_3}$	$\mathrm{CF_3SF_3, COF_2, Cl_2, CF_3Cl}$ (tr), $\mathrm{SF_4}$ (tr)	 $\mathrm{CF_3\overset{\overset{C(CF_3)_3}{O}}{\underset{\underset{C(CF_3)_3}{O}}{S}}SCF_3}$[e] (C)

[a] Reference 10. [b] References 3 and 4. [c] With $\mathrm{ClHgOC(CF_3)_3}$, $\mathrm{CF_3SCl \rightarrow CF_3SOC(CF_3)_3}$ and $\mathrm{CF_3S(O)Cl \rightarrow CF_3S(O)OC(CF_3)_3}$: ref 10. [d] Reference 23. [e] Reference 21.

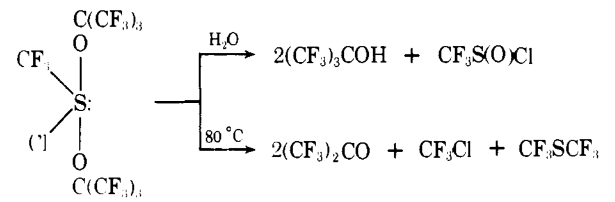


A

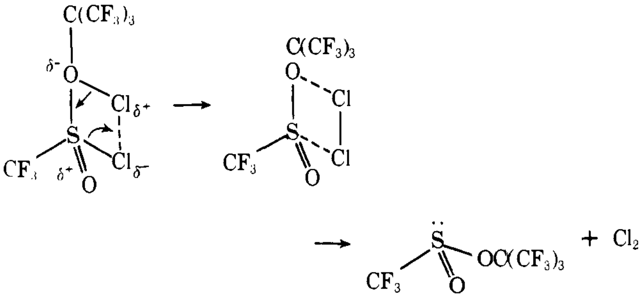


alkoxybromosulfurane (15% yield) which was thermally stable. Subsequently, these workers prepared a crystalline monocyclic alkoxychlorosulfurane in quantitative yield at 25 °C by treatment of 2-(2-hydroxy-2-propyl)-1-phenylthiobenzene or 2-(2-hydroxy-2-propyl)-1-phenylsulfinylbenzene with *tert*-butyl hypochlorite. This chlorosulfurane and its methyl analogue are stable at their melting points (125-126 and 107-109 °C). The former is less than 15% hydrolyzed after overnight exposure to Illinois air!

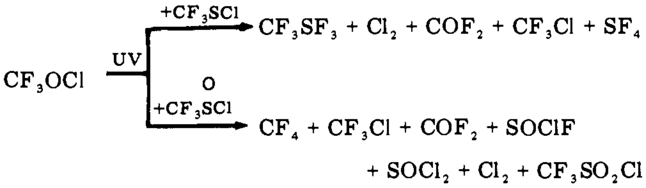
While our new acyclic chlorosulfurane is stable to exposure to air (~15-20% relative humidity) as monitored by infrared, in the presence of traces of water $\mathrm{CF_3S(OC(CF_3)_3)_2Cl}$ was hydrolyzed rapidly to give *F*-*tert*-butyl alcohol and *F*-methanesulfinyl chloride. At room temperature decomposition is slow, but after 2 h at 80 °C the compound is completely decomposed to give *F*-acetone, *F*-chloromethane, and bis(*F*-methyl) sulfide in quantitative amounts.



Compound B is identical with the product obtained when $\mathrm{CF_3S(O)Cl}$ is reacted with $\mathrm{(CF_3)_3COHgCl}$ or with $\mathrm{(CF_3)_3COH{\cdot}(CH_3)_3N}$.[19] That the reaction product is one resulting from replacement of chlorine by $\mathrm{(CF_3)_3CO}$, rather than of oxidative addition of $\mathrm{(CF_3)_3CO}$ to the central sulfur atom, must be due to the lower accessibility of the electron pair on the sulfur atom in $\mathrm{CF_3S(O)Cl}$ than in $\mathrm{CF_3SCl}$. It will be noted below that no reaction occurs with $\mathrm{CF_3SCF_3}$. The reaction intermediate likely is a four-center species which rearranges to give $\mathrm{CF_3S(O)OC(CF_3)_3}$ and $\mathrm{Cl_2}$. It is interesting to note that no reaction occurs between $\mathrm{CF_3SO_2Cl}$ and $\mathrm{(CF_3)_3COCl}$ under the conditions used, which explains the high-yield synthesis of chlorosulfates[8,9] by insertion of $\mathrm{SO_2}$ into OCl bonds of hypochlorites and is in agreement with the generally observed reduced reactivity of $\mathrm{CF_3SO_2Cl}$ and other sulfuryl compounds.



