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ULTRASONIC PHOTOLYSIS OF METHYL DISULFIDE AND HEXAFLUOROBUTADIENE

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SUMMARY

An ultrasonic photolytic method was described for preparing adducts of hexafluorobutadiene and methyl disulfide. In the presence of an excess CH_3SSCH_3, the major product was trans-1,4-bis(methylthio)hexafluoro-2-butene. The minor products were the 1:2 adducts ($CH_3SSCH_3 \cdot 2C_4F_6$) in the presence of a mixture, which consisted of a small amount of other oligomeric mixtures and isomeric 1:1 adducts.

INTRODUCTION

Several sonochemical syntheses in mixed phase systems were reported [1-3]. Recently, Ishikawa and Kitazume [4] reported the perfluoroalkylation of organic compounds assisted by ultrasound. In this paper, we report on a reaction in a vacuum-sealed quartz tube containing immiscible methyl disulfide and hexafluorobutadiene under ultrasonic photolysis.

RESULTS AND DISCUSSION

The addition of methyl disulfide to hexafluoro-2-butyne was reported to readily form an equal mixture of cis- and trans-2,3,-bis(methylthio)hexafluoro-2-butene under photolysis [5]; whereas the solution photolysis of hexafluorobutadiene and methyl disulfide from ambient to 100°C for 3 to 24 hours did not produce detectable products. Ultrasound facilitated the latter reaction to form adducts. The underlying reason of synthesizing hexafluorobutadiene/methyl disulfide adducts is to explore their oxidation products as multifunctional perfluorocarbon sulfonic acids.

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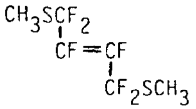
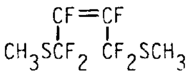
Since hexafluorobutadiene and methyl disulfide are immiscible, ultrasound was introduced to homogenize the reactants, but no products were detected. However, the combination of ultrasound and photolysis provides a convenient method to form trans-1,4-bis(methylthio)hexafluoro-2-butene(I) as the major product by using an excess of CH_3SSCH_3. The minor products were the isomeric 1:2 adducts ($CH_3SSCH_3 \cdot 2C_4F_6$), a mixture containing isomeric 1:1 adducts ($CH_3SSCH_3 \cdot C_4F_6$) [i.e., cis-1,4-bis(methylthio)hexafluoro-2-butene (II) and two other structurally undefined isomers] and other oligomeric adducts.



$CH_3SCF_2CF{=}CFCF_2SCH_3$

I



$CH_3SCF_2CF{=}CFCF_2SCH_3$

II

The proposed reaction sequence described below follows a free radical 1,4-addition of conjugated diene route [6] and is shown to be the prevailing reaction path consistant with the main product.

Initiation

$$CH_3SSCH_3 \xrightarrow{h\nu} 2CH_3S\bullet \qquad (1)$$

Propagation

$$CH_3S\bullet + CF_2{=}CFCF{=}CF_2 \longrightarrow CH_3SCF_2CF{=}CFCF_2\bullet \qquad (2)$$

Termination

$$CH_3SCF_2CF{=}CFCF_2\bullet + CH_3S\bullet \longrightarrow CH_3SCF_2CF{=}CFCF_2SCH_3 \qquad (3)$$

Besides the two common cis- and trans-1,4-adducts (I and II), there were another two isomeric $CH_3SSCH_3 \cdot C_4F_6$ adducts whose structures were partially elucidated by GC-mass spectroscopy and NMR spectra. The AB-pattern of ^{19}FNMR suggests three-membered ring structures [7,8]. These cyclic isomers were likely caused by ultrasound effect, as recently stated by Suslick that sonochemical products can be unpredictable by analogy to either their thermal or photochemical reaction [9].

The reaction products were subjected to fractional distillation to remove the excess CH_3SSCH_3 prior to gas chromatographic separation. The GC-ir data indicated, the products were in the second and third fractions, whereas the first fraction was CH_3SSCH_3, which showed an absorption band at 2940 cm^{-1}.

There was no noncondensable gas and only one small amount of volatile compound with absorptions at 1770, 1320, 1290, 1240, and 970 cm^{-1}, identified as hexafluorobutadiene [10], was detected. The gas chromatography was packed with 20% OV-210 on Chromasorb W and run at about 220°C with helium as the carrier gas at a flow rate of 30 ml/min.

Table I summarizes ^1H and ^{19}FNMR data of the two isomers (I and II). The ^{19}F chemical shifts are converted to ϕ-values upfield from fluorotrichloromethane by using the value of 61.9 ppm for 1,2-dichloro-1,1-difluoroethane. The latter compound CH_2ClCF_2Cl was added as an internal standard for both ^{19}FNMR and ^1HNMR of the sample. The singlet at δ 2.39 downfield from tetramethylsilane (Me_4Si) is the methyl groups of I and II. The ^1HNMR chemical shift of the methyl groups of $(CH_3S)_2C{=}C(SCH_3)_2$ was reported at δ 2.33 ppm in the literature [11].

