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SOME UNUSUAL REACTIONS OF DIMERS OF F-PROPENE WITH THIOLS

Masamichi MARUTA and Nobuo ISHIKAWA*

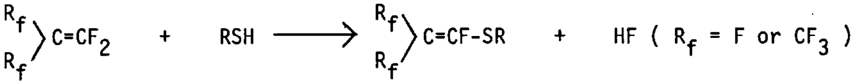
Department of Chemical Technology, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152 (Japan)

SUMMARY

Reactions of F-2- and -4-methyl-2-pentenes with thiols were found to involve an oxidation-reduction system. 1,4-Elimination of sulfenyl fluorides from thio-substituted perfluoroolefins to form 1,3-dienes and disulfides is suggested as the reaction pathway.

INTRODUCTION

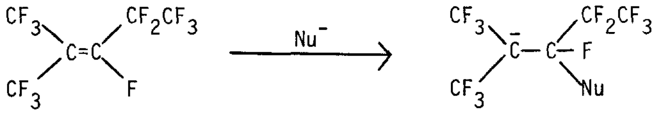
Several examples of the nucleophilic reactions of thiols with perfluoro terminal olefins have been reported. F-ethylene, F-propene and F-2-methylpropene are known to be substituted by alkyl- or arylthio groups at their terminal positions [1, 2].



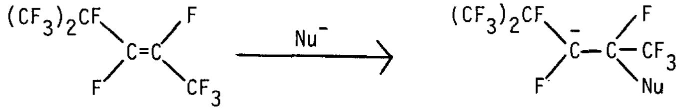
$$\begin{matrix}R_f\\R_f\end{matrix}\!\!\rangle C{=}CF_2 \quad + \quad RSH \longrightarrow \begin{matrix}R_f\\R_f\end{matrix}\!\!\rangle C{=}CF\text{-}SR \quad + \quad HF \ (R_f = F \text{ or } CF_3)$$

However, no reports on the reactions of perfluoro inner olefins with S-nucleophiles, except that of F-cyclobutene [3] giving usual RS-substituted products, have appeared in the literature.

In the course of our studies on the nucleophilic reactions of the oligomers of F-propene, we have found that the dimers of F-propene react with O- and N-nucleophiles giving various addition and substitution products [4 - 6]. Of these two dimers, F-2-methyl-2-pentene (1) is much more susceptible to the attack of nucleophiles than F-(E)-4-methyl-2-pentene (2), because the former forms a more stable carbanion (1') owing to the two adjacent trifluoromethyl groups.

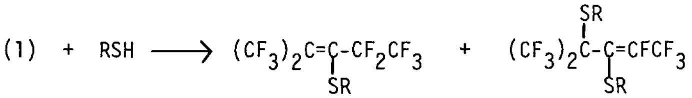


(1) (1')



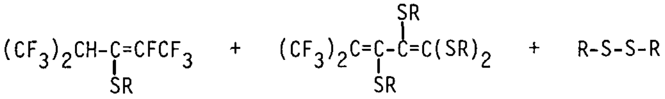
(2) (2')

Now we wish to report on the reactions of these dimers with thiols as nucleophile. Thiols are generally known to be more nucleophilic than alcohols or amines, and sometimes give unexpected products. In the reactions between F-propene dimers and thiols, we observed that the expected thio-substituted perfluoroolefins and their reduced derivatives, together with a considerable amount of disulfide of the thiol, were found in the reaction products.



$$(1) + RSH \longrightarrow (CF_3)_2C{=}\underset{SR}{C}{-}CF_2CF_3 + (CF_3)_2\overset{SR}{C}{-}\underset{SR}{C}{=}CFCF_3$$

(3) (4)



$$(CF_3)_2CH{-}\underset{SR}{C}{=}CFCF_3 + (CF_3)_2C{=}\underset{SR}{C}{-}\overset{SR}{C}{=}C(SR)_2 + R{-}S{-}S{-}R$$

(5) (6) (7)

RESULTS AND DISCUSSION

The reaction with phenylmethanethiol as nucleophile will be discussed first, as the characteristic nmr signal for its CH_2 protons was found to be useful in tracing the reactions.

