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SYNTHESIS AND TRANSFORMATIONS OF 1,1,1-TRIFLUORO-2-BENZYLTHIOPROPENE

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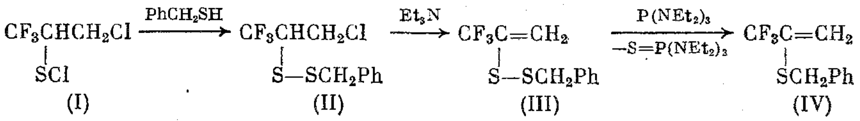
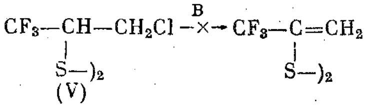
In our previous work [1, 2], we showed that perfluoroalkenyl benzyl sulfides may be used for the synthesis of stable perfluorinated enethiols and α,β-unsaturated sulfenyl chlorides (SC). In order to clarify the effect of substituents on the stability of these metastable compounds, we attempted to synthesize a partially fluorinated enethiol and α,β-unsaturated SC with one trifluoromethyl group at the double bond. The starting fluoroalkenyl benzyl sulfide (IV) was obtained from SC (I) described in our previous work [3]



$$\underset{\text{(I)}}{\underset{\text{SCl}}{\text{CF}_3\text{CHCH}_2\text{Cl}}} \xrightarrow{\text{PhCH}_2\text{SH}} \underset{\text{(II)}}{\underset{\text{S—SCH}_2\text{Ph}}{\text{CF}_3\text{CHCH}_2\text{Cl}}} \xrightarrow{\text{Et}_3\text{N}} \underset{\text{(III)}}{\underset{\text{S—SCH}_2\text{Ph}}{\text{CF}_3\text{C=CH}_2}} \xrightarrow[-\text{S=P(NEt}_2)_3]{\text{P(NEt}_2)_3} \underset{\text{(IV)}}{\underset{\text{SCH}_2\text{Ph}}{\text{CF}_3\text{C=CH}_2}} \quad (1)$$

Scheme (1) shows that disulfide (III) was obtained by the dehydrochlorination of disulfide (II) by the action of Et_3N. We should note that, in contrast to (II), it was not possible to carry out the dehydrochlorination of symmetrical disulfide (V), which does not react with a weak base, N-methylpyrrolidone but reacts with Et_3N to give a mixture of unidentified tarry products.

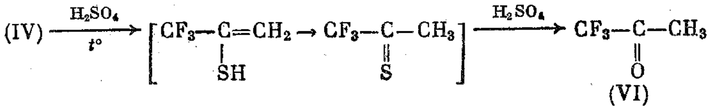


$$\underset{\text{(V)}}{\underset{\text{S—)}_2}{\text{CF}_3\text{—CH—CH}_2\text{Cl}}} \overset{B}{-\times\!\!\rightarrow} \underset{\text{S—)}_2}{\text{CF}_3\text{—C=CH}_2} \quad (2)$$

B = N-methylpyrrolidone, Et_3N.

The possibility of effecting the dehydrochlorination of disulfide (II) is apparently related to the electronic effect of the benzyl group which hinders attack of Et_3N at the sulfur atom.

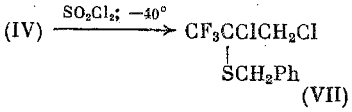
Fluorinated enethiols have been synthesized by the acid hydrolysis of perfluoroalkyl benzyl sulfides with simultaneous distillation of the products formed [1]. Under such conditions, the hydrolysis of (IV) gave 1,1,1-trifluoroacetone (VI)



$$\text{(IV)} \xrightarrow[t^\circ]{\text{H}_2\text{SO}_4} \left[\underset{\text{SH}}{\text{CF}_3\text{—C=CH}_2} \rightarrow \underset{\text{S}}{\underset{\|}{\text{CF}_3\text{—C—CH}_3}}\right] \xrightarrow{\text{H}_2\text{SO}_4} \underset{\text{(VI)}}{\underset{\text{O}}{\underset{\|}{\text{CF}_3\text{—C—CH}_3}}} \quad (3)$$

It is natural to assume that the initially formed enethiol isomerizes upon the action of H_2SO_4 to a thioketone and then is converted to ketone (VI). The possibility of such an isomerization was demonstrated in our previous work [1], while the oxidation of thioketones to their oxygen analogs was shown by Campaigne [4] and Ramnath [5].