Under the conditions tried we were not successful in isolating a chlorosulfurane or chlorosulfurane oxide or other products analogous to the $\mathrm{(CF_3)_3COCl}$ reactions from the reactions of $\mathrm{CF_3OCl}$ with $\mathrm{CF_3SCl}$ or $\mathrm{CF_3S(O)Cl}$, but rather only products of fluorination and hypochlorite decomposition were obtained.

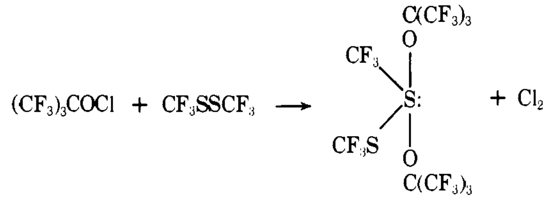


In the case of $\mathrm{CF_3SCl}$, it is unlikely that an unstable (unisolable) four-coordinate sulfur-containing intermediate was formed which subsequently decomposed since, based on the decomposition of $\mathrm{(CF_3)_3S(OCF_3)_2}$,[3] $\mathrm{CF_3OOCF_3}$ would be a likely product and it is not observed. Rather it appears that, in cases where the reactant contains a S-Cl bond, the favored reaction mode is one of fluorination with concomitant $\mathrm{Cl_2}$ and $\mathrm{COF_2}$ formation. Thus, in this instance, the behavior of $\mathrm{CF_3OCl}$ is analogous with that of the totally fluorinated hypofluorite, $\mathrm{CF_3OF}$, viz.

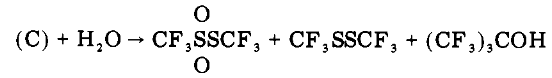
$$\mathrm{CF_3OF + 2CF_3SCl \xrightarrow{-78\ ^\circ C} CF_3SF_3 + Cl_2 + COF_2}^{20}$$

Essentially the same mode of reaction must occur for $\mathrm{CF_3OCl}$ with $\mathrm{CF_3S(O)Cl}$.

Because of the interesting sulfurane and sulfurane oxide which were obtained when $\mathrm{CF_3SCF_3}$ and $\mathrm{CF_3S(O)CF_3}$ were reacted with $\mathrm{CF_3OCl}$[3,4] (eq 1), we next examined the analogous reactions with $\mathrm{(CF_3)_3COCl}$. No reaction was found to occur when the sulfide and $\mathrm{(CF_3)_3COCl}$ were held at 0 °C for extended periods or when the mixture was photolyzed at 0 °C. A similar behavior was noted with $\mathrm{CF_3S(O)CF_3}$. At best, only the $\mathrm{(CF_3)_3COCl}$ was destroyed. However, upon using the disulfane, $\mathrm{CF_3SSCF_3}$, as the sulfur-containing species, it was possible to isolate a stable thiosulfurane in which four-coordinate sulfur(IV) is bonded to sulfur(II) (C).[21] Earlier, Gombler[22] reported a stable *F*-alkyl-containing compound in which three-coordinate sulfur(IV) is bonded to sulfur(II), $CF_3S(O)SCF_3$. In the case of the new thiosulfurane, the unsymmetric addition of the $(CF_3)_3CO\cdot$ to the disulfane is unexpected but is strongly supported by the ^{19}F NMR spectrum, where there are three resonances at ϕ 59.2 (nonadectet, J = 1.5 Hz) assigned to CF_3S^{IV}, 71.4 (quartet), $OC(CF_3)_3$, and 74.9 (singlet), CF_3S^{II}. The peak area ratio is 1:6:1. In addition, the mass spectrum, although it does not contain a molecular ion, has appropriate fragments, such as *m/e* 546 $(M - CF_3 - 3F)^+$, 364 $((CF_3)_2COSOC(CF_3)_2)^+$, 352 $((CF_3)_3COS(CF_3)O)^+$, and 283 $((CF_3)_3COSO)^+$, which strengthen the argument. This thiosulfurane, which is a colorless, involatile liquid, is stable indefinitely when stored under anhydrous conditions in Pyrex glass at 25 °C. However, it is readily hydrolyzed by water at 25 °C. Again, by contrast, the reaction of CF_3OCl with CF_3SSCF_3 which occurs at 0 °C results in the cleavage of the -S-S- bond to form CF_3SF_3, Cl_2, and COF_2 with trace amounts of CF_3Cl and SF_4.



