Formation of C–S Bond by the Elimination of Perfluorocarboxylic Acid

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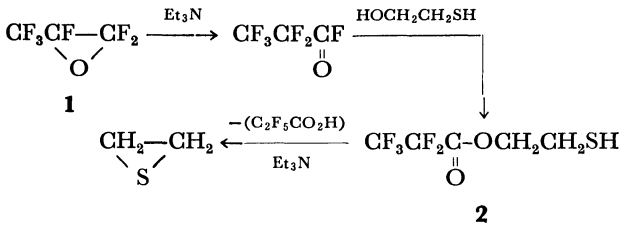
Synopsis. Thiirane was readily generated from 2-mercaptoethyl trifluoroacetate or pentafluoropropionate by the intramolecular elimination of the perfluorocarboxylic acid with triethylamine. Alkyl benzyl sulfides were also prepared from benzyl trifluoroacetate or pentafluoropropionate and alkanethiols by the intermolecular elimination of the perfluorocarboxylic acid

In a course of our studies on pentafluoropropionylation of various 1,2-bifunctional ethanes with hexafluoro-1,2-epoxypropane(**1**)–triethylamine system,[1] it was found that a considerable amount of thiirane was formed from 2-mercaptoethanol.

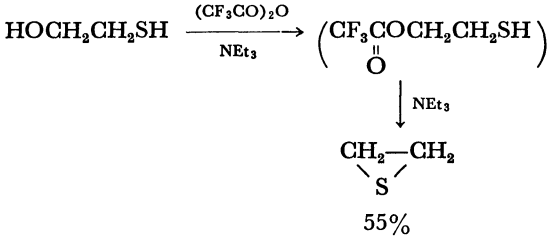


The reaction route shown above was supported by the experimental fact that pentafluoropropionic acid was eliminated very easily from 2-mercaptoethyl pentafluoropropionate (**2**) and thiirane was obtained in a yield of 60%. The formation of thiirane by decarboxylic acid reaction is not of novelty, because Miles and his co-workers have reported that thiirane was formed[2] when they examined the hydrolysis of 2-mercaptoethyl acetate with aqueous sodium hydroxide. However, the yield of thiirane in their reaction is very poor, as a mild base such as triethylamine is not strong enough for the formation of thiirane and this unstable compound easily polymerizes in the presence of aqueous sodium hydroxide.

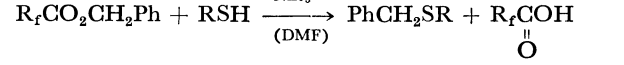
In our process, the reaction in diglyme proceeded smoothly at room temperature, in a short period such as 30 min, and the resulting thiirane was separated by only distillation under a reduced pressure (≈30 mmHg). Thus the perfluorocarboxylate seemed to be a much more convenient intermediate compound for the generation of thiiranes from 2-mercaptoethanols rather than a usual fluorine-free carboxylate.

Further we confirmed that thiirane can also be prepared by treating 2-mercaptoethanol with trifluoroacetic anhydride and two equivalents of triethylamine.

In the extention of the C–S bond formation by



the intramolecular elimination of perfluorocarboxylic acid described above, a similar intermolecular elimination was examined. We chose benzyl alcohol as an active alcohol and reactions of benzyl trifluoroacetate or pentafluoropropionate with several alkanethiols were tried. Several results of the preparation



of benzyl sulfides by this procedure are shown in Table 1. For these intermolecular condensations, it was necessary to apply more polar solvents and higher temperatures.

Table 1. Yields of $PhCH_2SR$ (%)

R	Yield (%) R_f		$PhCH_2SR$	
	CF_3[a]	CF_3CF_2[b]	Bp °C/mmHg [Mp/°C]	(lit)
n-Pr	15	55	88—89/10	(112/14)[c]
n-Bu	20	71	113—114/8	(123/13)[c]
$PhCH_2$	33	76	[48—49]	([49—50])[d]

a) GLC yield. b) Isolated yield. c) I. J. Buchi, M. Prost, H. Eichenberger, and R. Lieberherr, *Helv. Chim. Acta.*, **35**, 1527 (1952). d) "Handbook of Chemistry and Physics," 55th ed, CRC Press, Inc., Cleveland, Ohio (1974—1975), p. C498.

