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HIGH PRESSURE ISOMERIZATION OF 1,4-BIS(METHYLTHIO)HEXAFLUORO-2-BUTENE TO -1-BUTENE

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SUMMARY

The complete bond migration of the internal olefinic bond of trans-1,4-bis(methylthio)hexafluoro-2-butene(I) under high pressure to the terminal olefinic bond to form cis- and trans-1,4-bis(methylthio) hexafluoro-1-butene(II) is described. The Teflon-lined high pressure cell maintains a constant pressure at 16,000 atm and 180 to 200°C for 24 hours. The cis- and trans-II are elucidated from gas chromatography-mass spectroscopy, which shows two identical parent ions at m/e value of 255($C_6H_6F_6S_2^+$), but at different elution times. The ^{19}FNMR data of the isomeric products are summarized. Elemental analysis of II is verified by double focussing high resolution mass spectrometer.

INTRODUCTION

In the course of our investigation on the methyl disulfide addition reactions to hexafluoro-2-butyne by photolysis [1] and to hexafluorobutadiene under ultrasonic photolysis [2], we reported the formation of 1:1 adducts ($CH_3SSCH_3 \cdot C_4F_6$). In the former case an equal mole ratio of cis- and trans-2,3-bis(methylthio)hexafluoro-2-butene was formed; whereas in the latter example the main product was the trans-isomer of 1,4-bis(methylthio)hexafluoro-2-butene(I) in the presence of trace amounts of cis-I and other two structurally unidentified isomeric 1:1 adducts. The minor products of the latter example were the isomeric 1:2 adducts ($CH_3SSCH_3 \cdot 2C_4F_6$). The oligomeric adducts (e.g., $2CH_3SSCH_3 \cdot 2C_4F_6$, $CH_3SSCH_3 \cdot 3C_4F_6$ and $CH_3SSCH_3 \cdot 4C_4F_6$) in trace amounts from the latter example were only identified by gas chromatography-mass spectroscopy [3].

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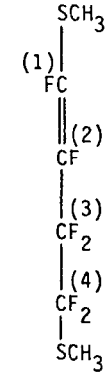
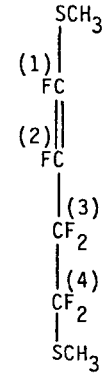
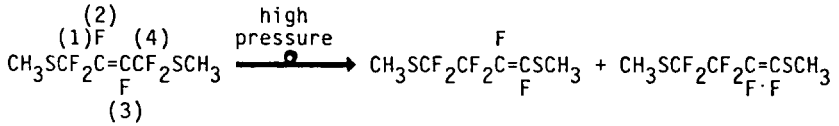
RESULTS AND DISCUSSION

In this paper we report that the isolated trans-I fraction underwent complete bond migration under high pressure from internal to terminal olefinic bond to form cis- and trans-bis(methylthio)hexafluoro-1-butene(II):

TABLE 1
^{19}FNMR spectral data of cis- and trans-1,4-bis(methylthio)hexafluoro-1-butene

Compound	Relative Intensity	Assignment	Chemical Shift ϕ(ppm from $CFCl_3$)	Coupling Constant J(Hz)
 trans-II	2	(4)	95.9	J(3,4)=7.5; J(2,4)=5.0; J(1,4)=6.5;
	2	(3)	118.0	J(2,3)=26; J(1,3)=15; J(1,2)=143
	1	(2)	128.0	
	1	(1)	157.8	
 cis-II	2	(4)	95.5	J(3,4)=8; J(2,4)=6; J(2,3)=13;
	1	(1)	104.2	J(1,3)=2(?); J(1,2)=5
	2	(3)	115.2	
	1	(2)	139.5	



trans-I trans-II cis-II

Table 1 summarizes the ^{19}FNMR data of the products, trans-II and cis-II. The assignment of trans-II's coupling constant 143Hz for its J(1,2) was based on the reported values for trans-olefinic fluorine in related compounds [4,5].

The ^{19}FNMR data of Table 1 are identical to the ^{19}FNMR of the previously unidentified isomeric 1:1 adducts, when we reacted CH_3SSCH_3 and CF_2=CFCF=CF_2 under ultrasonic photolysis. We reported the existence of four isomeric 1:1 adducts, but only two were structurally identified as cis- and trans-I [2]. The present high pressure study helped to clarify the previous results. The unidentified $CH_3SSCH_3 \cdot C_4F_6$ adduct isomers were cis- and trans-II. Their presence in trace quantities can be explained by the high local pressure charges caused by the ultrasonic cavitation phenomenon; whereas under continuous high pressure on the total sample, trans-I completely isomerized to cis- and trans-II.

The starting material (trans-I) was isolated from a GC-column as previously described [2]. It was the major product and was eluted from the column prior to cis-I and the other adduct products. The ^{19}FNMR data agreed with previous data [2]: ϕ84.5 ppm[doublet, J(1,4)=7.5Hz, relative peak area 4,4F,2CF_2] and 156.3 ppm [triplet, J(2,3)=7.5Hz, relative peak area 2,2F,2CF] from $CFCl_3$.

The trans-II fraction (0.01ml) and CH_3SSCH_3 (0.01ml) were added into a Teflon-TFE lined aluminum cell. After the liquid-filled high pressure cell with a fitted Teflon-TFE lined aluminum lid had been pressed in place and loaded into a steel block with a cylindrical hole and two high strength steel plugs at each end of the sample cell, the applied constant pressure reached 16,000 atm. Then the cell temperature was raised to 180 to 200°C for 24 hours at a constant pressure of 16,000 atm. Trans-I was completely isomerized to trans- and cis-II at the ratio of 57% and 43% respectively in the presence of some oligomers and black solid.

Table 1 summarizes the ^{19}FNMR of the trans- and cis-II. The GC-mass spectral data showed identical parent ion peaks at 256($C_6F_6H_6S_2^+$) and also same mass cracking patterns, except at different elution times.

Mass spectroscopic weight (CEC21-110-B) of trans- and cis-II: Found, 255.9815. Calculated for $C_6F_6H_6S_2$: 255.9801.

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