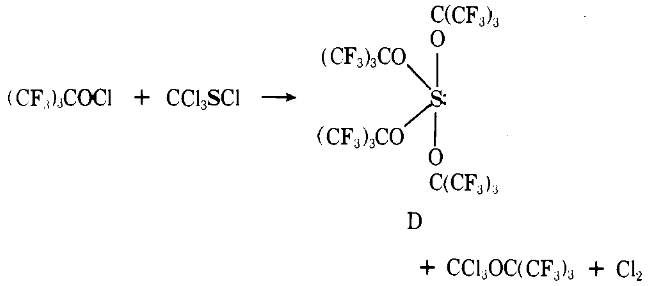
C



$$(C) + H_2O \rightarrow CF_3\overset{O}{\underset{O}{S}}SCF_3 + CF_3SSCF_3 + (CF_3)_3COH$$

The photolytic reaction of CF_3OCl with SF_4 provides a superior route to $SF_4(OCF_3)_2$ with yields approaching 90-95%.[23] However, when a mixture of $(CF_3)_3COCl$ and SF_4 is held at 0 °C for extended periods or when the mixture is photolyzed at 0 °C, no reaction occurs. The reaction was not carried out at higher temperatures because of the inherent thermal instability of $(CF_3)_3COCl$.

Continuing our efforts toward novel, substituted sulfuranes, we reacted $(CF_3)_3COCl$ with CCl_3SCl to obtain a white solid (mp 112 °C) which was very stable to hydrolysis for several hours at 25 °C. This hydrolytic stability of the new tetrakis-*F*-(*tert*-butoxy)sulfurane (D) is sharply different from other acyclic tetrakissulfuranes. The sole sulfuranes with four carbon-sulfur bonds are (a) unstable above 0 °C when the ligands are C_6F_5-, decomposing to $C_6F_5C_6F_5$ and $C_6F_5SC_6F_5$, or (b) unstable above −80 °C when the ligands are C_6H_5-.[24-26] Moreover, the hygroscopic solid, $(PhO)_4S$, is readily hydrolyzed to PhOH and $(PhO)_2SO$.[27] There are a variety of other acyclic diaryldialkoxysulfuranes which are hydrolytically unstable.[16a,b,18,28-31]



D

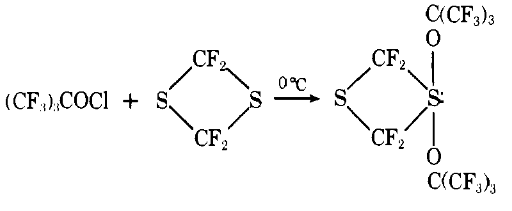
The ^{19}F NMR spectrum is composed of two broad resonances of equal area at ϕ 68.5 and 70.8. Although the molecular ion is not found in the mass spectrum, a peak at *m/e* 737 $(M - OC(CF_3)_3)^+$, coupled with excellent carbon, fluorine, and sulfur analyses for $S(OC(CF_3)_3)_4$, is strong evidence in support of this stable molecule.

It is interesting to compare the behavior of $(CF_3)_3COCl$ toward the two trihalomethanesulfenyl chloride compounds, CF_3SCl and CCl_3SCl. As noted above, oxidative addition of $(CF_3)_3CO$ to the sulfur in the former compound occurs with retention of the C-S and S-Cl bonds, whereas in the latter case oxidative addition of $(CF_3)_3CO$ groups to sulfur occurs with concomitant oxidative displacement of chlorine and replacement of the CCl_3-S bond by a CCl_3-O bond in the byproduct, $CCl_3OC(CF_3)_3$. In order to further investigate the nature of the S-Cl bond in these reactions, sulfur dichloride (SCl_2) was reacted with $(CF_3)_3COCl$ and was found to produce $S(OC(CF_3)_3)_4$ more efficiently, i.e., no side reactions which consume $(CF_3)_3COCl$.

