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PHOTOSONOSYNTHESIS OF 1,2,4-TRIS(METHYLTHIO)-3-H-HEXAFLUORO-n-BUTANE

MADELINE S. TOY and ROGER S. STRINGHAM
Science Applications International Corporation, 1257 Tasman Drive, Sunnyvale, CA 94089 (USA)

SUMMARY

The preparation of neat 1,2,4-tris(methylthio)-3-H-hexafluoro-n-butane is described. The mechanism, which involves the elimination of hydrogen fluoride with the subsequent isomerization in forming the cis- and trans-1,2,4-tris(methylthio)hexafluoro-1-butene, is discussed. This study also supports the presence of methanethiol as an intermediate during the photosonoreaction of bis(methylthio)hexafluoro-2-butene with an excess of methyl disulfide.

INTRODUCTION

For our synthesis of the perfluoroalkanepolysulfonic acids, we started with the unsaturated perfluorocarbons such as hexafluorobutadiene and hexafluoro-2-butyne in the presence of an excess of methyl disulfide to form the poly(methylthio) adducts as the precursors prior to the oxidations. Although the isomeric 1:1 adducts [i.e., the cis- and trans-2,3-bis(methylthio)hexafluoro-2-butene in an equal mole ratio] were readily formed from hexafluoro-2-butyne and methyl disulfide under photolysis [1] or thermolysis [2], the adducts with hexafluorobutadiene were difficult to form. The several attempted syntheses by photolysis alone with prior emulsification, solution photolysis, sonolysis singly or thermolysis up to 230° C for 24 hr were unsuccessful; but the combined photolysis and ultrasound provided a convenient path to synthesize the trans-1,4-bis(methylthio)hexafluoro-2-butene (I, the trans-1,4-adduct) as the major product in the presence of trace amounts of the other 1:1 adducts and a minor quantity of the oligomers (Eq. 1) [3]:

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$$CF_2{=}CFCF{=}CF_2 + XS.CH_3SSCH_3 \xrightarrow{UV))} CH_3SCF_2\underset{F}{\overset{F}{C}}{=}\underset{F}{\overset{F}{C}}CF_2SCH_3 +$$

trans-I (major product)

$$CH_3S(C_4F_6)_nSCH_3 +$$

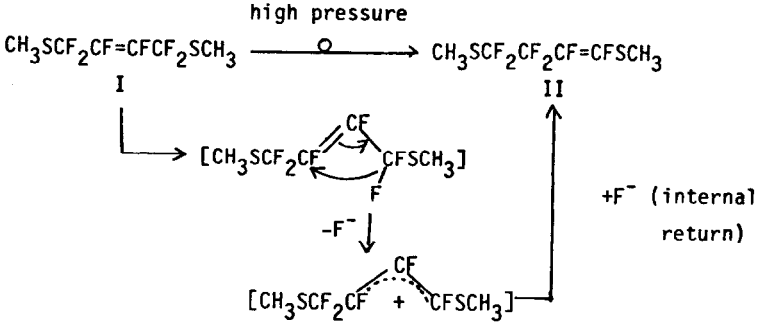
oligomers (minor)

$$CH_3SCF_2\underset{F}{\overset{F}{C}}{=}\underset{F}{\overset{F}{C}}CF_2SCH_3 + CH_3SCF_2CF_2CF{=}CFSCH_3 \qquad (1)$$

cis-I (trace) cis- and trans-II (trace)

The four 1:1 adduct products were the two commonly expected cis- and trans-I and the other two were very unusual adducts, which were later identified as the cis- and the trans-1,4-bis(methylthio)hexafluoro-1-butene (II). We then subjected the trans-I and CH_3SSCH_3 to a very high pressure of 16,000 atm at 200°C for 24 hr [4]. We obtained the cis- and trans-II as products instead of the saturated adduct. This high pressure isomerization result supports the trace amount of cis- and trans-II in Eq. 1 due to the sonication effect, which creates localized very high pressure and temperature. Although the localized 'hot spots' last only a few nanoseconds, new compounds have been reported to form and can be different from those arising by photochemical and thermal means [5].