When an equimolar amount of phenylmethanethiol was allowed to react with (1) in acetonitrile at 0 - 5 ^{o}C in the presence of triethylamine, mono- and bis-(benzylthio)-substituted derivatives (3) and (E-4), a hydrogen containing derivative (5), and dibenzyl disulfide (7), were formed in the ratios shown in Table 1.

TABLE 1

Yields of the products

RSH	Mol. ratio RSH/(1)	Yields (%)[a]						Recovd. RSH
		(3)	(E-4)	(5)	(6) cis	(6) trans	(7)	
$PhCH_2SH$	1	59*	32*	3*	—	—	6*	—
//	2	8*	23*	16*	—	—	44*	—
//	10	—	—	—	23	3	15	45
PhSH	10	—	—	—	30	—	32	19

a) Based on RSH. * : Calculated from the signal intensities of ^{19}F and ^{1}H nmr spectra.

The products were separated by means of column chromatography or recrystallizations from suitable solvents, and were subjected to various analyses. The structures were established mainly from ^{19}F and ^{1}H nmr spectra, by checking the chemical shifts and coupling constants. The figures are shown in Table 2.

Using two molar amount of thiol in the above reaction, (E-4) and (5) were formed as the major products, whereas with a much greater excess, (6) was mainly obtained [63% based on (1)]. The formation of the monosubstituted derivative (3) was most expected, because an analogous phenoxy compound was obtained in good yield in the similar reaction of (1) with phenol [5]. The easier formation of bis-substituted derivative (E-4) in this case should be ascribed to the stabilization of the carbanion (3') which occurs through the vacant 3d orbitals of the sulfur atom.

The formation of (5), (6), and (7) suggests that an oxidation-reduction system is involved in the reaction. We ascertained experimentally that no oxidation of the thiol to (7) by atmospheric oxygen occurs under these conditions, and that (1) is required for the oxidation.

The reaction pathway is speculated to be as shown in Fig. 1. In the disubstitution step, (Z-4) should have been formed together with (E-4), although the former was not detected in the reaction mixture. Model

TABLE 2

The ^{19}F and ^{1}H nmr spectra of reaction products

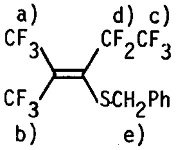
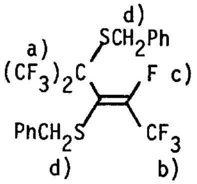
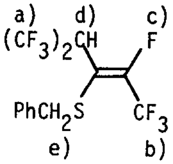
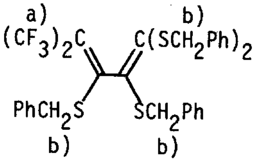
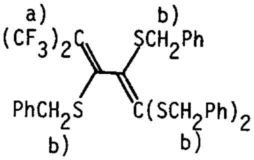
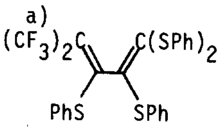
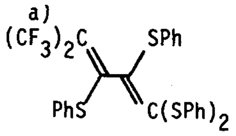
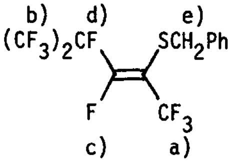
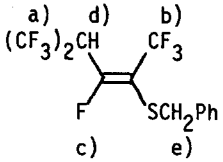
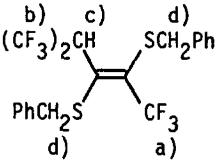
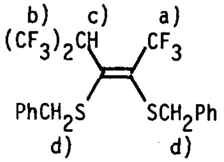
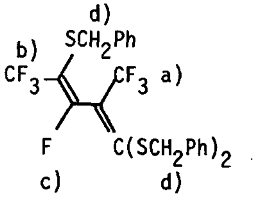
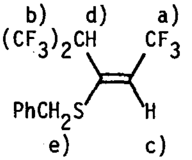
Compounds		^{19}F & ^{1}H Chemical shifts (δ ppm)*	Coupling constants (Hz)
No.	Structure		
(3)		a) 57.5(t,q,q) b) 62.9(q) c) 79.6(q) d) 103.8(q) e) 4.17(s)	J_{ab}= 9.4 J_{ac}= 9.0 J_{ad}= 18.8
(E-4)		a) 65.0(d) b) 65.9(d) c) 77.9(sep.br) d) 4.00(s)	J_{ac}= 26.2 J_{bc}= 3.4
(5)		a) 65.6(d,d) b) 67.1(d) c) 96.9(m) d) 4.23(sep) e) 3.92(s)	J_{ac}= 12.0 J_{bc}= 5.6 J_{ad}= 7.9
(cis-6)		a_1) 56.9(s), a_2) 59.1(s) b_1) 3.87(s) b_2) 3.86, 3.96 b_3) 3.72, 3.84 b_4) 3.12, 3.32	b_2) J_{AB}= 12.0 b_3) J_{AB}= 11.3 b_4) J_{AB}= 11.0
(trans-6)		a_1) 57.7(q), a_2) 59.9(q) b_1) 3.98(s) b_2) 3.94, 4.10 b_3) 3.91(s) b_4) 3.08, 3.38	$J_{a_1a_2}$= 3.4 b_2) J_{AB}= 12.0 b_4) J_{AB}= 10.8
(cis-6)		a_1) 55.9(s) a_2) 57.5(s)	

