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REARRANGEMENT OF ALLYL HEXAFLUOROISOPROPYL SULFIDES [1]

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SUMMARY

The rearrangement of terminal allylic hexafluoroisopropyl sulfides to the internal olefinic sulfide occurs under either photochemical or thermal conditions. In the case of the formation of E and Z isomers, the E isomer was predominant. The rearrangement is suggested as a unimolecular, associative radical mechanism, via kinetic studies, use of inhibitors, or radical initiator.

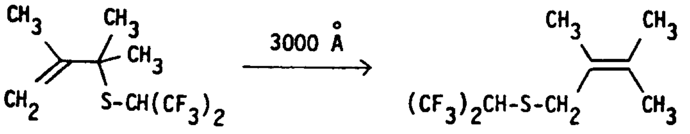
INTRODUCTION

During the course of the study of the ene reaction of hexafluorothioacetone (HFTA) generated in situ from tetrakis (trifluoromethyl)-1,3-dithietane (HFTA dimer) [2], a facile rearrangement of the allyl hexafluoroisopropyl sulfide was found. When 1,1,1,3,3,3-hexafluoro-2-propyl-1,1,2-trimethyl allyl sulfide was kept in a pyrex ampoule for several months, about half of it was changed to another component, but the mixture was still a clear liquid. When the mixture was subjected to 3000 Å light irradition for 24 hr, the starting allyl sulfide was totally changed to another component. Herein, we wish to report the rearrangement of allyl hexafluoroisopropyl sulfides.

α-Methylallyl methyl sulfide was reported to be rearranged to 2-butenyl methyl sulfide by light either in the presence or absence of methylmercaptan [3]. The major product was the Z-isomer. Also α,α-dimethylallyl phenyl sulfide was rearranged thermally to γ,γ-dimethylallyl phenyl sulfide in the presence of t-butyl hydroperoxide [4]. α-Methylallyl phenyl sulfide was rearranged thermally without a radical initiator or photochemically to 2-butenyl phenyl sulfide [5]. A detailed mechanistic study focused on the thermal rearrangement of allyl phenyl sulfides [6,7,8]. Both unimolecular and bimolecular pathways were involved in the rearrangement [6], and the associative transition state mechanism was suggested [7]. Interestingly, both triplet and singlet states of oxygen catalyzed the rearrangement [8]. However, a radical chain mechanism was also proposed for the thermal and photochemical rearrangement of aryl ally sulfide [9,10]. An acid catalyzed rearrangement of aryl allyl sulfide was also reported [9, 10].

RESULTS AND DISCUSSION

Freshly prepared 1,1,1,3,3,3-hexafluoro-2-propyl-1,1,2-trimethylallyl sulfide 1 was irradiated by 3000 Å light in a Pyrex ampoule. The rearrangement was completed within 24 hr to yield 1,1,1,3,3,3-hexafluoro-2-propyl-2,3-dimethyl-2-butenyl sulfide 2. The IR of 2 showed an C=C absorption at 1664 cm^{-1}. The terminal C=C absorption of 1 was 1622 cm^{-1}. ^{19}F NMR of 2 showed a doublet, J = 8 Hz, at ϕ^* 66.7 ppm. Although the chemical shift of 2 was very close to that of the starting sulfide 1 (66.4 ppm), these two doublets were clearly distinguishable. ^{1}H NMR of 2 showed overlapping signals at δ 3.46 ppm for the singlet of the methylene hydrogen and a heptet for the isopropyl hydrogen, J = 8 Hz. The chemical shifts of the three methyl groups of 2 coincided at δ 1.75 ppm [11]. However, ^{13}C NMR of 2 showed three different methyl groups at δ 17.4, 20.3, and 21.0 ppm.



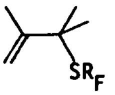
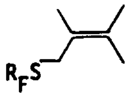
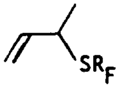
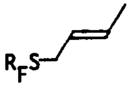
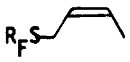
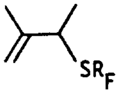
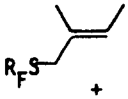
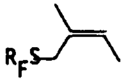
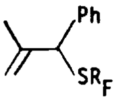
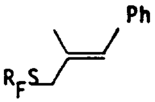
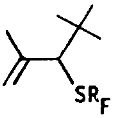
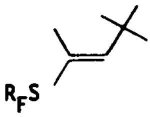
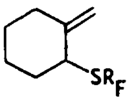
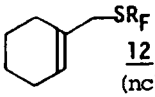
1 2

