Tetrahedron Letters Vol. 21, pp 1235 - 1238

0040-4039/80/0322-1235$02.00/0

DIRECT REDUCTION OF SULFONIC ACID TO THE CORRESPONDING THIOL WITH TRIFLUOROACETIC ANHYDRIDE/TETRABUTYLAMMONIUM IODIDE SYSTEM

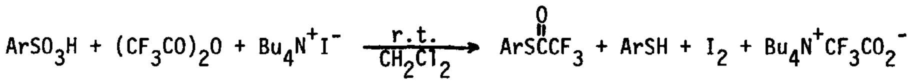
Tatsuo Numata, Hiroshi Awano, and Shigeru Oae*

Department of Chemistry, University of Tsukuba, Sakuramura, Ibaraki, 305 Japan

Arene- and alkane-sulfonic acids were easily reduced to the corresponding thiol derivatives in moderate yields with trifluoroacetic anhydride/tetrabutylammonium iodide mixture at room temperature.

Although sulfonic acid derivatives such as sulfonyl halide,[1-7] sulfonamide,[8-10] and sulfonate[11] are known to be reduced to the corresponding thiols or disulfides with typical reducing agents, no reductive method of free sulfonic acid to the corresponding lower oxidized compound such as sulfinic acid or thiol derivatives has been reported, while reductive C-S bond cleavage of arenesulfonic acids giving the corresponding arenes and sulfite are known to occur in the cathodic reduction[12] or in the treatment with aluminium-nickel alloy.[13]

Now we wish to report a first example of direct reduction of arenesulfonic acids to the corresponding thiols with trifluoroacetic anhydride - tetrabutylammonium iodide mixture[14] in moderate yields under mild conditions.



$$ArSO_3H + (CF_3CO)_2O + Bu_4N^+I^- \xrightarrow[CH_2Cl_2]{r.t.} ArS\overset{\overset{O}{\|}}{C}CF_3 + ArSH + I_2 + Bu_4N^+CF_3CO_2^-$$

p-Toluenesulfonic acid monohydrate (1 mmol) was dissolved in CH_2Cl_2 (30 ml) containing 5 - 20 equivalent amounts of $(CF_3CO)_2O$ and $Bu_4N^+I^-$, and the whole solution was allowed to stand at room temperature overnight (16 - 23 hr). The resulting dark red solution, colored with free iodine, was hydrolyzed with ice water and neutralized with 0.1 N NaOH aq. solution at 0° C, followed by decomposition of free iodine formed with aq. $Na_2S_2O_3$ solution at 0° C and drying with $MgSO_4$. After evaporation of CH_2Cl_2, the white crystalline residue, containing ammonium salt and the reduced products, was washed with benzene and the benzene extract was subjected to silica-gel column chromatography eventually giving a mixture of p-tolyl thiotrifluoroacetate as the main component and p-toluenethiol as a minor one. The ratio of these products was determined by both GLC and NMR measurements and results obtained are tabulated in Table 1. Among experiments with several compositions of the acid anhydride and ammonium iodide, the best

Table 1 Reduction of p-Tolenesulfonic Acid with $(CF_3CO)_2O/Bu_4N^+I^-$ in CH_2Cl_2

run	Sulfonic acid (mmol)		temp.	time (hr)	$(CF_3CO)_2O$ (mmol)	$Bu_4N^+I^-$ (mmol)	products (%)[a] p-TolSCOCF$_3$	p-TolSH
1	p-TolSO$_3$H.H$_2$O	(1)	r.t.	16	5	5	28	15
2	p-TolSO$_3$H.H$_2$O	(1)	r.t.	19	10	10	62	16
3	p-TolSO$_3$H.H$_2$O	(1)	r.t.	19	20	20	61	21
4	p-TolSO$_3$H.H$_2$O	(1)	r.t.	20	20	10	78	11
5	p-TolSO$_3$Na	(1)	r.t.	19	20	17	44	26
6	p-TolSO$_3$Na	(1)	r.t.	22	14	9	60	17

a) Amount of unreacted starting acid was not determined.

result was found to be obtained in the case with ten equivalent amounts of $Bu_4N^+I^-$ and twenty equivalent amounts of $(CF_3CO)_2O$ (run 4).