TABLE 2 (Cont.)

(trans-6)		a_1) 56.5(q) a_2) 59.3(q)	$J_{a_1a_2}$ = 3.8
(8)		a) 61.4(d) b) 76.1(d,d) c) 91.4(m) d) 178.2(d, sep) e) 3.95 (or 3.91)(s)	J_{ac}= 21.6 J_{bc}= 10.5 J_{bd}= 8.2 J_{cd}= 16.4
(9)		a) 65.0(d,d) b) 66.9(d) c) 95.9(m) d) 4.17(sep) e) 3.91 (or 3.95)(s)	J_{ac}= 7.1 J_{bc}= 5.6 J_{ad}= 7.5
(E-10)		a) 57.6(s) b) 63.9(d) c) 5.41(sep) d_1) 4.07(s) d_2) 3.93(s)	J_{bc}= 8.4
(Z-10)		a) 56.5(s, br) b) 64.4(d, q) c) 4.46(sep, br) d_1) 4.13(s) d_2) 3.93(s)	J_{ab}= 2.1 J_{bc}= 7.3
(11)		a) 51.8(s) b) 54.1(d) c) 81.5(q) d_1) 3.86, 4.02 d_2) 3.78, 3.88 d_3) 3.37, 3.58	J_{bc}= 15.0 d_1) J_{AB}= 12.0 d_2) J_{AB}= 11.3 d_3) J_{AB}= 11.3
(12)		a) 56.0(d, br) b) 64.9(d) c) 5.45(q) d) 4.28(sep, br) e) 3.88(s)	J_{ac}= 7.5 J_{bd}= 7.5

* Chemical shifts for ^{19}F and ^{1}H nmr spectra are given in δ ppm upfield from ext. $CFCl_3$ and in δ ppm from TMS respectively. All of the ^{1}H and a part of ^{19}F nmr spectra [(6), (11), and (12)] were taken in CCl_4, while the others of ^{19}F spectra were taken in neat.