(Eq. 1)

Such a photochemical rearrangement was also achieved on various allyl hexafluoroisopropyl sulfides and the results are given in Table 1. Sulfide 3 was rearranged to a mixture of E and Z isomers of sulfide 4. The major product was isolated by preparative GLPC. Its stereochemistry was determined by computer analysis [12]. The calculation indicated the vinyl

TABLE 1

Rearrangement of Allyl Hexafluoroisopropyl Sulfide by 3000 Å Light[a]

Entry	Starting Sulfide[b]	Rearranged Product(s)[b]	Irradiation Period	Conversion %	Yield %
1	 1	 2	24 hr	100	100
2	 3	 4-E (nc) +  4-Z (nc)	10 days	92	100
3	 5 (nc)	 6-E (nc) +  6-Z (nc)	6 days	90	100
4	 7 (nc)	 8 (nc)	5 days	100[c]	100[c]
5	 9 (nc)	 10 (nc)	3 days	82	100
6	 11 (nc)	 12 (nc)	3 days	84	100

[a] In neat. [b] R_F represents $-CH(CF_3)_2$ group. [c] In $CDCl_3$ solution.

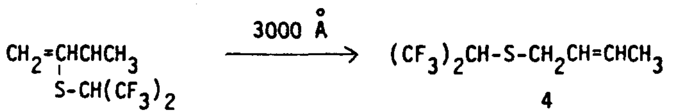
TABLE 2

Spectral Data of the Rearranged Product(s)

$(CF_3)_2CH\text{-}S\text{-}CH_2\text{-}CR_1{=}CR_2R_3$

Compound No.	^1H(δppm)					^{19}F(Ø*ppm)	IR^a(cm^{-1})
	$CH(CF_3)_2$	CH_2	R_1	R_2	R_3		
2	3.46 (hept) J = 8 Hz	3.46	1.75	1.75	1.75	66.7 (d) J = 8 Hz	1664
4 - E	3.61 (hept) J = 8 Hz	3.3	5.16 ~ 6.02		1.76	67.2 (d) J = 8 Hz	1668
6 - E	3.54 (hept) J = 8 Hz	3.26	1.73	1.73	5.41	67.2 (d) J = 8 Hz	1710^b
6 - Z	3.50 (hept) J = 8 Hz	3.41	1.64	1.64	5.50	67.2 (d) J = 8 Hz	
8	3.65 (hept) J = 8 Hz	3.5	5.85 ~ 6.71		7.36	66.4 (d) J = 8 Hz	1595 1576
10	3.63 (hept) J = 8 Hz	3.19	1.84	1.15	5.34	67.3 (d) J = 8 Hz	1657
12	3.60 (hept) J = 8 Hz	3.25	5.69	2.11	1.65	67.0 (d) J = 8 Hz	1662

^{a}Neat liquid ^{b}CCl_4 solution



$$\underset{S\text{-}CH(CF_3)_2}{CH_2{=}CHCHCH_3} \xrightarrow{3000\ \text{Å}} (CF_3)_2CH\text{-}S\text{-}CH_2CH{=}CHCH_3 \qquad \text{(Eq. 2)}$$

3 4 E and Z

protons coupling constant was 13.7 Hz, and this magnitude of coupling constant was in the range of trans proton-proton coupling [13]. The ratio of the above E and Z mixture was 4.8 : 1. Similarly, sulfide 5 gave a mixture of two products in a ratio of 5 : 1. By analogy to the predominant formation of the E-isomer of 4, the major product is assigned to the E-isomer of sulfide 6. In contrast to the formation of a mixture of E and Z isomers of 4 and 6, only one isomer was obtained from sulfide 7 and sulfide 9, respectively. The products are assumed to be the E-isomers.