An argument can be made for the formation of the observed products in the reactions of $(CF_3)_3COCl$ with $CF_3S(O)Cl$, CF_3SCl, CCl_3SCl, and SCl_2, based on the availability of unshared electron pairs as the main factor governing oxidative addition. For $CF_3S(O)Cl$, only a single pair is available and it will be the most tightly bound of any of the pairs in the other molecules; therefore, oxidative displacement is the main reaction mode. In each of the other three, two pairs of electrons are much more available for attack so that oxidative addition does occur. For CCl_3SCl and SCl_2, a six-member intermediate which undergoes subsequent collapse is possible. The fact that reaction does not occur between either of the hypochlorites and $(CF_3)_2SF_2$ supports the concept of tightly held electron pairs not being readily available for oxidative addition reactions.

Since sulfur dichloride proved to be the most efficient sulfur(II)-chloride precursor to $S(OC(CF_3)_3)_4$, its behavior with CF_3OCl was also examined. Once again the great tendency for fluorination to occur was the dominating force with the products being COF_2, Cl_2, and $SF_4(OCF_3)_2$.[23]

With *F*-1,3-dithietane, under photolytic conditions, CF_3OCl oxidatively adds to the sulfur atoms to give an unusual liquid cyclic sulfurane[3,4] as shown in eq 2. When $(CF_3)_3COCl$ is reacted at 0 °C with *F*-1,3-dithietane, a white, crystalline solid is formed which is sublimable at 25 °C and which melts at 61 °C in a sealed tube. Based on the *F*-methoxy cyclic sulfurane, it was tempting to expect an analogous compound for the *F*-*tert*-butoxy cyclic sulfurane. However, after the mass, ^{19}F NMR spectral, and elemental analysis data were analyzed, the compound which was formed was the disubstituted cyclic sulfurane. This was the sole product obtained, although a large excess of hypochlorite was employed in the reaction. The ^{19}F NMR spectrum consists of a pentet at ϕ 71.6 (J = 1.6 Hz) (assigned to $OC(CF_3)_3$) and a nonadectet at ϕ 62.1 (CF_2). The peak area ratio is 9:2. The X-ray crystal structure determination of this material is underway. Preliminary data indicate that the two $(CF_3)_3CO-$ groups occupy the axial positions and the CF_2SCF_2 ring is equatorial in a pseudo-trigonal-bipyramid structure. Complete details will be reported later.[32]



E

Agreement in the reaction behavior of the two hypochlorites is finally reached when neither can be reacted with $(CF_3)_2SF_2$ under any conditions tried. This is not surprising since the latter has a record of peculiar behavior which most likely results from the inaccessibility of the electron pair on sulfur.

Conclusion

The observed differences in behavior of these two hypochlorites can be attributed in large degree to the fact that CF_3OCl is more stable and most of its reactions require photolysis, which suggests a free-radical mechanism. $(CF_3)_3COCl$ is less stable to thermolysis, hydrolysis, photolysis, and insertion reactions. Reactions of $(CF_3)_3COCl$ normally are carried out at 0 °C. If photolytic conditions are employed, the $(CF_3)_3CO\cdot$ radical readily decomposes to the stable $(CF_3)_2CO$. It is not possible to carry out reactions of $(CF_3)_3COCl$ under rigorous conditions because of its overall lower stability. However, although the $CF_3O\cdot$ radical is stable, when CF_3OCl is reacted with materials which contain labile chlorine, the controlling reaction is one of fluorination with concomitant chlorine gas formation. In the case of reactions with $\overline{SCF_2SCF_2}$, the fact that two CF_3O groups add to each sulfur when CF_3OCl is the reacting species and two $(CF_3)_3CO$ groups add to only one sulfur when $(CF_3)_3COCl$ is the reactant must be attributed to steric factors. Confirmation of this awaits the crystal structure of E.

Experimental Section

Materials. *F*-1,3-Dithietane (PCR, Inc.), SCl_2, CCl_3SCl, S_2Cl_2, and CF_3SSCF_3 (PCR, Inc.) were used after distillation.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon tube gauge. Volatile starting materials and purified products were measured quantitatively by *PVT* techniques. Known products were confirmed, based on the spectral data of authentic samples.

Infrared spectra were taken by using a Perkin-Elmer 457 spectrometer with a 5-cm gas cell fitted with KBr windows. Solids were run as KBr disks and involatile liquids as capillary films. The ^{19}F and ^1H NMR spectra were obtained by using a Varian HA-100 spectrometer with CCl_3F or $(CH_3)_4Si$ as an internal standard. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6E spectrometer at 17 or 70 eV.

