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THE CHEMISTRY OF TRIFLUOROTHIOLACETIC ACID AND ITS DERIVATIVES. II*

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SUMMARY

Addition reactions of perfluorothiolacetic acid (TFTAA) with selected organic compounds were studied and six compounds containing the trifluoroacetyl group have been prepared. Two types of reactions were observed, free radical and nucleophilic addition. Under the influence of ultraviolet light, TFTAA (CF_3COSH) adds to olefins to form 1:1 adducts. The $CF_3COS\bullet$ radical appears to be the adding species. Three new olefin adducts were prepared: $CF_3COSCFHCF_2H$, $CF_3COSCH_2CF_2H$, and $CF_3COSCH_2CFH_2$. In addition, this was found to be a new way to prepare $CF_3COSCH_2CH_3$, which had been previously prepared by another route. Physical constants, analytical data, infrared, ultraviolet, NMR and mass spectra are presented supporting the proposed structures for these compounds.

Nucleophilic addition adducts were formed with TFTAA. TFTAA is a strong acid and the CF_3COS^- ion was found to act as a nucleophile with several substrates. With hexafluoroacetone, addition of TFTAA across the carbonyl group gave $CF_3COSC(CF_3)_2OH$, and with ethylene oxide the alcohol addition product, $CF_3COSCH_2CH_2OH$, was produced.

INTRODUCTION

The purpose of this project was to study methods and mechanisms of CF_3COSH (TFTAA) additions to unsaturated and strained carbon systems. Sheppard and Muetterties[1] found that fluorinated thioacids appeared to react similarly to the hydrocarbon analog. In particular they found ready addition to the double bond of hydrocarbon olefins:

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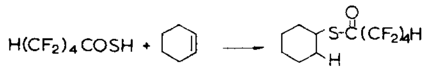


(1)

It was of interest to extend the scope of this reaction to fluorinated olefins and to investigate the mechanism and direction of addition.

RESULTS AND DISCUSSION

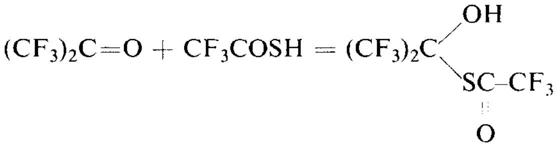
It was found that in the presence of UV light, TFTAA would add to olefins and fluoro-olefins. The following reactions were studied:

$$CF_3COSH + CH_2{=}CH_2 = CF_3COSCH_2CH_3 \quad (2)$$
$$CF_3COSH + CH_2{=}CHF = CF_3COSCH_2CH_2F \quad (3)$$
$$CF_3COSH + CF_2{=}CH_2 = CF_3COSCH_2CHF_2 \quad (4)$$
$$CF_3COSH + CF_2{=}CFH = CF_3COSCHFCHF_2 \quad (5)$$

Ethyl thioltrifluoroacetate, $CF_3COSCH_2CH_3$, has been prepared previously by Hauptschein, Stokes and Nodiff[2] by the reaction of ethyl mercaptan and trifluoroacetic anhydride.

The new fluoro-adducts are colorless liquids with an extremely strong onion-like odor. They decompose slowly at room temperature under a nitrogen atmosphere. The trifluoroethylene adduct was less stable than the others, darkening in a vacuum during the vapor pressure study while the others remained unchanged.

The observed nucleophilic behavior of TFTAA[3] led to an attempt to add it to hexafluoroacetone and ethylene oxide. The reaction of TFTAA with hexafluoroacetone occurs readily at room temperature:


$$(CF_3)_2C{=}O + CF_3COSH = (CF_3)_2C\begin{matrix}\diagup OH \\ \diagdown S\underset{\underset{O}{\|}}{C}{-}CF_3\end{matrix} \quad (6)$$

The product is a colorless sweet-smelling liquid, which is very stable in the liquid phase at room temperature, as was found to be true for other fluorinated olthiols reported by Harris.[4] In contrast, some unfluorinated compounds studied by Harris were found to be less stable, giving off H_2S or water. In the vapor phase, the hexafluoroacetone adduct behaved analogously to some of Harris' less stable fluorinated adducts by dissociating almost completely back into the starting materials.

