

## REDUCTION OF SULFONIC ACIDS WITH PHOSPHORUS PENTASULFIDE

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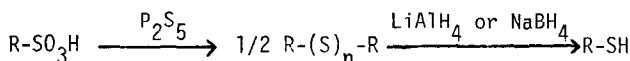
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Arene, and alkanesulfonic acids are easily reduced to the corresponding polysulfides  $R-(S)_n-R$  ( $n=2.9\sim 3.3$ ) by treatment with phosphorus pentasulfide. In this reaction, the formation of both P-O-S and P-S-H linkages is considered to be involved in the key step of the reduction.

Both arene, and alkanesulfonic acids are known to be so inert that they can not be reduced directly by ordinary procedures; for example sulfonic acids are unchanged upon treatment with  $LiAlH_4$  in refluxing  $Bu_2O$  for 3 days.<sup>1)</sup> Meanwhile, we have recently shown<sup>2)</sup> a few facile and convenient one-pot reduction procedures of sulfonic acids to thiols or disulfides in excellent yields. A similar reduction was found by Olah et al.<sup>3)</sup> In these reductions, iodide ion is the reducing agent which is oxidized eventually to iodine. Reduction of both arenesulfonic acids and sulfuric acid was found to be carried out successfully by treating these acids with a mixture of phosphorus pentoxide, polyphosphoric acid, or ethyl polyphosphate(PPE) and arenthiols. The initial step of this reduction is obviously the formation of  $RSO_2-O-\overset{O}{\underset{O-}{P}}-O-$  linkage of which the sulfur atom is attacked nucleophilically by thiol group.<sup>4)</sup> Phosphorus pentasulfide is a sulfur analog of phosphorus pentoxide and is considered to be attacked similarly by sulfonic acids at central phosphorus atom, generating an addition complex which possesses a thiol function, which can function as a reducing agent similar to iodide ion. Indeed, phosphorus pentasulfide has been found to be a new reducing agent which can reduce sulfonic acids directly to the corresponding polysulfides in good yields without any additional reagent. The reduction yields a mixture of mainly disulfide, trisulfide, tetrasulfide, as summarized in Table. The driving force of the reduction of the sulfonic acid with phosphorus pentasulfide is the formation of P-O- or P=O bond which has a higher bond energy than that of P-S- or P=S bond. Meanwhile, the thiol group combined to five coordinate phosphorus, such as  $(EtO)_2P(S)SH$  which is highly acidic ( $pK_a$  1.5~2)<sup>5)</sup> and known to be a good reducing agent, to reduce readily many organosulfur compounds<sup>6)</sup> such as sulfoxide,<sup>6a)</sup>

sulfinic acid,<sup>6b)</sup> and thiol-sulfonate.<sup>6c)</sup> Phosphorus pentasulfide alone is also known to reduce sulfoxides to corresponding sulfide.<sup>7)</sup>

**Table.** Reduction of Sulfonic Acids with Phosphorus Pentasulfide in Sulfolane



Substrate	Substrate/P <sub>2</sub> S <sub>5</sub>	Time(90~100°C) (h)	Polysulfide (%)	Reducing agent <sup>e)</sup>	Thiol (%) <sup>b)</sup>
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H	a)	24	-	LiAlH <sub>4</sub>	93
C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> H	a)	"	-	"	91
p-ClC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H	a)	"	-	"	73
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H·H <sub>2</sub> O	2/9	23	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -(S) <sub>n</sub> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -p n=3.30~3.35 d) (86) c)	"	68(68) <sup>c)</sup>
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na	2/9	24	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -(S) <sub>n</sub> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -p n=2.91~2.92 d) (73) c)	"	67
C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> Na·H <sub>2</sub> O	2/9	24	-	"	62
2,4, (CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SO <sub>3</sub> H	2/9	24	-	"	(62) <sup>c)</sup>
β-C <sub>10</sub> H <sub>7</sub> SO <sub>3</sub> Na	2/9	25	-	"	57
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> H	1.9/11.3	24	-	"	63 <sup>f)</sup>
m-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na	4/18	24	m-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> -(S) <sub>n</sub> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -m n=2.9~3.1 d)	NaBH <sub>4</sub>	(74) <sup>c)</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> SO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> N=C(SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NH <sub>2</sub>	1.2/9	24	-	LiAlH <sub>4</sub>	71
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> NH <sub>2</sub>	2/10.3	60	-	"	5 <sup>g)</sup>
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	2/9	27	-	"	16 <sup>h)</sup>
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	2/6	14	-	"	70

a) In this competition reaction, a mixture of p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H/C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>H/p-ClC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H=2/2/2(mmol) was carefully dehydrated by azeotropic distillation with benzene, and was placed in 15ml of sulfolane containing P<sub>2</sub>S<sub>5</sub>(27mmol). b) Overall yield(RSO<sub>3</sub>H→RSH), GC(SE-30, or OV-1, 1m glass column). c) Isolated yield. d) The number of sulfur atoms in the molecule was estimated from the elemental analysis. e) The reductions of polysulfides with LiAlH<sub>4</sub> and NaBH<sub>4</sub> were carried out in ether(30min) and ether-ethanol(3h) at room temperature respectively. f) In the hydrolysis of phosphoric derivatives, a mixture of 14% of pentanethiol and dipentyl polysulfide was obtained. g) Starting material was not recovered. h) Starting material was obtained in 26% yield.

Inspection of data in the Table reveals that the sulfinic acid is also reduced readily to the polysulfide. Thus the plausible reaction pathway is shown in the Scheme. Actually, the thiol



The mixture was extracted with a mixture of benzene and hexane(v/v=1/1), and chromatographed through column with a mixture of benzene and hexane(v/v=1/1) to obtain the polysulfide [ $R_f=0.25\sim 0.30$ , IR(NaCl)  $1345\text{cm}^{-1}$ ,  $1520\text{cm}^{-1}$ ,  $n=2.9\sim 3.1$ ]. In the reduction of other sulfonic acids, hexane was used for both extraction and column chromatography, in order to exclude sulfur, sulfolane, etc. Then, 430mg of di(m-nitrophenyl) polysulfide(a part of obtained polysulfide) was dissolved in a mixture of  $\text{Et}_2\text{O}-\text{EtOH}$  into which the 200mg of  $\text{NaBH}_4$  was slowly added at room temperature. After 3 hours, the mixture was poured into ether, and the whole mixture was acidified. The ether extract was washed with water and dried over  $\text{MgSO}_4$ . Thus 275mg of m-nitrobenzenethiol was obtained from the ether extract in 74% yield [IR(NaCl)  $1520\text{cm}^{-1}$ ,  $1345\text{cm}^{-1}$ ,  $2560\text{cm}^{-1}$ ].

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