TABLE 3

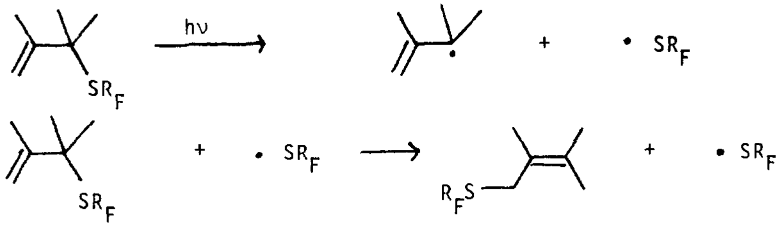
^{13}C NMR of the Rearranged Product(s)

Compound No.		$(CF_3)_2CH$ - S -	CH_2 -	CR_1 =	CR_2R_3	
	δ(ppm)	1 2	3	4	5	
	C_1	C_2	C_3	C_4	C_5	Others
2	123.9 (q) J = 279 Hz	50.0 (hept) J = 30.9 Hz	37.7	122.0	133.2	17.4, 20.3, 21.0
4 - E	123.4 (q) J = 282 Hz	48.9 (hept) J = 30.9 Hz	35.4	124.9	132.4	17.6
6 - E	123.4 (q) J = 276 Hz	48.6 (hept) J = 30.9 Hz	42.9	126.8	132.4	13.6, 14.0
6 - Z	123.6 (q) J = 274 Hz	49.0 (hept) J = 30.9 Hz	33.8	126.8	130.0	13.3, 21.6
8	123.1 (q) J = 278 Hz	48.9 (hept) J = 30.9 Hz	35.5			122.6, 126.4, 128.2 128.6, 135.3, 135.6
10	123.2 (q) J = 278 Hz	48.1 (hept) J = 30.9 Hz	44.9	127.7	143.2	15.1, 30.5, 35.5
12	123.3 (q) J = 273 Hz	48.7 (hept) J = 30.9 Hz	41.1	129.4	132.0	22.1, 22.6, 25.5, 26.1

Since the thermal rearrangement was known for aryl allyl sulfides [8, 9,10], 1 was subjected to a thermal rearrangement. At 135°C for 3.5 hr, 2 was formed in 94% yield, and 6% of 1 was found unrearranged. At 120°C for 24 hr, 2 was formed in 95%, and 5% of 1 was left unrearranged. After 3 days at 120°C, all of 1 was rearranged to 2. Trace amounts of four other peaks were detected by GLPC during the rearrangement at 135°C for 3.5 hr, but these did not increase or decrease during the rearrangement at 120°C for 3 days. These unidentified peaks were not detected in the photochemical rearrangement of 1. During the course of this study, Snider [14] reported the thermal rearrangement of 1 at 120°C for 12 hr in benzene solution. Under these conditions, the conversion of 1 was 55%, and 45% of 2 was found, and also 10% of 2,3-dimethyl-2-butene was detected. Interestingly, the thermal rearrangement of 3 was not clean. When 3 was heated at 130°C without solvent, 13% conversion of 3 was obtained after 21 hr, and the E and Z ratio of 4 was 2:1. After 2 days, 29% of conversion had occurred, and the E amd Z ratio of 1.6 was obtained. After 7 days, only a trace amount of 3 was left unchanged, but 14 other new peaks besides E and Z of 4 were detected by GLPC. These results suggested that the photochemical rearrangement was a better method than the thermal rearrangement.

MECHANISTIC ASPECTS OF THE PHOTOCHEMICAL REARRANGEMENT

Kinetic study of the photochemical rearrangement (3000 Å light) of 1 in benzene showed that the rearrangement was first order up to 86% conversion (Figure 1). From 86% to 97% conversion, the line deviated from first order, probably because of diffusion control. In the presence of radical inhibitors, such as p-benzoquinone, oxygen, and cumene, the rate of the rearrangement was depressed as shown in Figure 2. These results suggested that the rearrangement involved radical species. In contrast to the results obtained in this work, both triplet and singlet states of oxygen catalyzed the thermal rearrangement of phenyl ally sulfide [8]. A radical reaction mechanism was also suggested by the introduction of a radical intiator, instead of light irradiation. In the presence of a catalytic amount of azobisisobutyronitrile, 1 was heated in benzene at 75°C. 2 was formed in 58% yield in 5 min, 78% in 10 min, and 90% in 20 min. Under the same conditions in the absence of AIBN, 1 was not rearranged to 2 at all. Also various solvents were employed in the rearrangement. Polar solvents ($CHCl_3$, diglyme, acetophenone), and non-polar solvents (CCl_4, benzene) did not affect the rate of the rearrangement. Solvents with high dielectric constant (ε = 17.4 for acetophenone) and low dielectric constant (ε = 2.3 for benzene) also did not affect the rate of the rearrangement.