With ethylene oxide the reaction was found to proceed spontaneously and exothermically at room temperature, proceeding through a yellow intermediate which can be observed if the reactants are condensed together and warmed slowly to room temperature. The colorless, non-volatile liquid product when heated decomposes to a white solid, producing as a by-product trifluoroacetic acid, CF_3COOH:

$$nCF_3COSCH_2CH_2OH \xrightarrow{\text{heat}} nCF_3COOH + (CH_2CH_2S)_n \qquad (7)$$

All of the new compounds in reactions (3) through (7) were characterized *via* their infrared spectra, ultraviolet spectra, NMR spectra and mass spectra. Since isomers could be formed by CF_3COSH adding non-selectively to fluoro-olefins, the vapor phase chromatography of these compounds was studied. The results of this work are given in Table 1. Only one major component was found for these compounds.

TABLE 1

GAS CHROMATOGRAPHY DATA[a]

Compound	Retention time (min)
$CF_3COSCH_2CH_2F$	28.83
$CF_3COSCH_2CHF_2$	18.63
$CF_3COSCHFCHF_2$	11.93
CCl_4	5.59

[a] The column temperature was 35 ± 1°. Helium flow rate was 30 ml/min.

The physical properties of the olefin adducts are summarized in Table 2. The molecular weights were found from gas density measurements and compared reasonably well with the expected values. Vapor pressure data is presented in Table 3. The curves drawn from this data are shown in Figure 1. It is seen in Table 2 that the boiling point rises with increasing fluorine substitution until the di-substituted adduct is reached. The trifluoro adduct has a lower boiling point than any of the others. This is analogous to the series of fluorinated methanes compared by Sheppard and Sharts [5] which shows an increase in boiling point from methane to difluoromethane and a drop for the trifluoromethane, with the lowest value for carbon tetrafluoride. This is explained by the importance of intermolecular hydrogen bonding in partially fluorinated compounds. This intermolecular hydrogen bonding, promoted by the high polarization of the molecule is probably at a maximum for the difluoro-olefin adduct.

TABLE 2

PHYSICAL PROPERTIES OF THE OLEFIN ADDUCTS

Compound	B.p. °C (Extrap.)	$\Delta H_{vap.}$ kcal mole^{-1}	Trouton const.	Vapor density calc.	Expt'l. found	Index of refrac. 25°
$CF_3COSCH_2CH_3$	88.8	8.23	22.7	158	159.0	1.3750
$CF_3COSCH_2CFH_2$	97.8	9.64	26.0	176	179.5	1.3866
$CF_3COSCH_2CHF_2$	100.6	9.33	25.0	194	189.5	1.3632
$CF_3COSCHFCHF_2$	74.7	8.08	23.2	212	203.0	1.3482

TABLE 3

VAPOR PRESSURE–TEMPERATURE DATA FOR OLEFIN ADDUCTS

$CF_3COSCH_2CH_3$		$CF_3COSCH_2CFH_2$		$CF_3COSCH_2CHF_2$		$CF_3COSCHFCHF_2$	
T °K	P mm	T °K	P mm	T °K	P mm	T °K	P mm
273	8.0	283	12.9	282	13.1	282	52.4
283	31.0	294	25.0	295	26.8	284	54.9
293	54.6	304	42.9	302	39.0	294	86.35
303	82.0	312	64.6	303	42.4	304	138.0
313	128.0	313	69.4	308	53.1	312	193.6
		323	104.3	313	69.3	316	254.4
		324	107.8	322	96.3	322	302.1

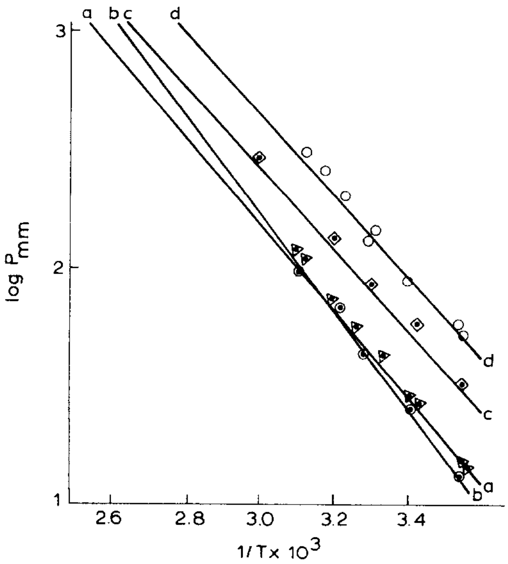


Fig. 1. Vapor pressure curves of olefin adducts.