Preparation of $CF_3S(OC(CF_3)_3)_2Cl$ (A). *F*-Methanesulfenyl chloride[33] (0.5 mmol) and *F*-(*tert*-butyl) hypochlorite[8] (1.0 mmol) were condensed into a 25-mL Pyrex vessel and reacted for 5 h at 0 °C. The chlorine and unreacted starting materials were removed under dynamic vacuum at 0 °C. The chlorosulfurane, which was a colorless, slightly volatile liquid at 0 °C (and at 25 °C), remained (68% yield). The ^{19}F NMR spectrum contained resonance bands at ϕ 59.7 (only 10 of 19 lines resolvable, $J = 1.4$ Hz) assigned to CF_3S and at ϕ 71.9 (quartet) assigned to $(CF_3)_3CO$. The peak area ratio was 1:6. The infrared spectrum (capillary film) had bands at 1385 w, 1275 vs, br, 1185 w, 1150 s, 1110 vs, 1055 vs, 980 vs, d, 770 m, d, 730 s, d, 695 m, 580 m, 545 m, 528 m, 475 cm^{-1} m. When the mass spectral data were recorded at 200 °C and 17 eV, a molecular ion was not observed; however, other fragment peaks, such as *m/e* 370, 368 $[CF_2S(OC(CF_3)_3)OCl]^+$, 352 $[CF_3S(OC(CF_3)_3O]^+$, 336 $[CF_3S(OC(CF_3)_3]^+$, 317 $[CF_2S(OC(CF_3)_3]^+$, 283 $[(CF_3)_3COSO]^+$, 267 $[(CF_3)_3COS]^+$, and 235 $[(CF_3)_3CO]^+$, were found. Anal. Calcd for $C_9O_2SClF_{21}$: C, 17.82. Found: C, 17.57.

Preparation of $CF_3S(O)OC(CF_3)_3$ (B). Approximately 1 mmol of $CF_3S(O)Cl$[20] was added to 0.63 mmol of $ClHgOC(CF_3)_3$[10] and the mixture was allowed to remain at 0 °C for 24 h. The volatile materials were separated by trap-to-trap distillation with $CF_3S(O)OC(CF_3)_3$ (~95% yield) being retained at −63 °C. It was identified by comparison of its published infrared and ^{19}F NMR spectra.[19] The mass spectrum had peaks at 352 $(M)^+$, 333 $(M - F)^+$, 283 $((CF_3)_3COSO)^+$, and 216 $((CF_3)_2CF_2CO)^+$ in addition to many characteristic smaller fragments.

Preparation of $CF_3(CF_3S)S(OC(CF_3)_3)_2$ (C). *F*-(*tert*-Butyl) hypochlorite (2.3 mmol) and CF_3SSCF_3 (1 mmol) were condensed into a 50-mL Pyrex vessel at −196 °C and then warmed to and allowed to remain at 0 °C for 72 h. After all of the volatile compounds were removed under dynamic vacuum at 0 °C, the colorless, nonvolatile thiosulfurane remained. Its infrared spectrum contained absorption bands at 1250 s, br, 1235 w, 1225 w, 1191 ms, 1153 s, 1100 s, 978 s, 965 s, 767 m, 758 m, 734-732 s, 692 cm^{-1} w. Anal. Calcd for $C_{10}O_2S_2F_{24}$: C, 17.86. Found: C, 17.70.

Reaction of CF_3OCl with CF_3SSCF_3. *F*-Dimethyldisulfane (1 mmol) was condensed with 4.3 mmol of CF_3OCl[8] at −196 °C and warmed to and allowed to remain at 0 °C for 12 h. The mixture was separated by trap-to-trap distillation and the products were identified as CF_3SF_3, Cl_2, and COF_2 with trace amounts of CF_3Cl and SF_4 from their infrared spectra. No evidence for unreacted starting materials was found.