Mechanism of the Rearrangement

When 1 was irradiated in the presence of 2-methyl-2-butene, trace amounts of 5 and 6 (E and Z) were detected by GLPC, but these peaks did not change during 3 days irradiation, while 1 was rearranged to 2 in 90% conversion. These results suggested that the radicals formed from 1 by the light would be a primary pair of Noyes' model.

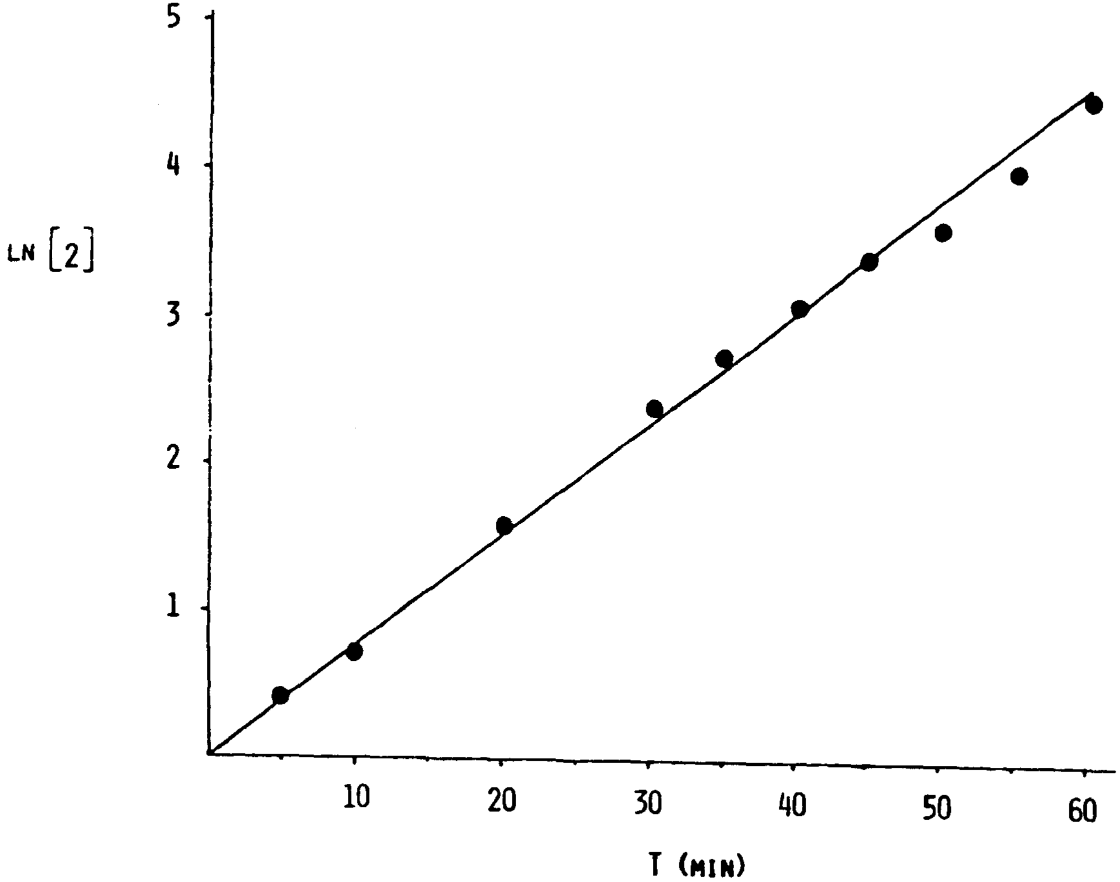


Fig.1. Kinetics of $\underset{\sim}{1}\xrightarrow{h\nu}\underset{\sim}{2}$; 0.47M in benzene at 35°C.