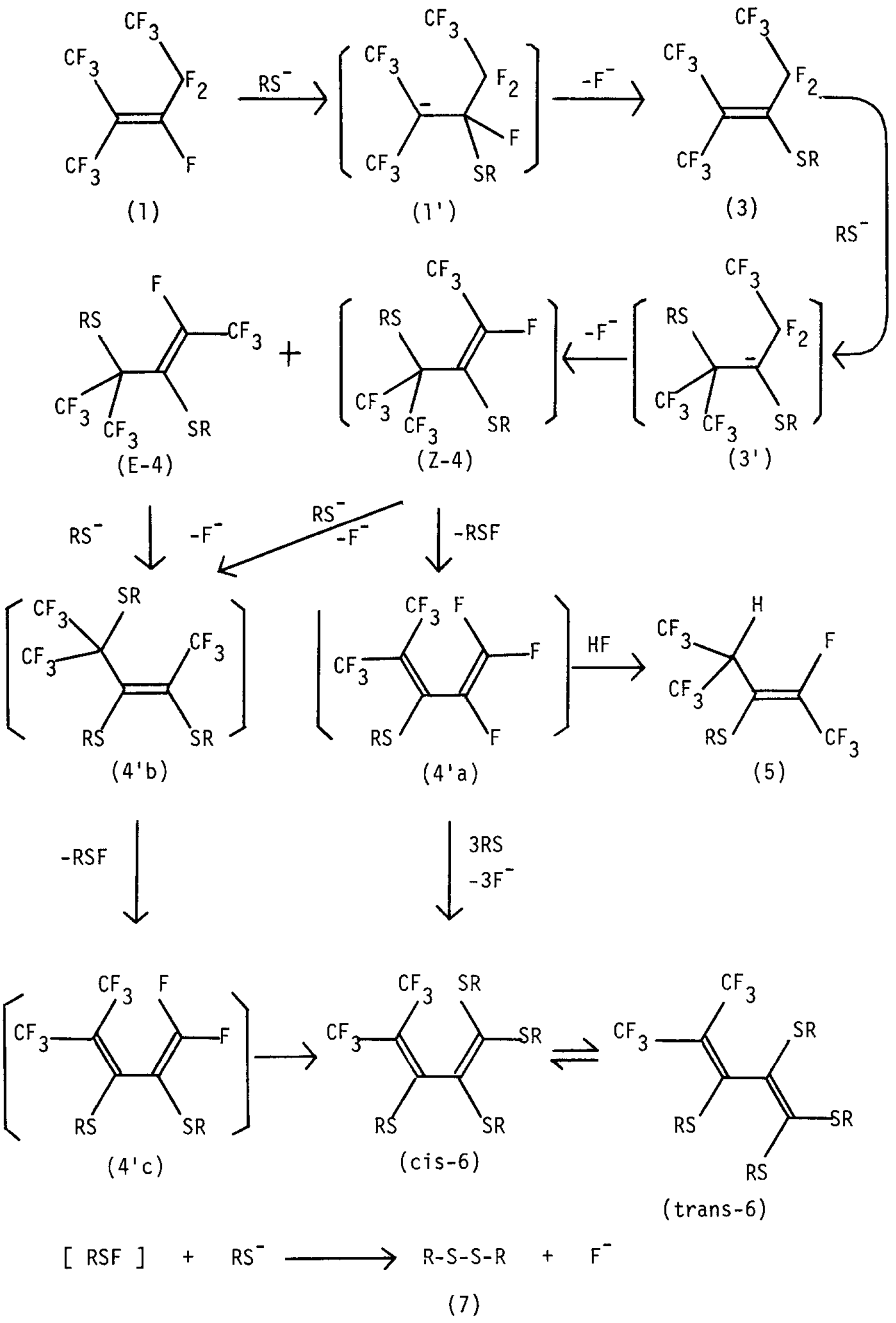
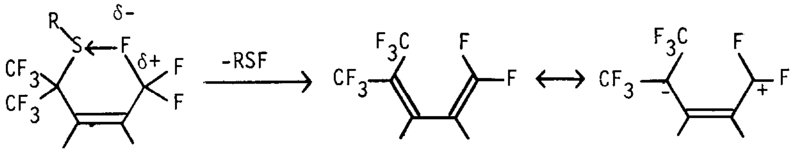


Figure 1. Reaction of (1) with RSH

inspections show that the interatomic distance between S and F, mutually 1,6-positioned in (Z-4), comes near 1.6Å, an average S-F bond length. This would make benzyl sulfenyl fluoride release easily from (Z-4) affording a 1,3-diene (4'a), which could be converted either to (5) by 1,4-addition of hydrogen fluoride, or to (6) by substitution of F by RS. The released sulfenyl fluoride must have reacted immediately with thiol to give (7) and HF.

