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Reduction of Sulfonic Acids with Triphenylphosphine–Diaryl Disulfide System

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Diaryl disulfides are effective catalysts to reduce arenesulfonic acids with triphenylphosphine to the corresponding arenethiols in good yields, while alkanesulfonic acids are transferred into the corresponding alkyl aryl sulfides. Arenesulfonic acids bearing electron-donating substituents can be reduced more readily than those having electron-withdrawing substituents, while diaryl disulfides bearing electron-withdrawing substituents are more effective catalysts than diaryl disulfides with electron-donating ring substituents.

The first example of one-pot reduction of sulfonic acids to thiols was recently reported from this laboratory, by using $(CF_3CO)_2O/(n\text{-}Bu)_4N^+I^-$. This method is the first break through in the direct deoxygenative reduction of sulfonic acids to thiols and thiol derivatives. However, it not only requires a large excess of expensive reagents but also affords a mixture of reduction products, *i.e.* thiols and thiol trifluoroacetates.(1) G. A. Olah *et al.* reported recently a second successful one-pot reduction of sulfonic acids to the corresponding disulfides with BX_3 (X=Cl, Br, I)/KI.(2) In the previous paper, we reported another facile and quantitative deoxygenative reduction of sulfonic acids and its derivatives by a new reducing system, *i.e.* triphenylphosphine-iodine system.(3) This paper deals with another facile and attractive reduction of sulfonic acids with triphenylphosphine–diaryl disulfide system. Although triphenyphosphine is known to be a relatively strong reducing agent, it does not react directly with sulfonic acids. Meanwhile, the mixture of triphenylphosphine with halogen(4) and that of triphenylphosphine with disulfide(5) respectively are known to give phosphonium salts. Several reactions are known to utilize such phosphonium salts *e.g.* the conversion of alcohol and phenol derivatives to the corresponding halides by treatment with the phosphine and halogen,(6) the desulfurization of disulfides to the corresponding sulfides with the phosphine,(7) the condensation of carboxylic acids and alcohols or amines to the corresponding esters or amides by treatment of the phosphine and diaryl disulfide(8) or diselenide,(9) and the conversion of alcohols to the corresponding sulfides by treatment with a mixture of the phosphine and the disulfide.(10) Thus a mixture of triphenylphosphine and a catalytic amount of diaryl disulfide or diaryl diselenide was our choice system for the reduction of sulfonic acids.

Results and Discussion

Reduction of Arenesulfonic Acids and Alkanesulfonic Acids to the Corresponding Arenethiols and Alkyl Aryl Sulfides with Triphenylphosphine and Diaryl Disulfide. Arenesulfeyltriphenylphosphonium arenethiolate is known to be formed upon treatment of diaryl disulfide with triphenylphosphine and has been utilized for the synthetic organic chemistry, *e.g.* syntheses of alkyl aryl sulfides,(10) peptide synthesis, *etc.*(8) This reagent system was found to reduce also arenesulfonic acids. The reducing ability of the system appears to depend on the choice of the disulfide used for the reduction. Some disulfides showed nearly the same activity as iodine, while others were found to be much weaker reducing catalysts than iodine.(3) In this reducing system, the amount of the disulfide did not affect the yield (Table 2) of the thiol, the reduction product, but changed the time to complete the reaction, suggesting that the disulfide acts as a catalyst. GLC analysis after the completion of reaction showed two kinds of thiols and three kinds of disulfides. These disulfides were then heated with an enough amount of triphenylphosphine and water, to be reduced to the thiols of which the yields were determined by GLC or isolation (Eq. 1).

$$\mathrm{ArSO_3H} + \left(3+\frac{1}{2}\right)\mathrm{Ph_3P} + \frac{1}{2}\,(\mathrm{Ar'S})_2 \xrightarrow[\text{2) H}_2\text{O}]{\text{1) reflux in benzene}} \mathrm{ArSH} + \mathrm{Ar'SH} + \left(3+\frac{1}{2}\right)\mathrm{Ph_3PO} \qquad (1)$$

The reaction is considered to be resulted by the following consecutive reactions (Eqs. 2—7) as postulated in the reaction of triphenylphosphine/iodine system.(3)

$$\mathrm{Ar'SSAr'} + \mathrm{Ph_3P} \rightleftharpoons \mathrm{Ar'S\text{–}\overset{+}{P}Ph_3\ Ar'S^-} \qquad (2)$$

$$\mathrm{ArSO_3H} + \mathrm{Ar'S\text{–}\overset{+}{P}Ph_3\ Ar'S^-} \overset{K_3}{\rightleftharpoons} \mathrm{ArSO_3^-\ Ar'S\text{–}\overset{+}{P}Ph_3} + \mathrm{Ar'SH} \qquad (3)$$