Preparation of $S(OC(CF_3)_3)_4$ (D). A. $CCl_3SCl + (CF_3)_3COCl$. Trichloromethanesulfenyl chloride (0.5 mmol) and $(CF_3)_3COCl$ (2.8 mmol) were condensed into a 50-mL Pyrex vessel and allowed to warm to and remain at 0 °C for 24 h. The volatile materials were then separated via trap-to-trap distillation. The white solid residue was purified by sublimation (~95% yield). The ^{19}F NMR spectrum contained two broad singlets of equal area at ϕ 68.5 and 70.8. The infrared spectrum (KBr pellet) had absorption bands at 1280 vs, br, 1085 s, 1058 s, 1019 s, 972 s, 830 s, sh, 771 w, 730 vs, 680 w, sh, 584 s, 476 s, and 405 cm^{-1} m. The mass spectrum contained peaks at *m/e* 737 $(M - OC(CF_3)_3)^+$, 502 $(M - (OC(CF_3)_3)_2)^+$, 283 $(OSOC(CF_3)_3)^+$, 198 $(SOC(CF_3)_2)^+$, 166 $(OC(CF_3)_2)^+$, and 147 $(OC(CF_3)(CF_2))^+$. Anal. Calcd for $C_{16}O_4SF_{36}$: C, 19.75; F, 70.37; S, 3.29. Found: C, 19.23; F, 70.0; S, 3.36.

B. $SCl_2 + (CF_3)_3COCl$. Sulfur dichloride (0.86 mmol) and $(CF_3)_3COCl$ (3.6 mmol) were retained at 0 °C for several hours. The volatile materials were removed and the white solid, $S(OC(CF_3)_3)_4$, was purified by sublimation (~95% yield).

C. $S_2Cl_2 + (CF_3)_3COCl$. Disulfur dichloride (0.42 mmol) and $(CF_3)_3COCl$ (3.4 mmol) were retained at 0 °C. The yield of $S(OC(CF_3)_3)_4$ was about 95% after volatile materials were removed.

D. $CS_2 + (CF_3)_3COCl$. Carbon disulfide (0.9 mmol) and $(CF_3)_3COCl$ (4 mmol) were held at 0 °C for several hours. The yield of $S(OC)CF_3)_3)_4$ was about 95%.

Reaction of CF_3OCl with SCl_2. To 1 mmol of SCl_2 in a quartz vessel was added 4.3 mmol of CF_3OCl. This mixture was photolyzed at 0 °C for 20 h. Products were separated by using fractional distillation and identified from infrared spectra. Materials found were $SF_4(OCF_3)_2$,[23] COF_2, and CF_4. Chlorine was also identified.

Preparation of $\overline{SCF_2S(OC(CF_3)_3)_2CF_2}$ (E). *F*-1,3-Dithietane (1 mmol) and $(CF_3)_3COCl$ (2.2 mmol) were condensed into a 50-mL Pyrex vessel at −196 °C. After warming to and remaining at 0 °C for 24 h, the volatile materials were separated by fractional condensation. The white solid remaining was recrystallized from anhydrous ether (~95% yield). The infrared spectrum (KBr pellet) had absorption bands as follows: 1200 vs, br, 950 vs, 900 vs, 768 s, 720 vs, 689 vs, 643 s, 575 s, and 535 cm^{-1} s. The mass spectrum contained peaks at *m/e* 615 $(M - F)^+$, 552 $(M - CF_2S)^+$, 533 $(M - CF_3S)^+$, 399 $(M - OC(CF_3)_3)^+$, 298 $(M - OC(CF_3)_3 - CF_3S)^+$, 219 $((CF_3)_3C)^+$, and 200 $((CF_3)_2(CF_2)C)^+$. Anal. Calcd for $C_{10}O_2S_2F_{22}$: C, 18.93; F, 65.9; S, 10.09. Found: C, 18.98; F, 67.0; S, 10.99.

Reaction of CF_3OCl with CF_3SCl. To 1.1 mmol of CF_3SCl was added 2.8 mmol of CF_3OCl. The mixture was either photolyzed at 0 °C through quartz for 12 h or held at 25 °C for 12 h in metal or Pyrex glass. It was separated by fractional distillation. Products identified were CF_3Cl, COF_2, SF_4, Cl_2, and CF_3SF_3. Approximately 0.4 mmol of CF_3SCl was recovered.

Reaction of CF_3OCl with $CF_3S(O)Cl$. A mixture of 4 mmol of CF_3OCl and 2 mmol of $CF_3S(O)Cl$ was photolyzed through quartz at 25 °C for 20 h. Products identified were COF_2, Cl_2, $SOClF$, $SOCl_2$, CF_3SO_2Cl, CF_4, and CF_3Cl.

Acknowledgment is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research. We thank Charles Barinaga and Dennis Gage for mass and ^{19}F nuclear magnetic resonance spectral data.