There is another possible route from (4) to (6). By an additional nucleophilic attack by RS^- on (4) (E or Z), the tri-RS-substituted product (4'b) would be formed. From this compound, 1,4-RSF-elimination would occur again, forming another 1,3-diene (4'c). Further nucleophilic attack on (4'c) could result in the formation of (6). We confirmed experimentally that (E-4) is converted into (6) in reaction with five molar amounts of the thiol. The 1,3-diene (6) thus obtained has as expected a cis-form, and was converted into the more stable trans-isomer by heating it in a solvent such as xylene.

In conclusion, the reaction pathway can only be well explained by assuming 1,4-elimination of RSF. Although this kind of elimination was so far unknown in the polyfluoroolefin series, it could very likely have taken place in the present case. Elimination of RSF from the inner monoenes, (Z-4) and (4'b), leave the conjugated dienes (4'a) and (4'c), respectively, which are both sterically less hindered by the crowd of substuents than are the monoenes. Further, (4'a) and (4'c) are stabilized by having two electron-attracting trifluoromethyl groups at one end and by two electron-repelling fluorine atoms at the other.



When benzenethiol was used instead of phenylmethanethiol, more complex products were formed. The reaction with a large excess of benzenethiol, however, gave the tetra(phenylthio)-substituted diene, (cis-6; R = Ph), in a yield of 75% based on (1), together with diphenyl disulfide (7; R = Ph).

F-(E)-4-methyl-2-pentene (2), another dimer of F-propene, also reacted with phenylmethanethiol under similar conditions. When an equimolar amount of the thiol was used, the products obtained were (8), (9), (10), and (7)