$$\mathrm{ArSO_3^-\ Ar'S\text{–}\overset{+}{P}Ph_3} \overset{K_4}{\rightleftharpoons} \mathrm{ArSO_2\text{–}O\text{–}\overset{+}{P}Ph_3\ Ar'S^-} \qquad (4)$$

$$\mathrm{ArSO_2\text{–}O\text{–}\overset{+}{P}Ph_3\ Ar'S^-} \longrightarrow \mathrm{ArSO_2SAr'} + \mathrm{Ph_3PO} \qquad (5)$$

$$\mathrm{ArSO_2SAr'} + 2\,\mathrm{Ph_3P} \longrightarrow \frac{1}{3}\,[\mathrm{ArSSAr} + \mathrm{ArSSAr'} + \mathrm{Ar'SSAr'}] + 2\,\mathrm{Ph_3PO} \qquad (6)$$

$$\mathrm{ArSSAr} + \mathrm{ArSSAr'} + \mathrm{Ar'SSAr'} + 3\,\mathrm{Ph_3P} + 3\,\mathrm{H_2O} \longrightarrow 3\,\mathrm{ArSH} + 3\,\mathrm{Ar'SH} + 3\,\mathrm{Ph_3PO} \qquad (7)$$

The reaction of alkanesulfonic acid such as 1-phentanesulfonic acid with triphenylphosphine/di-2-pyridyl disulfide gave the alkyl pyridyl sulfide.

$$\mathrm{CH_3(CH_2)_4SO_3H} + (\mathrm{PyS})_2 + 4\,\mathrm{Ph_3P} \longrightarrow \mathrm{CH_3(CH_2)_4\text{–}S\text{–}Py} + 3\,\mathrm{Ph_3PO} + \mathrm{Ph_3PS} + \mathrm{PySH} \qquad (8)$$

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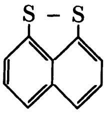
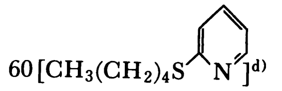
TABLE 1. REACTION OF SULFONIC ACID WITH TRIPHENYLPHOSPHINE/DIARYL DISULFIDE IN BENZENE UNDER NITROGEN ATMOSPHERE[a)]

$ArSO_3H$	$ArSO_3H/Ph_3P/(Ar'S)_2$	$(Ar'S)_2$	Time/h (Reflux)	Yields of products/%		
				$ArSH$[b)]	$Ar'SH$[b)]	Ph_3PO
2,4-$(CH_3)_2C_6H_3SO_3H$	2/8/1	(p-$ClC_6H_4S)_2$	21	(60)[c)]	(76)[c)]	—
p-$CH_3C_6H_4SO_3H$	2/10/1	(p-$ClC_6H_4S)_2$	24	75(60)[c)]	100(90)[c)]	—
$C_6H_5SO_3H$	2/10/1	(p-$ClC_6H_4S)_2$	24.5	90	94	—
p-$ClC_6H_4SO_3H$	2/8/1	(p-$ClC_6H_4S)_2$	24	26	100	—
2,4-$(CH_3)_2C_6H_3SO_3H$	2/8/1	(p-$CH_3C_6H_4S)_2$	28	46(42)[c)]	(78)[c)]	—
p-$CH_3C_6H_4SO_3H$	2/8/1	(p-$CH_3C_6H_4S)_2$	23.5	90(90)[c)]	100	90
$C_6H_5SO_3H$	2/8/1	(p-$CH_3C_6H_4S)_2$	36	14	85	—
p-$ClC_6H_4SO_3H$	2/8/1	(p-$CH_3C_6H_4S)_2$	22	Trace	100	—
p-$CH_3C_6H_4SO_3H$	2/8/1		24	63	—	—
p-$CH_3C_6H_4SO_3H$	1/4/0.5	$(C_6H_5Se)_2$	24	29	—	—
p-$ClC_6H_4SO_3H$	2/14(Bu_3P)/1.5	(p-$CH_3C_6H_4S)_2$	18	No reaction		
p-$CH_3C_6H_4SO_3H$	2/8/1/0.2(Bu_4NI)	(p-$ClC_6H_4S)_2$	2	91	100	—
$CH_3CH_2SO_3H$	2/11/3	(p-$ClC_6H_4S)_2$	29	No reaction		

a) After this reaction, the mixture of 300 mg of water and 2 ml of dioxane was added and refluxed for 0.5—1.0 h.
b) GLC yield (20% OV-1, 10 m glass column). c) Isolated yield.