References and Notes

(1) NSF Undergraduate Research Participant, summer 1977.
(2) On leave from Department of Chemistry, Marshall University, Huntington, W.Va.
(3) T. Kitazume and J. M. Shreeve, *J. Am. Chem. Soc.*, **99**, 4194 (1977).
(4) T. Kitazume and J. M. Shreeve, *Inorg. Chem.*, **17**, 2173 (1978).
(5) D. D. Moldavskii, V. G. Temchenko, V. I. Slesareva, and G. L. Antipenko, *Zh. Org. Khim.*, **9**, 694 (1973).
(6) W. Maya, C. J. Schack, R. D. Wilson, and J. S. Muirhead, *Tetrahedron Lett.*, 3247 (1969).
(7) L. R. Anderson, D. E. Young, D. E. Gould, R. Jurik-Hogan, D. Nuechterlein, and W. B. Fox, *J. Org. Chem.*, **35**, 3730 (1970).
(8) D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *J. Am. Chem. Soc.*,

92, 2313 (1970).

(9) D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *Tetrahedron Lett.*, 723 (1969).

(10) S. D. Morse, K. A. Laurence, G. H. Sprenger, and J. M. Shreeve, *J. Fluorine Chem.*, **11**, 327 (1978).

(11) D. E. Young and W. B. Fox, *Inorg. Nucl. Chem. Lett.*, **7**, 1033 (1971).

(12) D. E. Young, L. R. Anderson, and W. B. Fox, *Chem. Commun.*, 736 (1971).

(13) A. Haas and U. Niemann, *Adv. Inorg. Chem. Radiochem.*, **18**, 143 (1976).

(14) (a) H. W. Roesky and S. Tutkunkardes, *Chem. Ber.*, **107**, 508 (1974); (b) D. T. Sauer and J. M. Shreeve, *Inorg. Chem.*, **10**, 358 (1971); (c) D. T. Sauer and J. M. Shreeve, *Inorg. Nucl. Chem. Lett.*, **6**, 501 (1970); (d) C. A. Burton and J. M. Shreeve, *Inorg. Chem.*, **16**, 1039 (1977).

(15) T. Kitazume and J. M. Shreeve, *J. Fluorine Chem.*, **9**, 175 (1977); *J. Am. Chem. Soc.*, **99**, 3690 (1977).

(16) (a) J. C. Martin and R. J. Arhart, *J. Am. Chem. Soc.*, **93**, 2339 (1971); (b) R. J. Arhart and J. C. Martin, *ibid.*, **94**, 4997 (1972); (c) C. R. Johnson and J. J. Rigau, *ibid.*, **91**, 5398 (1969); (d) R. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *ibid.*, **91**, 5239 (1969); (e) G. H. Schmid and V. J. Nowlan, *J. Org. Chem.*, **37**, 3086 (1972).

(17) (a) J. C. Martin and E. F. Perozzi, *J. Am. Chem. Soc.*, **96**, 3155 (1974); (b) N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *ibid.*, **91**, 549 (1969); (c) O. Ruff, *Chem. Ber.*, 4513 (1904); (d) I. B. Douglass, K. R. Brower, and F. T. Martin, *J. Am. Chem. Soc.*, **74**, 5770 (1952).

(18) T. M. Balthazor and J. C. Martin, *J. Am. Chem. Soc.*, **97**, 5634 (1975); J. C. Martin and T. M. Balthazor, *ibid.*, **99**, 152 (1977).

(19) A. Majid and J. M. Shreeve, *Inorg. Chem.*, **13**, 1710 (1974).

(20) C. T. Ratcliffe and J. M. Shreeve, *J. Am. Chem. Soc.*, **90**, 5403 (1968).

(21) Q. C. Mir, D. P. Babb, and J. M. Shreeve, *J. Am. Chem. Soc.*, **101**, 3961 (1979).

(22) W. Gombler, *Angew. Chem., Int. Ed. Engl.*, **16**, 723 (1977).

(23) T. Kitazume and J. M. Shreeve, *J. Am. Chem. Soc.*, **100**, 492 (1978).

(24) W. A. Sheppard, *J. Am. Chem. Soc.*, **93**, 5597 (1971).

(25) W. A. Sheppard and S. S. Foster, *J. Fluorine Chem.*, **2**, 53 (1972).

(26) W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962).

(27) J. I. Darragh and D. W. A. Sharp, *Angew. Chem., Int. Ed. Engl.*, **9**, 73 (1970).