(a) $CF_3COSCH_2CH_3$ $\log P = 7.8 - \frac{1.8 \times 10^3}{T}$ ◬

(b) $CF_3COSCH_2CH_2F$ $\log P = 8.7 - \frac{2.2 \times 10^3}{T}$ ⊙

(c) $CF_3COSCH_2CHF_2$ $\log P = 7.9 - \frac{1.9 \times 10^3}{T}$ ▣

(d) $CF_3COSCHFCHF_2$ $\log P = 7.4 - \frac{1.7 \times 10^3}{T}$ ○

Vapor pressure versus temperature data were used to find $\Delta H_{\text{vap.}}$ and Trouton's constant for the four adducts. These constants are listed in Table 2 with the physical properties. One can see that these approximately follow the boiling point trends and support the above argument.

The infrared spectra are tabulated in Table 4. All the olefin adducts show the strong CF_3 symmetric and asymmetric stretching bands at 1285–1130 cm^{-1}, and the CF_3 deformation bands at 750–736 cm^{-1} [6]. The carbonyl stretching frequency for these compounds is found in the range 1710 cm^{-1} (ethylene adduct) to 1735 cm^{-1} (trifluoro adduct). Substitution with fluorines for hydrogens on the thiolester group reduces the mobile electronic field of the alkylsulfur, causing an enhancement of the attractive forces between the positive carbon and the negative oxygen of the carbonyl group which is reflected in the shift to higher frequencies. It is of interest to note that the absorption frequency of $CF_3COSCH_2CH_3$ is close to the "normal" value of 1715 cm^{-1} for a saturated aliphatic ketone.

TABLE 4

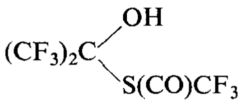
INFRARED ABSORPTION BANDS[a]

Compound	Wavenumber cm^{-1}
$CF_3COSCH_2CH_2F$	2940 (w), 1710 (s), 1463 (vw), 1395 (w), 1275 (s), 1210–1175 (s), 1120 (m), 1063 (m), 1020 (s), 955 (s), 818 (vw), 738 (m)
$CF_3COSCH_2CHF_2$	2940 (w), 1820 (vw), 1725 (s), 1398 (m), 1370 (m), 1280 (s), 1240–1175 (s), 1114 (s), 1076 (s), 1017 (w), 949 (s), 839 (w), 740 (m)
$CF_3COSCHFCHF_2$	2960 (w), 1872 (vw), 1825 (s), 1735 (m), 1373 (m), 1274 (s), 1205 (s), 1184 (s), 1108 (s), 1080 (m), 1058 (m), 983 (w), 938 (s), 893 (w), 807 (m), 779 (w), 738 (m)
$CF_3COSC(CF_3)_2OH$ (liquid)	3310 (w), 1709 (s), 1385 (w), 1279 (s), 1286 (s), 1242 (s), 1220 (s), 1184 (s), 1142 (s), 1074 (w)
$CF_3COSCH_2CH_2OH$	3570 (w), 2940 (w), 2560 (vw), 2270 (vw), 1790 (s), 1710 (m), 1545 (w), 1450 (m), 1415 (w), 1390 (m), 1340 (m), 1290 (m), 1230–1120 (s), 1080 (w), 1010 (m), 955 (m), 935 (m), 867 (w), 832 (w), 773 (m), 740 (w), 730 (m), 696 (vw)

[a] vw = very weak; w = weak; m = medium; s = strong; vs = very strong.

The C–H stretching modes in these adducts are in the region 2990–2960 cm^{-1}. The ethyl ester shows the CH_3 symmetric and asymmetric bending vibrations at 1460 and 1385 cm^{-1}. The bands in the vinyl and vinylidiene adducts at 1395 and 1370 cm^{-1} could be due to the CH_2 scissoring vibrations[2].