α,β-Unsaturated perfluorinated SC are obtained by the chlorolysis of the corresponding alkenyl benzyl sulfides [2]. However, in the case of sulfide (IV), chlorination of the double bond proceeds even at −40°C using SO_2Cl_2 to give only saturated sulfide (VII).



$$\text{(IV)} \xrightarrow{\text{SO}_2\text{Cl}_2;\ -40^\circ} \underset{\text{(VII)}}{\underset{\text{SCH}_2\text{Ph}}{\text{CF}_3\text{CClCH}_2\text{Cl}}} \quad (4)$$

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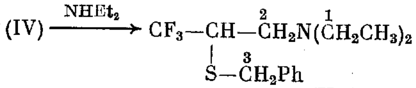
The reactions of sulfide (IV) show the amphoteric nature of the double bond with addition of both electrophilic (scheme (4)) and nucleophilic reagents (scheme (5)). Diethylamine reacts with (IV) to give only adduct (VIII).



$$\text{(IV)} \xrightarrow{NHEt_2} CF_3-\underset{S-\overset{3}{C}H_2Ph}{CH}-\overset{2}{C}H_2N(\overset{1}{C}H_2CH_3)_2 \qquad (5)$$

(VIII)

On the other hand, for the analog of sulfide (IV), 1,1,1-trifluoro-2-phenylthiopropene, in reactions with nucleophiles, stabilization of the anion formed upon attack of the nucleophile at the double bond is achieved due to β-elimination of a fluoride anion [6]. There is also probably some similar stabilization of the anion in reaction (5) since a small amount of $Et_2NH \cdot HF$ was found in the reaction mixture but only sulfide (VIII) could be isolated as a pure compound.

EXPERIMENTAL

The ^{19}F and ^1H NMR spectra (δ, ppm, J. Hz) were obtained on a Perkin-Elmer R-32 spectrometer at 84.6 and 90 MHz, respectively, relative to external CF_3CO_2H and TMS standard. The IR spectra were taken on a UR-20 spectrophotometer. The purity of the compounds was monitored by gas-liquid chromatography on an LKhM-8MD (model 3) chromatograph using a column packed with 20% QF on Chromatone. The mass spectrum of (VI) was taken by A. P. Pleshkova on a Hitachi M80A chromato-mass spectrometer with 70 eV ionizing electron energy and 50°C ionization chamber temperature, while the mass spectrum of (VIII) was taken on a Varian CH-6 with 70 eV ionizing electron energy. The m/z values are given along with the proposed ion structure.

(1-Trifluoromethyl-2-chloroethyl) benzyl disulfide (II). A sample of 21.0 g $PhCH_2SH$ was added with stirring to 20.82 g 1,1,1-trifluoro-3-chloropropanesulfenyl chloride-2 (I) [3] at 25-30°C. Then, the mixture was maintained for 24 h at about 20°C and poured into water. The organic layer was dried over $MgSO_4$ and distilled to give 26.8 g (89.5%) (II), bp 121-124°C (1 mm). Found: C 42.31; H 3.30; S 22.40%. Calculated for $C_{10}H_{10}F_3ClS_2$: C 41.88; H 3.52; S 22.36%. PMR spectrum: 3.0 m (CH), 3.5 m (CH_2Cl), 3.7 s (CH_2S), 7.1 s (Ph). The intensity ratio was 1:2:2.5. ^{19}F NMR spectrum: −10.7 d (CF_3, $J_{CF_3/CH}$ = 9.4 Hz).

(1-Trifluoromethyl)vinyl benzyl disulfide (III). A sample of 30 ml Et_3N was slowly added with stirring to 17.86 g (II) at −78°C and then the mixture was gradually warmed to ∿20°C. Dilute hydrochloric acid was added. The organic layer was dried over $MgSO_4$ and distilled to give 11.35 g (72.8%) (III), bp 105-110°C (1 mm). Found: C 47.98; H 3.62; F 22.77; S 25.62%. IR spectrum (ν, cm^{-1}): 1625 (C=C). PMR spectrum: 3.62 s (CH_2), 5.55 s (H^1), 6.23 s (H^2), 7.0 s (Ph), intensity ratio 2:1:1:5. ^{19}F NMR spectrum: −13.8 s (CF_3).

1,1,1-Trifluoro-2-benzylthiopropene (IV). A sample of 11.64 g $[Et_2N]_3P$ [7] was added dropwise to 11.78 g (III) at 25-30°C and maintained for 30 min at ∿20°C. A fraction with bp up to 80°C (1 mm) was distilled off the mixture. Redistillation gave 8.31 g (80.9%) (IV), bp 55-56°C (0.5 mm). Found: C 54.72; H 4.15; F 26.19; S 14.71%. Calculated for $C_{10}H_9F_3S$: C 55.03; H 4.16; F 26.12; S 14.69%. IR spectrum (ν, cm^{-1}): 1612 (C=C), PMR spectrum: 3.55 s (CH_2), 5.02 s (H^1), 5.6 (H^2), 7.0 s (Ph), intensity ratio 2:1:1:5. ^{19}F NMR spectrum: −12.0 s (CF_3).