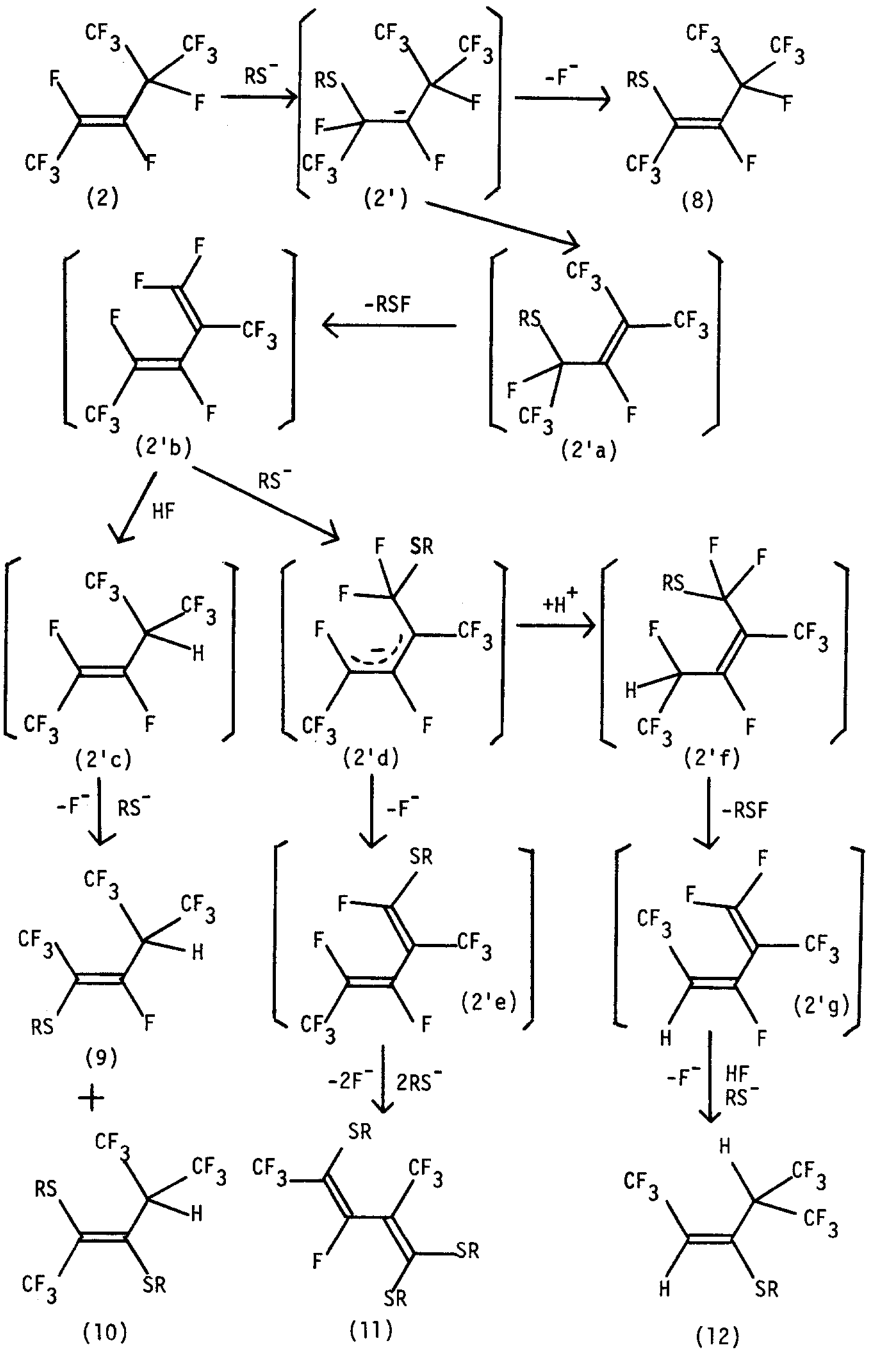


Figure 2. Reaction of (2) with RSH

in the ratios 4 : 5 : 28 : 52. Three equivalents of the thiol gave a tri-RS-substituted compound (11) and a dihydro compound (12) in addition to (8), (9), and (10).

Although the reactions are more complicated than those of (1), seemingly because of an S_N2'-like mechanism, the reaction pathway as shown in Fig. 2 involving 1,4-elimination can also be proposed.

Thus, the carbanion (2'), formed by nucleophilic attack of thiolate anion on (2), should lose fluoride ion to give (8) together with (2'a) through an S_N2'-like mechanism. The latter compound (2'a) should be susceptible to 1,4-RSF-elimination giving the 1,4-diene (2'b), which then undergoes 1,2-addition by HF to give (2'c). Nucleophilic attack on (2'c) by the thiolate ion leads to (9) and (10).

On the other hand, when the thiolate anions are abundant in the reaction mixture, they will attack the 1,4-diene (2'b) directly to give an allylic carbanion (2'd). This carbanion will either release a fluoride ion to give the 1,4-diene (2'e) or add a proton to give the hydro compound (2'f). The diene (2'e) will be attacked again by RS^- nucleophiles affording (11), whereas the hydro compound (2'f) will eliminate RSF to form the diene (2'g) , on which additions of HF and RS^- can occur to afford (12).

EXPERIMENTAL

Reaction between (1) and phenylmethanethiol in ratio 1 : 1

Into a mixture of (1) (3.00 g, 10 mmol), phenylmethanethiol (1.24 g, 10 mmol) and acetonitrile (20 ml) triethylamine (1.01 g, 10 mmol) was added dropwise under nitrogen at 0 - 5 ^oC over 20 min. After 100 min of stirring, the solvent was removed in vacuo leaving oily matter (4.18 g). This crude material was subjected to ^{19}F nmr analysis to determine the product ratios, using methanol and trifluoroethanol as solvent and internal standard, respectively. Then it was poured into dilute hydrochloric acid and the organic matter was extracted with diethyl ether. The ethereal exteact was washed with brine and dried over magnesium sulfate. The ether was evaporated in vacuo leaving an oily matter (3.40 g). A part of this matter was subjected to ^1H nmr analysis using carbon tetrachloride as the solvent and the ratios of the products were determined from their signal intensities based on phenyl protons. The ratios thus obtained agreed with those obtained by ^{19}F nmr, and the results are given in Table 1.