In the liquid spectrum of the hexafluoroacetone adduct, there is one carbonyl absorption at 1709 cm^{-1} which is in the region for the thioacid carbonyl. This shows that the SH group of the thioacid has added across the C=O group of hexafluoroacetone. The OH absorption at 3310 cm^{-1} further supports the proposed structure of:



The four strong peaks of the region 1286–1142 cm^{-1} are the CF_3 symmetric and asymmetric stretching frequencies. The peaks at 744 and 713 cm^{-1} are CF_3 deformation bands. The gas spectrum has a doublet in the carbonyl region for CF_3COSH and 6FK. This lends further support that the adduct dissociates in the vapor state into starting material. This result was further confirmed *via* gas chromatography.

For $CF_3COSCH_2CH_2OH$, the OH peak at 3570 cm^{-1} supports the alcohol structure.

The ultraviolet spectra of these adducts are compared in Table 5. There is a progressive blue shift from 242 mμ for the ethylene adduct to 232 mμ for the trifluoro adduct, which parallels increasing fluorine substitution on the olefin.

TABLE 5

ULTRAVIOLET ABSORPTION DATA[a]

Compound	$\lambda_{max.}$	$E_{max.}$
$CF_3COSCH_2CH_2F$	240	30700
$CF_3COSCH_2CHF_2$	238	87000
$CF_3COSCHFCHF_2$	232	55500
$CF_3COSC(CF_3)_2OH$	240	50000

[a] Solvent was cyclohexane.

These shifts are explained by Koch,[7] who accounts for the absorbance band by the formation of an excited state through charge transfer involving a sulfur electron:

It seems likely that a charge transfer, rather than a purely intra-atomic valency shell transition is involved in view of the relatively high intensity of the absorption band.

Koch[7] notes that substitution of chlorine on R produces a red shift (CH_3COSH $\lambda_{max.} = 220$ mμ, $E_{max.} = 220$; Cl_3COSH $\lambda_{max.} = 238$ mμ, $E_{max.} = 3800$). This he attributes to the inductive effect of chlorine, which would raise the ground state relative to the excited state. Rochat and Gard[3] found that substituting fluorines on R produces a red shift also, but to a lesser degree, (CF_3COSH $\lambda_{max.} = 230$ mμ).

Substitution of an alkyl group for hydrogen on sulfur causes a further red shift, ($CF_3COCH_2CH_3$ $\lambda_{max.} = 242$ mμ), due to the stabilizing electropositive effect of the alkyl group, which would help disperse the positive charge of the excited state:

The substitution of fluorines on one carbon removed from the sulfur should reduce the electron donating effect of the alkyl group slightly and result in a slight blue shift of 2 mμ for the vinyl adduct and 2 mμ more for the vinylidiene. Substituting fluorines on the adjacent carbon to the sulfur has a much larger counteracting effect, and for $CF_3COSCHFCF_2H$ the $\lambda_{max.}$ value is shifted 6 mμ from $CF_3COSCH_2CHF_2$ toward the blue and is almost the same as that found for CF_3COSH.

The structure of the addition products was determined from their magnetic resonance spectra. The proton and fluorine resonances were resolved into the various spin–spin components in order to identify the nearest neighbors. Coupling constants, corresponding to the various interactions, are listed in Table 6 as are the chemical shift values.

All the fluorine spectra contained the single CF_3– peak in the range +75.8 to +76.2 ppm upfield from $CFCl_3$, which is the region expected for the CF_3– group when it is attached to a carbonyl group[8]. Rochat and Gard[3] found that the CF_3 resonance for CF_3COSH was +77.2 and other substituted thioacids fell in the range of +73.5 to +75.8.

The fluorine spectrum of the vinyl adduct, $CF_3COSCH_2CH_2F$, consists of nine lines with a band center of 216 ppm upfield from $CFCl_3$, in the region expected for a fluorine in a CHF_2 group[9]. The ^{19}F resonance is split into a large triplet by the two protons of the CH_2F group, $J(F4, H4) = 47$ cps. Each of these triplets is further split into a triplet by the CH_2 protons, $J(F4, H3) = 24$ cps.