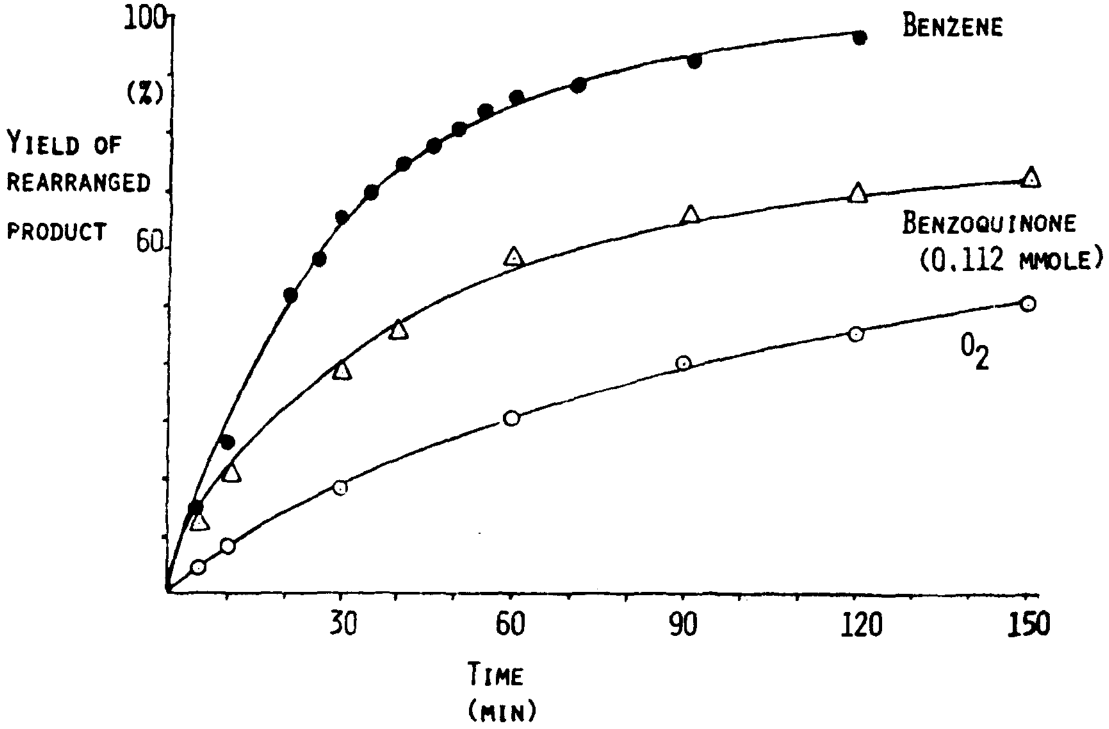


Fig.2. Radical inhibitor effect.

$CH_2{=}C(CH_3)C(CH_3)_2SCH(CF_3)_2 \xrightarrow{h\nu} (CF_3)_2CHSCH_2C(CH_3){=}C(CH_3)_2$;

0.2349 mmol/0.5 ml of solvent

CONCLUSION

The allyl hexafluoroisopropyl sulfides were rearranged to their internal olefinic sulfides by 3000 Å light irradiation or via thermal treatment. The E isomer was predominant. The rearrangement mechanism was first order and followed an associative radical mechanism.

EXPERIMENTAL

^{19}F NMR were recorded on a Varian HA-100 spectrometer operating at 94.075 MHz. ^{1}H NMR were obtained on a Varian A-60 spectrometer. Analytical GLPC were determined on Hewlett Packard 5750 Research Chromatograph. The column used in this work was a 10' x 1/4" column packed with 20% (w/w) SE-30 coated on 80-100 mesh Chromosorb P. A Varian Aerograph Model 700 was used for preparative GLPC, with a 10' x 1/2" column packed with 20% (w/w) SE-30 coated on 80-100 mesh Chromosorb P. Photochemical reactions were carried out in a Rayonet Photochemical Chamber Reactor.

Preparation of 1

The preparation of the starting allyl hexafluoroisopropyl sulfides were carried out by the ene reaction of HFTA generated *in situ* from HFTA dimer and potassium fluoride [2,15].

Potassium fluoride was dried over a Bunsen burner, well calcined, and again dried by flame. Potassium fluoride was weighed in a flask while it was hot.