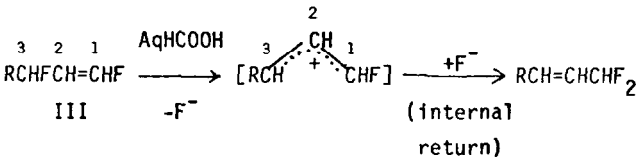
The high pressure isomerization of I to II is an example, where the internal olefinic bond migrates to the terminal position [4]. The suggested mechanism involves an allylic fluoride (Eq. 2):



(2)

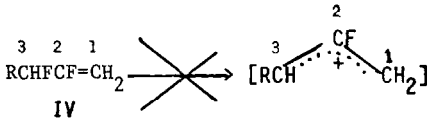
It is believed that the intermediate proceeds through an ion-pair and is analogous to the 'internal return' of S_Ni' (substitution-nucleophilic-internal-with rearrangement) reaction [6,7] to form II.

Another similar example is III, which involves the solvolysis of an allylic fluoride, where fluorine at the 1-position is postulated to stabilize an attached carbonium ion (Eq. 3); whereas in the case of its isomer IV, the fluorine at the 2-position appears to be unfavorable and solvolysis does not occur (Eq. 4) [8]:



(3)

(R=$CF_3CH_2CHFCH_2$-)



(4)

RESULTS AND DISCUSSION

Recently when we reacted the trans-*I and an excess of methyl disulfide* under a previously described photosonosynthetic condition [3] but with a prolonged reaction time, the yield of the fully saturated methylthio adduct $CH_3SCF_2CF(SCH_3)CF(SCH_3)CF_2SCH_3$ [V, 1,2,3,4-tetrakis(methylthio)-hexafluoro-n-butane] was extremely poor. When we increased the pressure by adding an inert perfluoropropane in the sealed quartz reactor with the same reactants, we obtained about 50% of the product V and 40% of the *by-product 1,2,4-tris(methylthio)-3-H-hexafluoro-n-butane* VI [9].

In order to improve the yield of V, we aimed to understand how the by-product VI was formed. We reasoned that the formation of VI may be due to the presence of methanethiol in the reaction mixture. The commercial CH_3SSCH_3 was redistilled, but the presence of VI was unaffected. We then proposed that CH_3SH formation is from the hydrogen atom abstraction by a *methylthio radical* ($CH_3S\cdot$) *from the reactant* CH_3SSCH_3 *or another* $CH_3S\cdot$ radical.

The following reaction sequence (Eq. 5 to 10) explains methanethiol as an intermediate to form VI, when I reacted with an excess of CH_3SSCH_3. The process is initiated by the homolytic S-S bond breaking of CH_3SSCH_3 to yield a pair of methylthio free radicals (Eq. 5).

$$CH_3SSCH_3 \overset{\text{UV}}{\rightleftharpoons))\longrightarrow} 2CH_3S\cdot \qquad (5)$$

where))) indicates sonication. The $CH_3S\cdot$ radical abstracts a hydrogen atom from another CH_3SSCH_3 molecule (Eq. 6):

$$CH_3S\cdot + CH_3SSCH_3 \longrightarrow CH_3SH + CH_3SSCH_2\cdot \qquad (6)$$

or from another $CH_3S\cdot$ radical by disproportionation (Eq. 7):

$$CH_3S\cdot + CH_3S\cdot \longrightarrow CH_3SH + CH_2{=}S \qquad (7)$$

where thioformaldehyde is likely to be polymerized or formed an adduct in the presence of $CH_3S\cdot$ radicals (Eq. 8):

$$2CH_3S\cdot + nCH_2{=}S \longrightarrow CH_3S(CH_2S)_nSCH_3 \qquad (8)$$

where n=1 or greater. Our unpublished result has shown oligomers, which contain no fluorine. The methanethiol from Eq. 6 and 7 dissociates under UV and ultrasound to form the hydrogen atom and $CH_3S\cdot$ radical (Eq. 9):

$$CH_3SH \overset{\text{UV}}{\longrightarrow))\longrightarrow} CH_3S\cdot + H\cdot \qquad (9)$$

to add to the olefinic bond of I to form VI. The rate of the radical addition from CH_3SH (i.e., $H\cdot$ and $CH_3S\cdot$ of Eq. 9) to I is much faster than the radicals from CH_3SSCH_3 (i.e., $2CH_3S\cdot$ of Eq. 5) to form the saturated adduct. This point is confirmed below.

