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MILD AND SELECTIVE REDUCTION OF SULFOXIDES IN THE MIXTURE WITH OTHER SULFINYL COMPOUNDS WITH TRIFLUOROACETIC ANHYDRIDE — HYDROGEN SULFIDE SYSTEM

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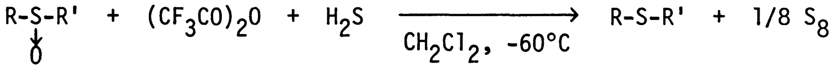
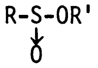
A rapid and convenient method for selective reduction of sulfoxides to the corresponding sulfides in the mixture with other sulfinyl compounds, i.e., sulfinic esters and t-butyl thiolsulfinates, with $(CF_3CO)_2O$ — H_2S system is described.

Recently many preparatively useful methods to deoxygenate sulfoxides to sulfides have been reported.$^{1)}$ The reduction of sulfoxides was shown by us to be very facile with trifluoroacetic anhydride — sodium iodide system.$^{2)}$ However this reducing system is not selective and reduces sulfinic esters and thiolsulfinates.$^{3)}$ Now we wish to report a selective method to deoxygenate sulfoxides(1) to sulfides(2) in a mixture with sulfinic esters(3) or thiolsulfinates(4) by treating with trifluoroacetic anhydride — hydrogen sulfide system. (Equation 1)



$$R\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}R' + (CF_3CO)_2O + H_2S \xrightarrow[CH_2Cl_2,\ -60^\circ C]{} R\text{-}S\text{-}R' + 1/8\ S_8 \qquad \text{---- (1)}$$

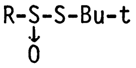
(1) (2)



$$R\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}OR'$$

(3)

a: R=p-Tol, R'=Me;
b: R=p-Tol, R'=Neopentyl;
c: R=Ph, R'=Me



$$R\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}S\text{-}Bu\text{-}t$$

(4)

a: R=Ph;
b: R=p-Cl-C_6H_4

This reaction proceeds rapidly (5 min.) even under cooling at -60°C when hydrogen sulfide gas is passed into a dichloromethane solution of the sulfoxide(1) and sulfinyl compounds, (3) or (4), together with $(CF_3CO)_2O$. After sulfur formed was filtered off, the organic layer was washed with Na_2CO_3 solution and water and dried over $MgSO_4$. Removal of solvent gave a mixture of sulfide(2) and non-reduced (3) or (4). Purification was performed by filtration through a short silica-gel column with hexane as eluent. Several representative examples are listed in Table.

The data reveal that sulfoxides are reduced selectively to the corresponding sulfides in yields exceeding 90%. Thin layer chromatography of the crude product indicated the reduction of the sulfoxide to be quantitative with each of these compounds. The selective reduction of sulfoxides in the mixture with (3) or (4) is undoubtedly due to the difference in nucleophilicity of sulfinyl oxygen atom of sulfoxides and those of the sulfinic acid derivatives, (3) or (4). The oxygen atom of sulfoxide is much more nucleophilic than that of sulfinic ester(3) or thiolsulfinate(4) and hence the formation of acyloxysulfonium salts (see Equation 2), which

Table

Selective reduction of sulfoxides(1) in a mixture with sulfinyl compounds, (3) or (4), with trifluoroacetic anhydride — hydrogen sulfide system[a]

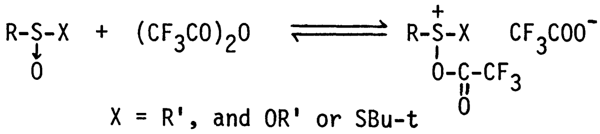
sulfoxide(1) R	R'	Sulfinyl compound added	Yield of sulfide(2) (%)
Ph	Me	-	92[b]
$PhCH_2$	$PhCH_2$	-	95[b]
n-Bu	n-Bu	-	89[b]
Ph	Ph	-	92[b]
p-Tol	Me	-	90[b]
$PhCH_2$	$PhCH_2$	3a	~95[c]
$PhCH_2$	$PhCH_2$	3b	~95[c]
$PhCH_2$	$PhCH_2$	3c	~90[c]
Ph	Me	4a	~90[c]
p-Tol	Me	4b	~90[c]

a: 5 mmole of (1) and (3) or (4), and 12 mmole of $(CF_3CO)_2O$ in CH_2Cl_2. Time 5 min. Temp. -60°C.

b: isolated yields after chromatography.

c: based on NMR analysis of chromatographed mixture (2) and (3) or (4).

is an intermediate in this equilibrium reaction, is attained much readily with the sulfoxides (X=R') than with either (3) or (4)[X=OR' or SBu-t, respectively].



$$R\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}X + (CF_3CO)_2O \rightleftharpoons R\text{-}\underset{\underset{O\text{-}\underset{\overset{\|}{O}}{C}\text{-}CF_3}{|}}{\overset{+}{S}}\text{-}X \quad CF_3COO^- \qquad \text{---- (2)}$$

X = R', and OR' or SBu-t

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References and Notes

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