Potassium fluoride (3.5 g, 60.3 mmole) was weighed into a flask equipped with septum capped side arm, magnetic stirring bar and glass stopper. The flask was connected to a condenser and dry nitrogen inlet tee. After cooling, 10 ml of DMF, 10 ml of 2,3-dimethyl-2-butene (92.8 mmole) and 10 ml of HFTA dimer (46.6 mmole) were injected. The reaction mixture was stirred at room temperature overnight. Then it was poured into water, and shaken vigorously. After the separated oil was collected, the aqueous phase was extracted with ether (3 x 10 ml), and the extract was combined with the oil and the ether solution was dried over anhydrous magnesium sulfate. Distillation at 44-45°C under 8 mm Hg gave 17.7 g of 1, 72% yield. Reported bp 61°C/20 mm Hg [16];IR 1622 cm^{-1} (terminal C=C). Reported 1639 cm^{-1} [16] ^{19}F NMR ϕ^* ppm 66.7 (d, J = 8 Hz, Reported 67.3 (d, J = 8 Hz) [16] ^1H NMR δ ppm 1.48 (6H), 1.88 (3H), 3.34 (heptet, J = 8 Hz) (1H), 4.95 (1H) 5.04 (1H). Reported δ 3.4 ppm (heptet, J = 8 Hz) [16] ^{13}C NMR δ ppm 19.1 (CH_3), 27.4 (CH_3) 49.7 (heptet, J = 30.9 Hz) (CH), 52.6 (C), 113.5, 147.3 (vinyl C), 123.3 (q, J = 279 Hz) (CF_3).

Similarly, 5, 9, and 11 were prepared from 2-methyl-2-butene, 2,4,4-trimethyl-2-pentene and 1-methylcyclohexene, respectively. Physical properties and spectral data are given as follows.

5 59°C/40 mm Hg, 64% yield. ^{19}F NMR Ø* ppm 66.4 (pentet, J = 8 Hz), 67.5 (pentet, J = 8 Hz) [17]. ^1H NMR δ ppm 1.38 (d, J = 7 Hz)(CH_3), 1.76 (CH_3), 3.53 (heptet, J = 8 Hz)(CH) 4.88, 5.02 (vinyl H). ^{13}C NMR δ ppm 15.8, 18.1 (CH_3), 49.5 (CH), 50.7 (heptet, J = 30.9 Hz)(CH), 115.8, 144.2 (vinyl C) 124.2 (q, J = 283 Hz), 124.4 (q, J = 283 Hz)(CF_3). IR 1642 cm^{-1} (terminal C=C). Analysis: Found: C, 37.79; H, 3.71%. $C_8H_{10}F_6S$ requires C, 38.10; H, 3.99%.

9 34°C/1.5 mm Hg, 60% yield. ^{19}F NMR Ø* ppm 66.3 (pentet, J = 8 Hz), 67.5 (pentet, J = 8 Hz) [17]. ^1H NMR δ ppm 1.1 (t-butyl), 1.86 (CH_3), 3.32 (CH), 3.51 (heptet, J = 8 Hz), 4.85, 5.08 (vinyl H). ^{13}C NMR δ ppm 18.4 (CH_3), 28.5 (t-butyl CH_3), 34.4 (CH), 50.2 (heptet, J = 30.9 Hz) (CH), 67.5 (t-butyl C), 118.3, 142.5 (vinyl C), 122.9 (q, J = 283 Hz), 123.8 (q, J = 283 Hz)(CF_3). IR 1638 cm^{-1} (terminal C=C). Analysis: Found: C, 44.74; H, 5.30%. $C_{11}H_{16}F_6S$ requires C, 44.88; H, 5.48%.

11 38°C/1.5 mm Hg, 65% yield. ^{19}F NMR Ø* ppm 66.1 (pentet, J = 8 Hz), 67.4 (pentet, J = 8 Hz) [17]. ^1H NMR δ ppm 1.71-2.55 (CH_2), 3.53 (heptet, J = 8 Hz), 3.8 (CH), 4.78, 4.98 (vinyl H). ^{13}C NMR δ ppm 21.0, 27.7, 29.5, 31.7 (CH_2), 50.5 (CH), 50.5 (heptet, J = 30.9 Hz) (CH), 123.2 (q, J = 282 Hz), 124.1 (q, J = 280 Hz) (CF_3), 113.1, 146.2 (vinyl C). IR 1645 cm^{-1} (terminal C=C). Analysis: Found: C, 43.03; H, 4.22%. $C_{10}H_{12}F_6S$ requires C, 43.16; H, 4.35%.