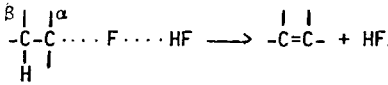
In the present experiment, CH_3SH is added as a reactant at a 1:1 mole ratio to the trans-I in an excess of CH_3SSCH_3 and is not as solely derived from a secondary product (e.g., Eq. 6 and 7). The reaction (Eq. 10) was carried out to 20% completion and the product was pure VI in the absence of V.

$$\underset{\text{I}}{CH_3SCF_2CF{=}CFCF_2SCH_3} + \underset{\text{XS. } CH_3SSCH_3}{CH_3SH} \xrightarrow{UV} \underset{\text{VI}}{CH_3SCF_2\overset{(4)}{C}FH\overset{(3)}{C}F(SCH_3)\overset{(2)}{C}F_2\overset{(1)}{S}CH_3} \qquad (10)$$

When VI was passed through a GC-column (capillary, DB-5, 30 m) at 200°C, VI was resolved into the two isomers at a 1:2 ratio with the identical parent ions at 304 ($C_7F_6H_{10}S_3^+$) and the same fragmentation patterns. When the GC-mass spectral data show, that the two species have the identical parent ions and fragmentation patterns but with a different elution time, the two species are considered isomeric [1,10]. With the reference to the isomeric product ratio of VI from the ^{19}FNMR data (under Experimental), the GC elutes the isomer B (relative peak area 2) before the isomer A (relative peak area 1). Since VI (Eq. 10) contains the two dissimilar asymmetric carbons (*), the two isomers A and B, which are separable by GC, are suggested to be the two diastereomers, dl-VI and d'l'-VI, although the resolution of the optical isomers has not been carried out.

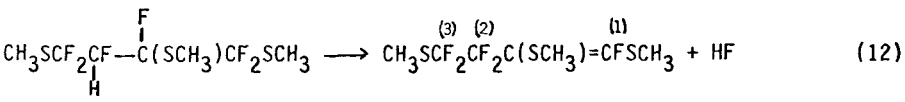
When VI was passed through the GC-columns (OV-17 at 0.9 m and 3.2 m of 0.63 cm od) at a higher temperature (280°C), the ease of hydrogen fluoride elimination with the subsequent isomerization to form 1,2,4-tris(methylthio)hexafluoro-1-butene (VII) was noted. These columns gave a broad single peak with no product separation of VII. From the ^{19} FNMR analysis, the isomers of VI were converted to a mixture of cis- and trans-VII (1:5 ratio) at a 59% conversion for the 0.9 m column (8.5 min at 280°C) and at a 71% for the 3.2 m column (29 min at 280°C). However, with a longer GC-column (capillary, DB-5, 30 m) and at a lower temperature (200°C), VII was resolved into the two isomers at a 1:5 ratio, which with the reference to the isomer ratio of VII from the ^{19}FNMR data (under Experimental) indicates that the cis-isomer elutes before the trans-isomer. Since the two species (i.e., with different elution times) have the identical parent ions at 284 ($C_7F_5H_9S_3^+$) and the same fragmentation patterns, the results confirm the existence of the two isomers for VII.

In general, the elimination of HF has been reported to be autocatalytic, due to the assistance in ionization by the hydrogen bonding between the leaving fluoride ion and hydrogen fluoride produced in the reaction (Eq. 11) [11]:



(11)

It is thus suggested that the β-elimination of HF from VI is one possible path and the other is the direct HF elimination from the CF_2 group. The concerted or subsequent isomerization in the GC-column is likely due to some catalytic substance on the column forming VII (Eq. 12):



(12)

VI VII

EXPERIMENTAL

The preparation of the trans-I, the photosonosynthetic apparatus and the analytical instruments were previously described [3].