Distillation of the material in vacuo gave an oil (2.10 g), b.p. 115 - 117 °C/ 24 mmHg, a mixture of (3) and (5), together with a heavier oil (0.51 g), b.p. 157 - 158 °C/ 3 mmHg (E-4).

Pure (3) and (E-4) were separated by means of repeated silica-gel column chromatography using hexane as eluent.

(3) (nc) Found: C, 38.43; H, 1.86%. $C_{13}H_7SF_{11}$ requires C, 38.63; H, 1.75%. MS : m/e 404 (M^+), 335 (M^+-CF_3), 285 (M^+-C_2F_5), 91 ($PhCH_2^+$).

(E-4) (nc) Found : C, 47.90; H, 2.83%. $C_{20}H_{14}S_2F_{10}$ requires C, 47.25; H, 2.78%. MS : m/e 385 (M^+-$PhCH_2S$), 316 (385-CF_3), 262 (385-$PhCH_2S$), 123 ($PhCH_2S^+$), 91 ($PhCH_2^+$).

Reaction between (1) and phenylmethanethiol in ratio 1 : 2

In the above reaction, phenylmethanethiol (2.48 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) were used, and the reaction mixture was worked up in a similar way. The resulting material, a mixture of oil and solid, was subjected to ^{19}F and ^{1}H nmr analyses (Table 1) and then purified further The solid product was recrystallized from ethanol, giving dibenzyl disulfide (0.61 g, m.p. 68 - 69 °C), which was identified with an authentic sample. The oily matter was distilled in vacuo giving a mixture of (3) and (5) (1.35 g, b.p. 101 - 103 °C/ 14 mmHg), together with a mixture (2.50 g) of (E-4) and dibenzyl disulfide as residue. The distillate was subjected to repeated silica-gel column chromatography using hexane as eluent, affording pure (5).

(5) (nc) Found : C, 40.82; H, 2.12%. $C_{13}H_8SF_{10}$ requires C, 40.43; H, 2.09%. MS : m/e 386 (M^+), 317 (M^+-CF_3), 262 (M^+-$PhCH_2SH$), 91 ($PhCH_2^+$).

Reaction between (1) and phenylmethanethiol in ratio 1 : 10

Perfluoroolefin (1) (0.90 g, 3 mmol), phenylmethanethiol (3.72 g, 30 mmol) and triethylamine (3.03 g, 30 mmol) were allowed to react under the same conditions. The reaction mixture was poured into dilute hydrochloric acid and extracted with diethyl ether. The extract was treated with a 1N-aqueous solution of sodium hydroxide to remove phenylmethanethiol (1.69 g, 45%), which was recovered by acidification of the alkaline solution. The remaining ether extract was subjected to evaporation and the residue (2.45 g) was recrystallized several times from hexane, giving (cis-6) (1.17 g, 23%), m.p. 115 - 116 °C.

(cis-6) (nc) Found: C, 60.29; H, 4.17%. $C_{34}H_{28}S_4F_6$ requires C, 60.16; H, 4.16%. MS : m/e 587 (M^+-$PhCH_2$), 463 (587-$PhCH_2S$), 123 ($PhCH_2S^+$), 91 ($PhCH_2^+$).

The mother liquor from the recrystallization was subjected to repeated silica-gel column chromatography, using hexane as eluent, giving dibenzyldisulfide (0.58 g, 15%), m.p. 70 - 72 °C and (trans-6) (0.12 g, 3%), m.p. 106 - 107 °C.

(trans-6) (nc) Found: C, 60.62; H, 4.37%. $C_{34}H_{28}S_4F_6$ requires C, 60.16; H, 4.16%. MS: m/e 587 (M^+-$PhCH_2$), 123 ($PhCH_2S^+$), 91 ($PhCH_2^+$).

When (cis-6) (0.05 g) was heated in xylene (1 ml) at 140 °C for 5 h, an equilibrium mixture of (cis-6) and (trans-6) (cis/trans = 0.2) was obtained. This result was confirmed by ^{19}F nmr spectrum.