Preparation of 3

A mixture of potassium fluoride (9.1 g, 157 mmole), trans-2-butene (10 g, 178 mmole), HFTA dimer (10 ml, 46.4 mmole) and 20 ml of DMF was stirred at room temperature in a flask equipped with magnetic stirring bar, dry ice-condenser, and dry nitrogen inlet tee. After overnight stirring, the reaction mixture was poured into water. After a normal work-up, 3 was distilled at 46°C/45 mm Hg., 9.1 g, 41% yield. ^{19}F NMR Ø* ppm 66.5 (pentet, J = 8 Hz), 67.5 (pentet, J = 8 Hz) [17]. ^1H NMR δ ppm 1.38

(d, J = 7 Hz)(CH_3), 3.58 (heptet, J = 8 Hz)(CH), 3.66 (q, J = 7 Hz)(CH), 4.93 ~ 6.00 (vinyl H). ^{13}C NMR δ ppm 19.5 (CH_3), 45.4 (CH), 50.3 (heptet, J = 30.9 Hz)(CH), 123.0 (q, J = 281 Hz), 123.9 (q, J = 281 Hz)(CF_3), 117.8, 138.6 (vinyl C). IR 1639 cm^{-1} (terminal C=C). Analysis: Found: C, 35.26; H, 3.19%. $C_7H_8F_6S$ requires C, 35.29; H, 3.39%.

Preparation of 7

A mixture of potassium fluoride (3.6 g, 62 mmole), β-methylstyrene (10 ml, 77.5 mmole), HFTA dimer (5 ml, 23.2 mmole) and 10 ml of DMF was stirred at room temperature and at 70°C for 2 days. The reaction mixture was poured into water. After a normal work-up, 7 was distilled at 50-52°C/0.2 mm Hg. 4.6 g, 33% yield. ^{19}F NMR Ø* ppm 66.1 (pentet, J = 8 Hz), 66.5 (pentet, J = 8 Hz) [17]. ^1H NMR δ ppm 3.56 (heptet, J = 8 Hz) (CH), 4.66 (d, J = 9 Hz)(CH), 5.1 ~ 6.4 (vinyl H), 7.36 (phenyl). ^{13}C NMR δ ppm 50.9 (heptet, J = 30.9 Hz)(CH), 54.7 (CH), 128.2, 128.8, 129.4, 136.0, 137.4 (phenyl and CF_3). IR 1622 cm^{-1} (terminal C=C), 1590 cm^{-1} (phenyl). Analysis: Found: C, 48.36; H, 3.44%. $C_{12}H_{10}F_6S$ requires C, 48.00: H, 3.36%.

Photo-rearrangement of 1

After about four months in a Pyrex ampoule, 1 was changed to 2 in about 1:1 ratio, but the mixture was still a clear, colorless liquid. ^{19}F NMR of the mixture showed two doublets centered at Ø* 66.4 and 67.0 ppm (J = 8 Hz). ^1H NMR of the mixture showed methyl groups at δ ppm 1.46, 1.75 and 1.86 ppm, two heptets at 3.33 and 3.46 ppm, and vinyl protons at 4.95 and 5.05 ppm. This mixture was irradiated with 3000 Å light in a Pyrex ampoule for 24 hr. All 1 disappeared and 2 was formed. Distillation gave 2 at 48°C/7 mm Hg. The spectral data of 2 are shown in Tables 2 and 3. Analysis: Found: C, 40.41, H, 4.44%. $C_9H_{12}F_6S$ requires C, 40.59; H, 4.54%.

Freshly prepared 1 was irradiated with 3000 Å light in an nmr tube in a $CDCl_3$ solution. A quantitative yield of 2 was obtained after 12 hr. A neat sample of 1 was also irradiated with 3000 Å light in an nmr tube. Again, quantitative yield of 2 was obtained after 24 hr.

Thermal rearrangement of 1

A small amount of 1 was added to an nmr tube and the tube was capped by rubber septum. 1 was heated in an oil bath at 135°C (bath temperature) for 3.5 hr. 94% of 1 was converted to 2, and 6% of 1 remained unchanged. Also, trace amounts of four other peaks were detected by GLPC, but these were not identified. When the thermal rearrangement was carried out neat at 120°C, 95% conversion of 1 to 2 was obtained after 24 hr. After 3 days, all 1 was converted to 2.

Photo-rearrangement of 3

Freshly prepared 3 was irradiated with 3000 Å light in a Pyrex ampoule neat. Two days irradiation gave 85% conversion of 3 to 4, and the ratio of 4-E and 4-Z was 4.0. After 5 days, the conversion of 3 was 90% and the ratio was 4.8. After 10 days, the conversion of 3 was 92% and the ratio was 5.1. 4-E was isolated by preparative GLPC. Spectral data of 4-E are given in Tables 2 and 3. Analysis: Found: C, 34.45; H, 2.74%. $C_{17}H_8F_6S$ requires C, 35.29; H, 3.38%.