The GC-mass spectral data of the main fraction (i.e., the second fraction, 60%) show four peaks with one predominant peak (I) over the other three peaks (II and two isomers) at the ratio of 50:5:1:3. The m/e values of parent ions of the four peaks are identical at 256 ($C_6H_6F_6S_2^+$), but at four different elution times, indicating the presence of four isomers. The mass fragments of the isomer (II) immediately following the eluted first predominant peak (I) are identical; whereas the latter two peaks' mass fragments are the same, but differ from the fragment patterns of I and II. In particular, it is the presence of mass fragment 209 peaks (i.e., parent ion at 256 minus the mass of SCH_3 at 47) for I and II, but absent for the other two isomers; while mass fragment 159 peaks (i.e., the parent ion at 256 minus the mass of CF_2SCH_3 at 97) are present for all four isomers.

The complex product mixture of the third main fraction (15%) consists chiefly of 1:2 adducts ($CH_3SSCH_3\cdot 2C_4F_6$) of m/e value of parent ion at 418 ($C_{10}H_6F_{12}S_2^+$) in the presence of trace amounts of other oligomeric adducts [e.g., at mass 512 for 2:2 adducts ($2CH_3SSCH_3\cdot 2C_4F_6$) and 580 for 1:3 adducts ($CH_3SSCH_3\cdot 3C_4F_6$)].

EXPERIMENTAL

Materials and Apparatus

Hexafluorobutadiene was purchased from PCR and methyl disulfide from Aldrich Chemical. These reagents were checked by infrared spectroscopy and used as received.

TABLE I

^{1}H and ^{19}F NMR spectra of <u>cis</u>- and <u>trans</u>-1,4-bis(methylthio)hexafluoro-2-butene

		^{19}FNMR				^{1}HNMR	
Compound	Relative Intensity (No. F)	Chemical Shift ϕ(ppm from $CFCl_3$)	Coupling Constant Hz	Assign-ment	Relative Intensity (No. H)	Chemical Shift δ(ppm from TMS)	Assign-ment
b 1a 2a 3a4a b $CH_3SCF_2CF{=}CFCF_2SCH_3$							
Trans-isomer (I)	4	84.5 doublet	7.5	1a, 4a	6	2.39 singlet	b
	2	156.3 triplet	7.5	2a, 3a			
Cis-isomer (II)	4	84.4 doublet*	17	1a, 4a			
	2	139.5 triplet*	17	2a, 3a			
b a CH_2ClCF_2Cl**	2	61.9 triplet		a	2	4.04 triplet	b

* with second order effect
** internal standard

A sonicator (Model W-370) was purchased from Heat Systems-Ultrasonic with a cup horn attachment. The horn was the resonant body, which vibrated at 20 kHz (20,000 cycles per second) and served as a second stage of acoustic amplification. The standard tapped titanium disrupter horn was immersed in water during sonication.

Vacuum manipulations were carried out in a copper-Monel system with copper traps. Pressures were measured with a Heise gauge (0-100 cm Hg absolute with 500 increments) to accuracy of 1 mm Hg. The amount of volatile reactant was determined by P-V-T measurements, assuming ideal gas behavior. A quartz reaction vessel was used. The quartz bottom end, which contained the reactants, was suspended under the water level in the horn cup. A 200-watt high pressure mercury arc lamp was the outside irradiation source.

^{1}HNMR and ^{19}FNMR were recorded on a Nicolet spectrometer operating at 200 and 188 MHz and 35°C. Mass spectra were determined on a LKB 9000 Model GC/MS instrument. The elemental analysis was obtained by a CEC21-110-B mass spectrometer. The infrared spectra were measured on a Perkin-Elmer 567 spectrophotometer and with a chromatographic infrared analyzer (CIRA 101).

Procedure

Hexafluorobutadiene (10 mmol) was condensed onto an evacuated frozen excess of methyl disulfide in a quartz reaction tube at -196°C. The quartz tube was vacuum-sealed, warmed to ambient temperature, and suspended vertically with the immiscible reactants in the quartz bulb under the water level in the cup horn. The immiscible reactants easily homogenized under ultrasound and were simultaneously subjected to photolysis for 24 hours. After the sealed tube had been removed from the horn cup, the colorless immiscible liquids turned to a homogenous dark orange liquid, which was cooled to -196°C and the tube was opened and evacuated without detection of noncondensable gas.

The dark orange residual liquid was fractionally distilled to remove the excess CH_3SSCH_3, prior to gas chromatographic separation. The GC-ir and GC-mass spectral data are described in the Results and Discussion section. The ^{19} F and ^{1}H NMR of I and II are summarized in Table I.

Mass spectroscopic molecular weight (CEC21-110-B) of a mixture of the four $CH_3SSCH_3 \cdot C_4F_6$ adduct isomers: Calcd. for $C_6F_6H_6S_2$: 255.9801. Found: $C_6F_6H_6S_2$: 255.9815.

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