The fluorine spectrum of the vinylidiene adduct, $CF_3COSCH_2CHF_2$, consists of six lines, with a band center of 115.5 ppm upfield from $CFCl_3$, as expected for a fluorine in a CHF_2 group. The ^{19}F resonance is split into a large doublet by the CHF_2 proton, $J(F4, H4) = 55$ cps. Each component of the doublet becomes a triplet as a result of coupling between ^{19}F and the CH_2 protons, $J(F4, H3) = 16.0$ cps.

The fluorine spectrum of the trifluoro adduct, $CF_3COSCHFCHF_2$, is more complex. In addition to the CF_3 peak, there are two ^{19}F resonance bands representing the CHF group and the CHF_2 group. The CHF resonance has a band center at 179.1 ppm upfield from $CFCl_3$ and contains 12 lines. The resonance is first split into a wide doublet by the CHF proton, $J(F3, H3) = 47$ cps. Each doublet is further split into a triplet by the CF_2H fluorine, $J(F3, FH) = 19$ cps, which is further split into a doublet, $J(F3, H4) = 5$ cps, by the CF_2H proton resulting in a total of 12 lines.

The CHF_2 resonance consists of 16 lines with a band center of 127.0 ppm upfield from $CFCl_3$. The band is initially split into a large doublet by the CHF_2 proton, $J(F4, H4) = 54$ cps. Each doublet is further divided into a doublet by the CHF fluorine, $J(F3, F4) = 19$ cps. One would then expect each of these doublet elements to be further split into doublets by the CHF proton with a coupling constant of approximately 5 cps as in the CHF resonance coupling. However, in

TABLE 6

NUCLEAR MAGNETIC RESONANCE DATA

Compound[c]	Chemical shifts, band centers[a]								Coupling constants[b]					
Skeletal carbon atom number	CF_3	CF_2	CF	CH_2		CH		OH	J(F4,H3)	J(F4,H4)	J(F3,H3)	J(F3,F4)	J(H3,H4)	J(H4,OH4)
1 2 3 4				3	4	3	4							
$CF_3COSCH_2CH_2F$	76.1		216.2	3.36	4.56				24	47			5.5	
$CF_3COSCH_2CHF_2$	76.0	115.5		3.45			5.9		16	55			4.0	
$CF_3COSCHFCHF_2$	76.2	127.0	179.1			6.39	6.06		5	54	47	19		
$CF_3COSCH_2CH_2OH$	75.7			4.45	2.86			1.53					6.5	9

[a] Chemical shifts in ppm upfield from $CFCl_3$ internal standard or downfield from $Si(CH_3)_4$ internal standard.

[b] Measured in cycles per second.

[c] Data for hexafluoroacetone adduct unavailable as a detailed analysis of this compound is incomplete.

this case the doublet is split into a doublet with a coupling constant of 10.2 cps and each of these is again split into a doublet with a coupling constant of 3.8 cps, giving a total of 16 lines when only eight are expected. The difference between band centers, $\Delta\nu$, here is 52 cps and the largest coupling constants are on the order of 50 cps, giving a $\Delta\nu/J$ ratio of 1. Whenever the ratio falls below 6 or 7, first-order spectra are not expected. In this spectrum it appears that the two CHF_2 fluorine atoms are not equivalent. Apparently the two fluorines have the same chemical shift and after splitting by the coupled fluorines and protons they further mutually interact to split each other into two pairs of resonances. The additional splitting results in the observed 16 line pattern which is, in fact, two sets of lines predicted by the first-order theory from CHF and H splitting. If this is the case, the CHF spectrum would still look the same if the coupling constant of the two non-equivalent fluorines are the same.

The ^{19}F NMR analysis shows that the CF_3COS radical has attached itself to the carbon of the olefin carrying the most hydrogens.