TABLE 2. REACTION OF SULFONIC ACID WITH TRIPHENYLPHOSPHINE/DIARYL DISULFIDE IN BENZENE UNDER NITROGEN ATMOSPHERE[a)]

$ArSO_3H$	$ArSO_3H/Ph_3P/(Ar'S)_2$	$(Ar'S)_2$	Time/h (Reflux)	Yields of products/%		
				$ArSH$[b)]	$Ar'SH$[b)]	Ph_3PO
2,4-$(CH_3)_2C_6H_3SO_3H$	2/8/1	$(PyS)_2$[e)]	2	(92)[c)]	—	(88)[c)]
p-$CH_3C_6H_4SO_3H$	2/8/1	$(PyS)_2$[e)]	2	87(73)[c)]	—	—
2-$C_{10}H_7SO_3H$	2/8/1	$(PyS)_2$[e)]	4	(76)[c)]	—	—
p-$ClC_6H_4SO_3H$	2/8/1	$(PyS)_2$[e)]	4	60(53)[c)]	—	(65)[c)]
$C_6H_5SO_3H$	2/8/1	$(PyS)_2$[e)]	2	85	—	(76)[c)]
p-$CH_3C_6H_4SO_3H$	2/8/0.2	$(PyS)_2$[e)]	5	(73)[c)]	—	—
p-$CH3C_6H_4SO_3H$	2/8(Bu_3P)/1	$(PyS)_2$[e)]	4	(26)[c)]	—	—
$CH_3(CH_2)_4SO_3H$	2/10/2	$(PyS)_2$[e)]	3.5 (room temperature)	 60 [$CH_3(CH_2)_4S$-2-pyridyl][d)]		
$C_6H_5SO_3H$	2/9/1/2(Bu_3N)	$(PyS)_2$[e)]	2	18	—	—
2-$C_{10}H_7SO_3H$	2/8/1	$(Cl_3C_6H_2S)_2$[f)]	32	Trace	—	—
p-$CH_3C_6H_4SO_3H$	2/8/1	$(Cl_3C_6H_2S)_2$[f)]	3	75(60)[c)]	(100)[c)]	(75)[c)]
$C_6H_5SO_3H$	2/8/1	$(Cl_3C_6H_2S)_2$[f)]	5	68	—	—
2,4-$(CH_3)_2C_6H_3SO_3H$	2/8/1	$(Cl_3C_6H_2S)_2$[f)]	5	(66)[c)]	(97)[c)]	(61)[c)]
p-$ClC_6H_4SO_3H$	2/8/1	$(Cl_3C_6H_2S)_2$[f)]	25	Trace	—	—

a) After this reaction, the mixture of 300 mg of water and 2 ml of dioxane was added and refluxed for 0.5—1.0 h. GLC yield (20% OV-1, 10 m glass column). c) Isolated yield. d) Pentyl 2-pyridyl sulfide was obtained, and Ph_3PS was also obtained in 83% isolated yield. e) Di-2-pyridyl disulfide. f) Bis(2,4,5-trichlorophenyl) disulfide.

When dialkyl disulfide, such as lipoic acid or dibutyl disulfide was used, the following known desulfurization reaction took place rather than the reduction to the thiol.[11)]

$$RSSR + Ph_3P \longrightarrow RSR + Ph_3PS \qquad (9)$$

Thus, diaryl disulfides had to be used for this purpose. Inspection of the data in Tables 1, 2, and Fig. 1 reveals that the diaryl disulfide which bears a stronger electron-withdrawing aryl group is a better catalyst in the reduction of sulfonic acids with triphenylphosphine; *e.g.* unsubstituted diphenyl disulfide exhibits only a trivial catalytic activity, however, the catalytic ability of bis(2,4,5-trichlorophenyl) disulfide is nearly as strong as that of iodine.[3)] Di-2-pyridyl disulfide was found to be the best among several disulfides tested (Tables 1 and 2), while 1,2-dithiaacenaphthene was not a good catalyst, probably due to the unfavorable equilibrium (Eq. 2) because of its unusually high stability of the stereoelectronic arrangement, or due to the formation of a very stable phosphorane intermediate by the reaction between triphenylphosphine and 1,2-dithiaacenaphthene. Diphenyl diselenide displayed only a weak catalytic

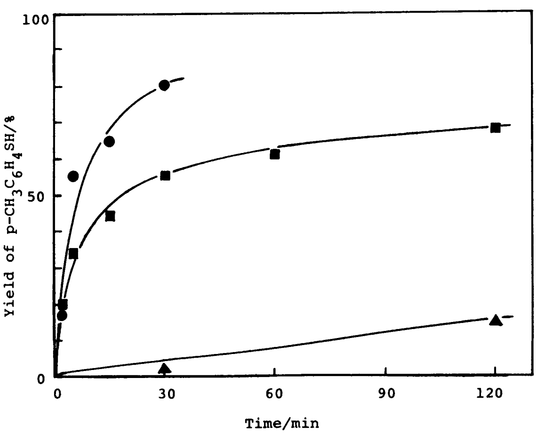


Fig. 1. Reaction of p-$CH_3C_6H_4SO_3H$ with $Ph_3P/(ArS)_2$ in benzene under reflux conditions. p-$CH_3C_6H_4SO_3H/Ph_3P/(ArS)_2=2/8/1$ (mmol). ●: Di-2-pyridyl disulfide, ■: Bis(2,4,5-trichlorophenyl) disulfide, ▲: Bis(p-chlorophenyl) disulfide.