Reaction of bis(1-trifluoromethyl-2-chloroethyl) disulfide (V) with N-methylpyrrolidone. A sample of 2.0 g (V) [3] was added with stirring to 10 ml N-methylpyrrolidone, maintained for 10 min and poured into water. The organic layer was analyzed by gas-liquid chromatography and NMR spectroscopy and found identical to authentic (V).

1,1,1-Trifluoroacetone (VI) [8]. A sample of 2.0 g (IV) and 1 ml of a mixture of concentrated H_2SO_4 and P_2O_5 were placed in a distillation apparatus and then heated to 140°C, collecting the volatile fraction in two traps connected in series at −8 and −78°C.

An analogous procedure was carried out using 1.83 g (IV) and 1 ml of the mixture of H_2SO_4 and P_2O_5 with the same traps. In the two experiments, the trap at −8°C gave 0.83 g (42.0%) (VI). Raman spectrum (ν, cm^{-1}): 1767 (C=O). PMR spectrum: 1.89 s (CH_3). ^{19}F NMR spectrum: 2.89 s (CF_3). Mass spectrum: 112 M^+, 97 $[M-CH_3]^+$, 69 $[CF_3]^+$, 43 $[CH_3CO]^+$.

1,1,1-Trifluoro-2,3-dichloro-2-benzylthiopropane (VII). Freshly distilled SO_2Cl_2 (1 ml) was slowly added dropwise to 2.68 g (IV) cooled to −40°C. Then, the mixture was warmed to ∿20°C and distilled to yield 2.76 g (76.7%) (VII), bp 115-117°C (0.5 mm). Found: C 42.15; H 3.28; F 19.57; S 10.99%. Calculated for $C_{10}H_9F_2Cl_2S$: C 41.54; H 3.13; F 19.71; S 11.09%. PMR spectrum: 3.94 s (CH_2^1), 4.07 s (CH_2^2), 7.25 s (Ph), intensity ratio 2:2:5. ^{19}F NMR spectrum: –6.23 s (CF_3).

1-Trifluoromethyl-2-(N,N-diethylamino)ethyl benzyl sulfide (VIII). A sample of 2.5 ml Et_2NH was added dropwise to 0.72 g (IV) cooled to –40°C. The mixture was warmed to ∿20°C and maintained at this temperature for several days. The end of the reaction was monitored by gas-liquid chromatography. Distillation of the filtrate gave 0.63 g (66%) (VIII), bp 105-107°C (0.5 mm). Found: C 57.84; H 6.97; F 19.17; S 11.11%. Calculated for $C_{14}H_{20}F_2SN$: C 57.70; H 6.92; F 19.56; S 11.00%. PMR spectrum: 0.8 t (CH_3), 2.1-2.6 m (CH_2^1, CH_2^2, CH), 3.7 br. s (CH_2^3), 7.2 br. s (Ph), intensity ratio 6:7:2:5, J_{CH_2/CH_2} = 7 Hz. ^{19}F NMR spectrum: –8.6 d (CF_3, $J_{CF_3/CH}$ = 9 Hz). Mass spectrum: 291 M^+, 216 $[CF_3C_2SC_7H_7]^+$, 140 $[CF_3C_2HSCH_2]$, 127 $[CF_3C_2H_2S]^+$, 126 $[CF_3C_2HS]^+$, 91 $[C_7H_7]^+$, 86 $[N_2C_4H_{10}]$, 77 $[C_6H_5]^+$, 72 $[NC_4H_{10}]^+$, 69 $[CF_3]^+$, 58 $[C_4H_{10}]^+$, 57 $[C_2HS]^+$, 45 $[CHS]^+$, 43 $[NC_2H_5]^+$, 39* (86 → 58), 29 $[C_2H_5]^+$, 28 $[N_2]^+$.

CONCLUSIONS

1,1,1-Trifluoro-2-benzylthiopropene was synthesized and the reactions of this sulfide with electrophiles and nucleophiles (H_2SO_4, SO_2Cl_2 and $NHEt_2$) leading 1,1,1-trifluoroacetone, 1,1,1-trifluoro-2,3-dichloro-2-benzylthiopropane and 1-trifluoromethyl-2-(N,N-diethylamino)-ethyl benzyl sulfide, respectively, were studied.

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