For practical purposes, the resulting mixture of the thiol ester and the thiol obtained was treated with sodium hydroxide methanol solution at room temperature for 30 min giving the thiol predominantly.[15] Thus, after the overall reductive procedure arenesulfonic acids gave the corresponding thiols in good yields (run 8, 10 and 12 in Table 2).

Meanwhile, arenesulfonic acids can give the corresponding disulfides in good yields by this reducing system under the following work-up procedure. The resulting reduced solution, obtained after being kept standing overnight, was hydrolyzed with a highly alkaline solution (1.5 N NaOH aq. solution) at room temperature, followed by treatment with aq. $Na_2S_2O_3$. A yellow colored crystalline residue, obtained after evaporation of CH_2Cl_2, was suspended with benzene, and the whole solution was washed several times with diluted aq. $Na_2S_2O_3$ solution until the crystalline mass was completely dissolved into aqueous layer. The resulting benzene layer was dried and evaporated to yield the corresponding disulfides in 81 - 93 % yields (runs 7, 9 and 11 in Table 2). In the case of sodium p-toluenesulfonate similar results were obtained, but the yields were slightly lower than those of the free sulfonic acid (runs 5, 6 and 13).[16]

Alkanesulfonic acids were also reduced by this system, but the yields of the disulfides were substantially low because of the formation of the corresponding thiolsulfonates (RSO_2SR) as the side products. The yield of sulfide was improved under a somewhat drastic condition

Table 2 Reduction of Sulfonic Acid with $(CF_3CO)_2O/Bu_4N^+I^-$ in CH_2Cl_2[a]

run	sulfonic acid	(mmol)	time (hr)	$(CF_3CO)_2O$ (mmol)	$Bu_4N^+I^-$ (mmol)	products (%) RSSR[b]	RSH[c]	$RSSO_2R$
7	p-$TolSO_3H.H_2O$[d]	(2)	22	30	17	93		
8	p-$TolSO_3H.H_2O$[d]	(2)	20	30	17		81	
9	p-$ClC_6H_4SO_3H.H_2O$[d]	(2)	22	30	17	85		
10	p-$ClC_6H_4SO_3H.H_2O$[d]	(2)	19	30	17		70	
11	$C_6H_5SO_3H.H_2O$[d]	(1.1)	22	23	10	81		
12	$C_6H_5SO_3H.H_2O$[d]	(2)	19	30	17		59[e]	
13	p-$TolSO_3Na$	(1)	24	20	9	76		
14	$C_8H_{17}SO_3H.H_2O$[g]	(1)	21	20	10	38		48
15	$C_8H_{17}SO_3H.H_2O$[g]	(1)	45[f]	20	10	57		6
16	$C_5H_{11}SO_3H.H_2O$[g]	(2)	23	30	20	36		h)
17	$C_8H_{17}SO_2SC_8H_{17}$	(0.35)	68	7	3.5	30		60[i]

a) All reactions were carried out at room temperature except run 15.
b) Reaction mixture was treated with 1.5 N NaOH aq. solution overnight (see text).
c) Products mixture of thiol and aryl thiotrifluoroacetate was treated with NaOH/MeOH (see text)
d) Commertially available sulfonic acids were dried in a vacuum desicator and partially dried sulfonic acids were used in the experiments. But the molar amount of the acid used was calculated as a monohydrate form. e) Benzenethiol is known to be substantially volatile.
f) reflux g) These aliphatic sulfonic acids were prepared by acidification of the corresponding sodium sulfonates by passing through a cation exchange resin(Dowex-50W-X8, 200-400 mesh, H^+ form). The molar amount of the acid was based on the amount of the sodium sulfonate used. h) not determined i) unreacted recovered thiolsulfonate.