Thus, benzyl perfluorocarboxylate and an alkanethiol were allowed to react in *N*,*N*-dimethylformamide at ≈120 °C in the presence of triethylamine. Pentafluoropropionate gave much higher yields of sulfides than trifluoroacetate did and this should be due to the fact that a pentafluoropropionyloxyl group is a better leaving group compared with a trifluoroacetoxyl group. As the electronegativities of trifluoromethyl and pentafluoroethyl groups are almost similar,[3] the difference should be due to the bulkiness of these leaving groups. Thus in comparison with a trifluoroacetyl group, the bulkier pentafluoropropionyl group should make the ester less stable thermodynamically.

Perfluorocarboxylates of other alcohols, such as cyclohexyl-, allyl-, and *t*-butyl alcohol, were tried for this reaction, but none of good results were obtained.

Experimental

2-Mercaptoethyl Pentafluoropropionate. In a sealed glass vessel, 2-mercaptoethanol (1.56 g, 20 mmol) was treated with hexafluoro-1,2-epoxypropane (bp −27 °C, 3.32 g, 20 mmol) and a catalytic amount of triethylamine (≈0.1 g) in acetonitrile (20 ml) for 30 min at room temperature. The reaction mixture was poured into water and the lower oily layer was separated. It was washed with water, dried ($MgSO_4$) and distilled to give 2-mercaptoethyl pentafluoropropionate (3.23 g, 72%). Bp 67—68 °C/77 mmHg (1 mmHg=133.322 Pa) (lit,[1] 68 °C/77 mmHg).

2-Mercaptoethyl trimethylsilyl ether and diethyl ether

were used instead of 2-mercaptoethanol and acetonitrile in the previous experiment. 2-Mercaptoethyl pentafluoropropionate was obtained in 85% yield.

Thiirane 2-Mercaptoethanol (1.56 g, 20 mmol), triethylamine (2.02 g, 20 mmol), and diglyme (10 ml) were placed in a sealed glass tube, and the mixture was cooled to −70 °C. Liquefied hexafluoro-1,2-epoxypropane (3.32 g, 20 mmol) was introduced into this vessel and the whole was brought to room temperature with stirring. After the reaction was continued for 30 min at this temperature, the pressure was reduced to about 30 mmHg, and the gas evolved was trapped in a Dry Ice–acetone bath. The trapped material was identified to thiirane (0.72 g, 60%). Bp 53—54° C (lit,[4] bp 54.0—54.5 °C).

Triethylamine (2.02 g, 20 mmol) was added to a solution of 2-mercaptoethyl pentafluoropropionate (4.48 g, 20 mmol) in diglyme (10 ml) in an ice bath. The mixture was stirred for 30 min at room temperature. The pressure was then gradually reduced to ≈30 mmHg and evolved thiirane was collected in a Dry Ice–acetone bath (0.84 g, 70%).

To a solution of 2-mercaptoethanol (1.56 g, 20 mmol) and triethylamine (4.04 g, 40 mmol) in diglyme (10 ml), trifluoroacetic anhydride (4.20 g, 20 mmol) was added slowly in an ice bath. After 1 h of stirring at room temperature, thiirane was obtained by a similar treatment (0.60 g, 50%).

Alkyl Benzyl Sulfides. A typical procedure is as follows. The benzyl perfluorocarboxylate (10 mmol) was mixed with a thiol (12 mmol) and triethylamine (15 mmol) in *N,N*-dimethylformamide (5 ml). The mixture was heated at 120 °C for 3 h with stirring and the resulting mixture was subjected to distillation *in vacuo* to give the corresponding sulfide.

References

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