Since these olefin reactions occur at a negligible rate when the reactants are combined at room temperature, but proceed readily when irradiated with UV light, it seems likely that free radicals play an important part in the mechanism. Harris and Stacey[10] found in their free radical studies with CF_3SH and fluoroolefins, that the $CF_3S\bullet$ radical was the adding species. In this work only one isomer was found (as with CF_3SH) for each reaction, and the products were correlated on the basis of the intermediate radical stability, postulated by Haszeldine and co-workers[11,12]. The products found are those deriving from the predictably more stable intermediate radical. Haszeldine found that the order of radical stability is tertiary > secondary > primary, and that the order of stability of primary and secondary radicals can be very dependent upon the substituents involved. The designations "tertiary," "secondary" and "primary" are determined solely by the number of atoms or groups other than hydrogen on the carbon atom bearing the odd electron and do not necessarily refer to the carbon skeleton. Substituents vary in their stabilizing ability, *e.g.* $H < F <$ (Cl, CF_3, RO). Thus, the relative order of stability of free radicals produced here would be $CF_3COSCH_2CHF\bullet > CF_3COSCHFCH_2\bullet$; $CF_3COSCH_2CF_2\bullet > CF_3COSCF_2CH_2\bullet$; $CF_3COSCHFCF_2\bullet > CF_3COSCF_2CHF\bullet$.

However, it is known that reactions involving thiyl radicals are reversible and that the observed orientation could be the result of an equilibrium process.

The major mass spectra peaks for the olefin, alcohol and olthiol adducts are listed in Table 7. A comparison of the major peaks shows that all of the spectra had strong peaks at $m/e = 69$, the CF_3^+ peak, as would be expected. The vinyl, vinylidiene and ethyl adduct had good parent peaks, while the trifluoro adduct showed only a weak parent peak. The unit COS + olefin ($COSCH_2CH_3^+$, $COSCH_2CH_2F^+$, $COSCH_2CHF_2^+$ and $COSCHFCHF_2^+$) was present in all. It was surprising that other units of the thioacid were not consistently present.

CF_3CO^+ was present in all of the spectra, although it was very weak in the vinyl and trifluoro adduct spectra. CF_3COS^+ was very weak in the fluorinated adducts and not present in the ethyl adduct. CF_3COSH^+ was found only in the vinyl and vinylidiene adducts. A 131 peak, however, was present in all but the vinylidiene spectra and was quite strong in the vinyl adduct spectrum. This might correspond to $CF_3COSH_2^+$.

TABLE 7

MASS SPECTRUM DATA

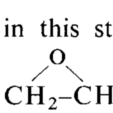
Compound	Peak *m*/*e* and identity[a]
$CF_3COSCH_2CH_3$	28(CO^+, N_2^+), 29($CH_3CH_2^+$, COH^+), 45 (CSH^+), 61($CH_3CH_2S^+$), 69(CF_3^+), 89($COSCH_2CH_3^+$), 158($CF_3COSCH_2CH_3^+$)
$CF_3COSCH_2CH_2F$	29(COH^+), 47($CH_2CH_2F^+$, COF^+), 69(CF_3^+), 100(?), 107($COSCH_2CH_2F^+$), 131($CF_3COSH_2^+$), 176($CF_3COSCH_2CH_2F^+$)
$CF_3COSCH_2CHF_2$	28(CO^+, N_2^+), 45(CSH^+), 46(CH_2S^+), 47(COF^+), 51(CF_2H^+), 65($CH_2CHF_2^+$), 69(CF_3^+), 77(?), 97(CF_3CO^+), 125($COSCH_2CHF_2^+$), 194($CF_3COSCH_2CHF_2^+$)
$CF_3COSCHFCHF_2$	28(CO^+, N_2^+), 32(CHF^+, O_2^+, S^+), 69(CF_3^+), 143 ($COSCHFCF_2H^+$), 212($CF_3COSCH_2CHF_2H^+$)[b]
$CF_3COSC(CF_3)_2OH$	18(H_2O^+), 31(CF^+), 32(O_2^+, S^+), 33(SH^+), 44(CS^+), 50(CF_2^+), 51(?), 60(COS^+), 61($COSH^+$), 63(?), 69(CF_3^+), 78(?), 97(CF_3CO^+), 100(?), 130(CF_3COSH^+), 147($CF_3COCF_2^+$), 166($CF_3COCF_3^+$)
$CF_3COSCH_2CH_2OH$	27($C_2H_3^+$), 43(CH_2CHO^+), 45($CH_2CH_2OH^+$), 47(CH_2SH^+), 59($C_2H_3S^+$), 60(COS^+), 61($COSH^+$), 69(CF_3^+), 141(CF_3COSC^+), 155($CF_3COSC_2H_2^+$), 156($CF_3COSC_2H_3^+$), 174($CF_3COSCH_2CH_2OH^+$)

[a] Only peaks over 10 % intensity are included unless of special interest.