In order to simplify the second order splitting of vinyl protons, the methyl protons were decoupled in ^{1}H NMR, and the obtained signals were used for a computer simulation. The calculated coupling constant was J = 13.7 Hz. The magnitude of this coupling constant indicated the *trans* isomer.

Alternatively, 4-E and Z were synthesized from the reaction of 1-butene, HFTA dimer and potassium fluoride in DMF: bp 43°C/22 mm Hg, 60% yield. The product 4-E, was isolated *via* preparative GLPC. This sample was identical to the above rearranged product on the basis of ^{19}F, ^{1}H NMR and IR.

Thermal rearrangement of 3

3 was heated in a flask neat at 130°C. After 21 hr, 13% of 3 was converted to 4-E and Z. The ratio of E and Z was 2.1. Two days heating gave 29% conversion and the ratio of E and Z was 1.6. After seven days, the mixture became black, and only a trace amount of 3 was left unchanged, but 14 new peaks in addition to 4-E and Z were detected by GLPC.

Photo-rearrangement of 7

A small amount of freshly prepared 7 was irradiated with 3000 Å light in $CDCl_3$ solution in an nmr tube for five days. All 7 was converted to 8. GLPC analysis showed only one isomer. 8 was alternatively prepared from the reaction of allyl benzene, HFTA dimer, and potassium fluoride in DMF. Only one isomer was obtained in this reaction, bp 74°C/0.5 mm Hg; 50% yield. Spectral data of 8 are given in Tables 2 and 3. The second order splitting of vinyl protons of 8 was similar to the methyl decoupled splitting of 4-E. 8 was assigned as the E isomer. Analysis: Found: C, 48.10; H, 3.29%. $C_{12}H_{10}F_6S$ requires C, 48.00; H, 3.36%.

Photo-rearrangement of 9

Freshly prepared 9 was irradiated with 3000 Å light in a Pyrex ampoule for three days. 82% of 9 was converted to 10. 10 was isolated by preparative GLPC. Spectral data of 10 are given in Tables 2 and 3. Analysis: Found: C, 44.60; H, 5.55%. $C_{11}H_{16}F_6S$ requires C, 44.88; H, 5.48%.

Photo-rearrangement of 11

Freshly prepared 11 was irradiated with 3000 Å light in a Pyrex ampoule for three days. 84% of 11 was converted to 12, which was separated by preparative GLPC. Spectral data of 12 are given in Table 2 and 3. Analysis: Found: C, 43.36; H, 4.28%. $C_{10}H_{12}F_6S$ requires C, 43.16; H, 4.35%.

Kinetic study of photo-rearrangement of 1

To an nmr tube were added 50 μl of 1 (0.234 mmole), 50 μl of benzotrifluoride and 0.5 ml of benzene. The tube was flushed with dry nitrogen and capped by rubber septum. The mixture was irradiated with 3000 Å light at 35°C. The results are shown in Figure 1.

Photo-rearrangement of 1 in the presence of a radical inhibitor

To an nmr tube were added 50 μl of 1 (0.235 mmole), 12.1 mg of p-benzoquinone (0.112 mmole), 50 1 of benzotrifluoride and 0.5 ml of benzene.

The tube was flushed with dry nitrogen and capped by rubber septum. The mixture was irradiated with 3000 Å light. The results are shown in Figure 2.

Oxygen gas was bubbled into a mixture of 50 μl of 1 (0.235 mmole), 50 μl of benzotrifluoride, and 0.5 ml of benzene in an nmr tube. The tube was capped by rubber septum and a mixture was irradiated with 3000 Å light. The results are shown in Figure 2.

Photo-rearrangement of 1 in 2-methyl-2-butene

In a Pyrex ampoule, 30 μl of 1 (0.141 mmole) was dissolved in 0.1 ml of 2-methyl-2-butene. The mixture was irradiated with 3000 Å light. The ratio of 2 to 1 was 0.75 after 20 hr, 2.78 after 40 hr, and 10.0 after 3 days irradiation. Trace amounts of 5 and 6 (E and Z) were detected by GLPC after 20 hr irradiation, but the amounts of 5 and 6 did not increase after 3 days irradiation.

Solvent effect

In an nmr tube, 50 μl of 1 (0.235 mmole) and 50 μl of benzotrifluoride were dissolved in 0.5 ml of solvent. The mixture was irradiated with 3000 Å light. No significant rate effects were observed.

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