(28) J. C. Martin and R. J. Arhart, *J. Am. Chem. Soc.*, **93**, 2341 (1971).

(29) L. J. Kaplan and J. C. Martin, *J. Am. Chem. Soc.*, **95**, 793 (1973).

(30) I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Am. Chem. Soc.*, **93**, 6674 (1971).

(31) I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Am. Chem. Soc.*, **94**, 5010 (1972).

(32) D. Schomburg, private communication.

(33) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

Novel Meso-Substitution Reactions of Metalloporphyrins

Kevin M. Smith,*[1a] Graham H. Barnett,[1b] Brian Evans,[1b] and Zoya Martynenko[1a]

Contribution from the Department of Chemistry, University of California at Davis,
Davis, California 95616, and The Robert Robinson Laboratories, University of Liverpool,
Liverpool, England.

Received March 29, 1979

Abstract: Solutions of octaalkyl metalloporphyrin π cation radicals react with nucleophiles such as nitrite, chloride, pyridines, imidazole, cyanide, triphenylphosphine, thiocyanate, acetate, and azide, to produce the corresponding meso- (methine) substituted metalloporphyrins. Demetalation then gives the appropriate meso-substituted porphyrin. Circumstantial evidence suggests that the π cation radical reacts (possibly in a complexed or aggregated form) with the nucleophile, and that the corresponding π dication of the metalloporphyrin or the radical (produced by oxidation of the nucleophile) is not involved in the combination step of the reaction.

Introduction

The classical methods for introduction of substituents into the meso (methine) positions of porphyrins involve electrophilic substitution upon the porphyrin nucleus.[2] However, since the classical deuteration, nitration, halogenation, sulfonation, formylation, and acetylation procedures require use of acidic reagents, and because the N,N′-diprotonated porphyrin salt is nonnucleophilic, it is necessary to protect the inner porphyrin nitrogens against protonation in situ by formation of a metal complex. Nickel(II), copper(II), and iron(III) complexes are most often used, but these suffer two disadvantages in that they (1) are relatively difficult to demetalate after the reaction and (2) are relatively electron withdrawing, thereby causing a decrease of electron density in the porphyrin ligand which is being employed as a nucleophile. Both of these disadvantages are assessed relative to zinc(II), cadmium(II), or magnesium(II) complexes which are easy to demetalate in high yield and which "release" electron density to the porphyrin ligand; unfortunately, use of these more favorable metal complexes for classical electrophilic meso substitution in porphyrins causes almost instantaneous demetalation (even in the relatively mild Vilsmeier formylation procedure employing phosphoryl chloride and dimethylformamide).

The prospect of using alternative methods[3] for meso substitution was brought to our attention by a report which showed that aromatics (e.g., perylene) can be nitrated using nitrite and the corresponding aromatic π cation radical.[4] It transpires that there now exists an extensive literature on the reactions of such π cation radicals with a whole variety of nucleophiles, and the mechanistic pathway of these transformations has many times been demonstrated to involve reactions of the π cation radical rather than, for example, the π dication.[5] Our interest was yet further stimulated by the fact that metalloporphyrin π cation radicals can be readily formed, either chemically or electrochemically; moreover, though metalloporphyrin π cation radicals had been shown to be stable in methanol,[6] a relatively good nucleophile, the corresponding π dications are extremely potent electrophiles,[7] so we considered that at the least we could use these two-electron oxidation products as substrates. We were hopeful, however, that, if the metalloporphyrin π cation radicals were found to be as reactive as other aromatic π cation radicals, then it would be possible to prepare the porphyrin analogues in methanol and to dissolve the nucleophiles in the same solvent without the danger of obtaining meso methoxy-substituted products.

Results and Discussion

Nitration. Treatment of magnesium(II) etioporphyrin I (**1**) in chloroform with an excess of iodine (i.e., 4 oxidizing equiv) in methanol gave a green solution of the π cation radical possessing a characteristic electronic absorption spectrum.[6] Addition of sodium nitrite (as a suspension in methanol) caused a rapid color change to give a red solution, the visible spectrum of which, though of the normal metalloporphyrin type, suggested that a chemical transformation of the porphyrin ligand had occurred. Demetalation and chromatography gave a small amount of etioporphyrin I (**2**) and an 84% yield of the corresponding meso mononitro derivative **3.** A similar procedure

0002-7863/79/1501-5953$01.00/0