[b] Peaks under 10 % intensity.

In all cases, the mass spectra did re-affirm the proposed structures.

EXPERIMENTAL

The chemicals used in this study ($CH_2{=}CH_2$, $CH_2{=}CHF$, $CH_2{=}CF_2$, $CHF{=}CF_2$, CF_3COCF_3,  $\overset{O}{CH_2{-}CH_2}$ were purchased as reagent grade and used as received. The infrared spectra of the chemicals were taken where possible and agreed with the published spectra.

All handling of liquids and gases at room temperature was performed with a Pyrex glass vacuum system equipped with Eck and Krebs stopcocks.

Ultraviolet reactions were performed using a 5 l round-bottom flask fitted with a water-cooled quartz cold-finger. A 100 W Hanovia mercury arc lamp was used to irradiate the reactants.

The infrared spectra were recorded on a Perkin–Elmer 137 Infracord Spectrophotometer. The infrared cell was made of monel metal and equipped with a Whitey-brass valve. Path length of the cell was 8.25 cm. The infrared spectra of solids and non-volatile liquids were taken neat between NaCl plates.

The proton magnetic resonance spectra were obtained with a Varian Model A-60 analytical NMR spectrometer. The fluorine spectra were obtained with a Varian Model HA-100 high resolution NMR spectrometer operating at 99.7 Mcps. Frequencies were determined using the audio side-band technique.

Mass spectra were taken on a CEC 21-110B double-focus mass spectrometer equipped with a 6 kV ion accelerator and operated at 72 V. Polyfluoroamine (PFA) was used as an internal standard.

The ultraviolet spectra were recorded using a Cary Model 14 recording spectrophotometer. The liquid spectra were taken with a cell having a path length of 1.00 cm. The cyclohexane used in this work was Gas Chromatographic–Spectrophotometric quality (J. T. Baker Co.).

Indices of refraction were determined using a Bausch and Lamb Abbe-3L refractometer. Vapor pressure data were obtained by holding the compound in a liquid state at various temperatures and reading the pressure on a mercury manometer.

General Preparation

The same general method was used for all of the fluoro-olefin reactions. In a typical reaction, a slight excess of TFTAA was condensed with a fluoro-olefin in a 5 l Pyrex round-bottom flask. The reactants were warmed to room temperature. Excess nitrogen was found to improve the yield for all but the vinyl fluoride reactions, and was then added to all but this reaction. The reactants were exposed to UV light and the course of the reaction was followed on a manometer. When the pressure stopped decreasing (approximately 30 min) irradiation was stopped. The products were pumped slowly through a liquid nitrogen trap which permitted collection of all products and excess reactants, while removing the nitrogen and possibly CO produced during the reaction. In all cases there remained behind a colorless pool of liquid at the bottom of the reaction vessel, which was assumed to be a higher polymer. The infrared spectra of this material showed more peaks than for the monomer product, in addition to having the carbonyl and CF_3 peaks present. The transferred product was distilled under reduced pressure, yielding 30 to 70% of the monomer.

Preparation of $CF_3COSCH_2CH_3$

In a 1 l Pyrex glass reaction vessel, 2.15×10^{-2} mole of CF_3COSH and 2.05×10^{-2} mole of $CH_2{=}CH_2$ were irradiated for 10 min. The volatile materials were pumped away through a trap cooled to −195.8°, leaving behind a non-volatile polymeric oil. The product (1.2×10^{-2} mole) was a colorless liquid (yield *ca.* 49%), and was found to be $CF_3COSCH_2CH_3$. Calcd. mol. wt. for $CF_3COSCH_2CH_3$ 158; found 158.