(run 15).[17] Thus this reduction procedure is not so effective to reduce alkanesulfonic acids in one-pot reaction, however, the product mixture obtained was successfully reduced to the corresponding thiol with any one of common reducing agents, since thiolsulfonates are known to be reduced easily in good yields with several simple reducing agents.[4, 5 and 18]

Incidentally, aromatic sulfonic acid derivatives such as p-toluenesulfonyl chloride and phenyl benzenethiolsulfonate ($PhSO_2SPh$), and benzenesulfinic acid ($PhSO_2H$) have been found to be reduced much faster to the corresponding disulfides in moderate yields by simple treatment with $(CF_3CO)_2O$/NaI in acetone under mild conditions as shown in Table 3.

Table 3 Reduction of Sulfonic Acid Derivatives with $(CF_3CO)_2O$/NaI in Acetone[a)]

run	substrate	(mmol)	temp.	time	$(CF_3CO)_2O$ (mmol)	NaI (mmol)	products (%)
18	p-$TolSO_2Cl$	(2)	r.t.	15 min	6	20	p-TolSSTol-p (66)
19	$PhSO_2SPh$	(0.1)	-78° C	5 min	0.4	1	PhSSPh (83)
20	p-$TolSO_3H$	(10)	r.t.	13 hr	30	70	p-TolSSTol-p (6) + p-$TolSO_3Na$ (84)
21	$PhSO_2H$	(1.4)	-78° C	90 min	5	10	PhSSPh (58)

a) under argon atmosphere

References and Notes

1) R. Adams and C. S. Marvel, Organic Syntheses, Coll. Vol. 1, 504 (1956).
2) O. Litvay, E. Riesz and L. Landau, Chem. Ber., 62, 1863 (1929).
3) W. A. Sheppard, Organic Syntheses, 40, 80 (1960).
4) J. I. G. Cadogan, Quart. Rev. (London), 16, 223 (1962).
5) D. Cipris and D. Pouli, Synthetic Commun. 9, 207 (1979).
6) H. Alper, Angew. Chem., Int. Ed. Engl., 8, 677 (1969).
7) a) S. Smiles and C. M. Bere, Organic Syntheses, Coll. Vol. 1, 7 (1941).
   b) S. Krishna and H. Singh, J. Am. Chem. Soc., 50, 792 (1928).
   c) M. Kulka, J. Am. Chem. Soc., 72, 1216 (1950).
8) a) C. S. Marvel and P. D. Caeser, J. Am. Chem. Soc., 73, 1097 (1951).
   b) D. Klamann, Monatsh. Chem., 84, 651 (1953).
9) E. Fisher, Chem. Ber., 48, 93 (1915).
10) T. Cuving and M. Larcheveque, J. Organomet. Chem., 64, 315 (1974).
11) A. Zobacova, V. Hermankova, J. Jary, Collect. Czech. Commun., 42, 2540 (1977).
12) Reviewed by A. I. A. Khodair, A. Swelim and F. El-Sheikh, Inst. J. Sulfur Chem., B, 6, 213 (1971).
13) E. Schwenk, D. Papa, B. Whitman and H. Ginsberg, J. Org. Chem., 9, 1 (1944).
14) $(CF_3CO)_2O$/NaI system was previously reported to act as a good reducing agent for reduction of sulfoxide to sulfide [J. Drabowicz and S. Oae, Synthesis, 404 (1977)].
15) Authentic phenyl thiotrifluoroacetate (400 mg) was converted to benzenethiol (194 mg) in 89 % yield by treatment with solid NaOH (5 pellets) in 20 ml of methanol at room temperature for 30 min.
16) A mixture of trifluoroacetic anhydride and either tetramethylammonium iodide, phenyltrimethylammonium iodide, ammonium iodide or tetrabutylammonium bromide as the halide reagent was found to have no or little ability to reduce sulfonic acid.
17) Thiolsulfonate ($C_8H_{17}SO_2SC_8H_{17}$) was found to be reduced to disulfide below 30 % after keeping the mixture to stand for 3 days at room temperature (run 17).
18) J. Strating and H. J. Baker, Rec. Trav. Chim. Pays-Bas, 69, 638 (1950).

(Received in Japan 9 November 1979)