Reaction between (1) and benzenethiol in ratio 1 : 10

Benzenethiol (3.30 g, 30 mmol) was used instead of phenylmethanethiol, in a reaction similar to that described above. In addition to benzenethiol (0.63 g, 19%) and diphenyl disulfide (1.04 g, 32%), m.p. 59 - 61 °C, (cis-6; R = Ph) (1.39 g, 30%), m.p. 121 - 122 °C, was obtained.

(cis-6; R = Ph) (nc) Found: C, 57.86; H, 3.20%. $C_{30}H_{20}S_4F_6$ requires C, 57.86; H, 3.24%. MS: m/e 513 (M^+-PhS), 404 (513-PhS), 109 (PhS^+).

The presence of (trans-6) in the mother liquor was confirmed by ^{19}F nmr. The cis-isomer was converted to an equilibrium mixture (cis/trans = 0.3), by heating it in xylene at 140 °C for 36 h.

Reaction between (E-4) and phenylmethanethiol in ratio 1 : 5

A mixture of (E-4) (0.2 g, 0.4 mmol), phenylmethanethiol (0.25 g, 2 mmol) triethylamine (0.2 g, 2 mmol) and acetonitrile (4 ml) was stirred for 2 h at 0 - 5 °C, under nitrogen. The solvent was removed in vacuo and diethyl ether was added to give a solution, which was washed with dilute aqueous solution of sodium hydroxide, then with brine, and dried over magnesium sulfate. The solvent was evaporated in vacuo, and residue (0.38 g) was subjected to silica-gel column chromatography, using hexane as eluent. Dibenzyl disulfide (0.16 g, 65%), (cis-6) (0.11 g, 32% based on the thiol or 40% based on (E-4), m.p. 103 - 105 °C, and unidentified products (0.12 g) were obtained.

Reaction between (2) and phenylmethanethiol in ratio 1 : 1

Into a mixture of (2) (3.00 g, 10 mmol), phenylmethanethiol (1.24 g, 10 mmol) and acetonitrile (20 ml), triethylamine (1.01 g, 10 mmol) was added dropwise over a 20 min period. After 100 min of stirring, the solvent was removed in vacuo to give a residue (2.78 g). This reaction product was treated as usual and a white solid material (1.92 g) was obtained. Glc analysis showed this to be a mixture of 11 components, and repeated recrystallization from ethanol gave dibenzyl disulfide (0.59 g), m.p. 70 - 72 °C. The mother liquor was subjected to silica-gel column chromatography, using hexane as eluent, and a mixture (0.16 g) of (8) and (9) (1 : 1), (10) (0.25 g)(E/Z = 1), and (7) (0.06 g), m.p. 70 - 71 °C were obtained.

(8) (nc) MS: m/e 404 (M^+), 313 (M^+-$PhCH_2$), 91 ($PhCH_2^+$).

(9) (nc) MS: m/e 386 (M^+), 295 (M^+-$PhCH_2$), 91 ($PhCH_2^+$).

(10) (nc) Found: C, 49.42; H, 2.99%. $C_{20}H_{15}S_2F_9$ requires C, 48.98; H, 3.08%. MS: m/e 490 (M^+), 399 (M^+-$PhCH_2$), 308 (399-$PhCH_2$), 91 ($PhCH_2^+$).

When 3 molar amounts of the thiol were used in a different run, (12), m.p. 52.5 - 54.5 °C, and (11), m.p. 84 - 85 °C, were obtained though in poor yields.

(12) (nc) Found: C, 42.23; H, 2.53%. $C_{13}H_9SF_9$ requires C, 42.40; H, 2.46%. MS: m/e 368 (M^+), 91 ($PhCH_2^+$).

(11) (nc) Found: C, 56.79; H, 3.67%. $C_{28}H_{21}S_3F_7$ requires C, 56.43; H, 3.68%. MS: m/e 574 (M^+), 483 (M^+-$PhCH_2$), 451 (M^+-$PhCH_2S$), 123 ($PhCH_2S^+$), 91 ($PhCH_2^+$).

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