Methanethiol (10 mmol) was condensed onto an evacuated frozen mixture of the trans-I (10 mmol) and an excess methyl disulfide in a quartz reaction tube at -196°C. The quartz tube was vaccum-sealed, warmed to ambient temperature, and suspended vertically with the liquid-liquid interphase in the quartz bulb under the water level in the sonicator's cup horn. The mixture was simultaneously subjected to ultraviolet irradiation and sonication for 8 hours. The temperature of the circulating water in the cup horn was maintained at 50°C. At the end of the reaction time, the sealed tube was removed from the horn cup, the homogeneous liquid was cooled to -196°C and the tube was opened and evacuated. The volatile fraction consisted mainly of methanethiol in the presence of some methyl disulfide. The residual liquid constituted the product VI (20% yield) and the reactants (trans-I and CH_3SSCH_3) in the absence of V.

The ^{19}FNMR ($CFCl_3$) of VI consists of the two isomers A and B at a 1:2 ratio. Isomer A: δ87.3 [center AB system, J(1A, 1B)=228 Hz, relative peak area 2,2F,$\underline{CF}_2$(1)], 161.3 [septet, J(2,5)=18 Hz, realtive peak area 1,1F,$\underline{CF}$(2)], 193.6 [doublet of quartets, J(3,5)=56 Hz, relative peak area 1,1F,$\underline{CF}$(3)], 86.0 [center AB system, J(1A,1B)=228 Hz, relative peak area 2,2F,$\underline{CF}_2$(4)]. Isomer B: δ84.1 [coalesced AB system, relative peak area 2,2F,$\underline{CF}_2$(1)], 165.7 [complex singlet, relative peak area 1,1F,$\underline{CF}$(2)], 195.4 [doublet of sextet, J(3,5)=54 Hz, relative peak area 1,1F,$\underline{CF}$(3)], 84.4 [center AB system, J(1A,1B)=231 Hz, relative peak area 2,2F,$\underline{CF}_2$(4)]. The GC-mass spectral data of VI show two species (i.e., with different elution times) with identical parent ions at 304($C_7F_6H_{10}S_3^+$) and the same fragmentation patterns. This confirms the ^{19}FNMR data for the two isomers of VI. See Results and Discussion.

Mass spectroscopic weight of the two isomers of IV: Calcd. for $C_7F_6H_{10}S_3$: 303.9849. Found 303.9851.

When the isomeric VI was passed through the GC-columns (OV-17 at 0.9 m and 3.2 m of 0.63 cm od) at 280°C, both columns gave VII as a broad single peak with no isomeric product separation at 8.5 min for the 0.9 m column and 29.0 min for the 3.2 m column. VII gives a strong ir absorption at 1590 cm^{-1} indicating an olefinic bond.

The ^{19}FNMR($CFCl_3$) of VII shows the cis- and trans-isomers at a 1:5 ratio. Cis-VII: δ 63.6 [complex singlet, J(1,2)=4 Hz, J(1,3)=8 Hz, relative peak area 1, 1F,$\underline{CF}$(1)], 105.5 [doublet triplet, J(2,3)=10 Hz, relative peak area 2,2F,$\underline{CF}_2$(2)], 93.5 [quartet, relative peak area 2,2F,$\underline{CF}_2$(3)]. Trans-VII: δ67.1 [pentet, J(1,2)=26 Hz, J(1,3)=10 Hz, relative peak area 1,1F,$\underline{CF}$(1)], 106.8 [doublet triplet, J(2,3)=10 Hz, relative peak area 2,2F,$\underline{CF}_2$(2)], 94.65 [quartet, relative peak area 2,2F,$\underline{CF}_2$(3)]. The GC-mass spectral data of VII show the two species. Its GC-column (capillary, DB-5, 30 m) at 200°C resolves the two isomers of VII at a 1:5 ratio. See Results and Discussion. The two species have different elution times but with the identical parent ions at 284 ($C_7F_5H_9S_3^+$) and the same fragmentation patterns. These results confirm the ^{19}FNMR data for the cis- and trans-isomers of VII.

Mass spectrosopic weight of the two isomers of VII: Calcd. for $C_7F_5H_9S_3$: 283.9787. Found: 283.9787.

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