The infrared spectrum agreed with the published value.

Preparation of $CF_3COSCH_2CH_2F$

In a 5 l Pyrex round-bottom ultraviolet apparatus, 3.22 × 10^{-2} mole of CF_3COSH and 3.22 × 10^{-2} mole of $CH_2{=}CHF$ and excess N_2 were irradiated together for 40 min. The product (1.0 × 10^{-2} mole) is a colorless liquid with a strong onion-like odor (yield *ca.* 31%), (nc). Calcd. for $C_4H_4F_4OS$: C, 27.3; H, 2.3; F, 43.2; S, 18.1; mol. wt. 176. Found: C, 27.2; H, 2.2; F, 43.1; S, 17.9; mol. wt. 179.5.

Preparation of $CF_3COSCH_2CHF_2$

In a 5 l Pyrex round-bottom ultraviolet apparatus, 4.13 × 10^{-2} mole CF_3COSH and 3.89 × 10^{-2} mole $CH_2{=}CF_2$ and excess N_2 were irradiated for 40 min. The product (1.13 × 10^{-2} mole) is a colorless liquid with a strong disagreeable odor (yield *ca.* 29%), (nc). Calcd. for $C_4H_3F_5OS$: C, 24.7; H, 1.5; F, 49.0; S, 16.5; mol. wt. 194. Found: C, 24.8; H, 1.5; F, 48.9; S, 16.5; mol. wt. 201.5.

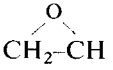
Preparation of $CF_3COSCHFCHF_2$

In a 5 l Pyrex round-bottom ultraviolet apparatus, 3.88 × 10^{-2} mole CF_3COSH and 3.51 × 10^{-2} mole $CHF{=}CF_2$ and excess N_2 were irradiated for 30 min. The product (2.31 × 10^{-2} mole) is a colorless liquid with a strong disagreeable odor (yield *ca.* 66%), (nc). Calcd. for $C_4H_2F_6OS$: C, 22.6; H, 0.9; F, 53.8; S, 15.2. Found: C, 22.6; H, 1.8; F, 47.4; S, 14.2.

Preparation of $CF_3COSC(CF_3)_2OH$

In a 1 l Pyrex vessel, 1.46 × 10^{-3} mole CF_3COSH and 1.33 × 10^{-3} mole $(CF_3)_2CO$ were condensed together at −195.8°. Warming slowly from −195.8° to room temperature resulted in disappearance of the yellow thio acid and the appearance of a colorless liquid. 0.8 × 10^{-2} mole of product was produced (yield *ca.* 60%): b.p. 48.5°C (760 mm Hg), n^{25} 1.3244, (nc). The product dissociates in the vapor phase into the starting materials. Two peaks were obtained from gas chromatography on a 1.5 m × 1 cm 60/80 chromosorb W column coated with 5% QF-1 at 35°, flow rate 30 ml/min. One peak was at 1.75 min and the other at 2.83 min (same as for CF_3COSH). Calcd. for $C_5HF_9O_2S$: C, 20.3; H, 0.3; S, 10.8. Found: C, 20.3; H, 0.4; S, 10.9.

Preparation of $CF_3COSCH_2CH_2OH$

In a 1 l Pyrex vessel, 3.19 × 10^{-2} mole  $\overset{O}{CH_2{-}CH}$ was condensed with 2.69 × 10^{-2} mole CF_3COSH at −195.8°. Warming slowly resulted in the production of a bright yellow liquid at −78°. Upon further warming to room temperature, a very exothermic reaction occurs which produces a colorless liquid that is solid at −78°: 1.61×10^{-2} mole of product was produced (yield *ca.* 54%): b.p. 134° (760 mm Hg), n^{25} 1.3918, (nc). Calcd. for $C_4H_5F_3O_2S$: C, 27.6; H, 2.9; S, 18.4. Found: C, 27.6; H, 2.7; S, 18.1.

The compound forms a white solid and CF_3COOH when heated, m.p. 193–194°. Calcd. for C_2H_4S: C, 40.0; H, 6.67; S, 53.3. Found: C, 39.1; H, 6.55; S, 51.8.

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