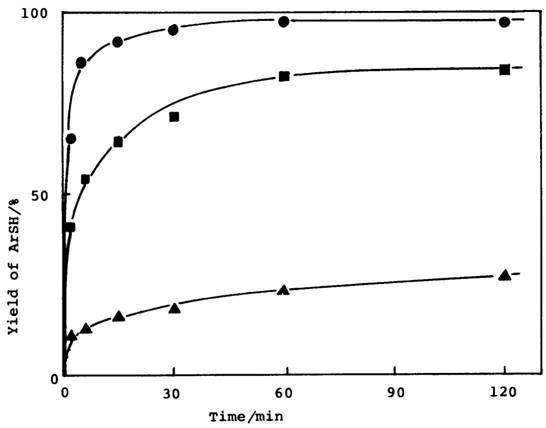


Fig. 2. Reaction of $ArSO_3H$ with $Ph_3/(PyS)_2$ in benzene at 15 °C. p-$CH_3C_6H_4SO_3H/C_6H_5SO_3H/p$-$ClC_6H_4SO_3H/Ph_3P/(PyS)_2=1/1/1/13/1.5$ (mmol). ●: p-$CH_3C_6H_4SO_3H$, ■: $C_6H_5SO_3H$, ▲: p-$ClC_6H_4SO_3H$. $(PyS)_2$: Di-2-pyridyl disulfide.

activity. The use of tributylphosphine instead of triphenylphosphine led to a sluggish reaction even when it was used in combination with di-2-pyridyl disulfide.

Inspection of the data in Tables 1, 2, and Fig. 2, reveals that the introduction of an electron-releasing substituent on the aromatic ring of arenesulfonic acid accelerates the reduction with $Ph_3P/(Ar'S)_2$ system. Typical examples are shown in Fig. 2. In contrast to the reaction with triphenylphosphine/iodine system, addition of tertiaryl amine in the reaction of the arenesulfonic acid with triphenylphosphine/diaryl disulfide system did not accelerate the reaction but slightly retarded the reaction (Table 2). The rate of the reaction of sodium arenesulfonate in the presence of crown ether was found to be much lower than that of the corresponding acid. This opposite behavior with bases in the reaction of $Ph_3P/(Ar'S)_2$ system to that with Ph_3P/I_2 system suggests that since arenethiolate anion is a much stronger base than sulfonate anion in the reduction with $Ph_3P/(Ar'S)_2$ system, K_3 is quite large and hence a higher concentration of the sulfonate anion can be maintained, however K_4 is very small. Whereas in the case of Ph_3P/I_2 system, since hydrogen iodide would be a strong acid comparable to the sulfonic acid in an aprotic solvent, K_{10} would not be sufficiently large

$$ArSO_3H + Ph_3\overset{+}{P}\text{-}I\ I^- \overset{K_{10}}{\rightleftharpoons} ArSO_3^-\ Ph_3\overset{+}{P}\text{-}I + HI \quad (10)$$

$$ArSO_3^-\ Ph_3\overset{+}{P}\text{-}I \overset{K_{11}}{\rightleftharpoons} ArSO_2\text{-}O\text{-}\overset{+}{P}Ph_3\ I^- \quad (11)$$

enough to maintain a high concentration of the sulfonate anion in the absence of any base catalyst, however, K_{11} is larger than K_4.[3] These considerations along with the actual observations would suggest that the rate-determining step involves the nucleophilic substitution on the phosphorus atom of the arenesulfenyltriphenylphosphonium ion by the sulfonate anion. This hypothesis is also in accordance with the observation that a diaryl disulfide bearing an electron-withdrawing group is a better catalyst than that which bears an electron-donating substituent in the reduction of arenesulfonic acids with triphenylphosphine as shown in Figs. 1 and 2; *i.e.* the better leaving ability of $Ar'S^-$ and the stronger nucleophilicity of $ArSO_3^-$ facilitate the reactions Eqs. 2 and 4. If the following elemental reaction, Eq. 5, is the rate-determining step of this reaction, the observed electronic demand should be the opposite, since the nucleophilicity of $Ar'S^-$ increases with the decrease of electronegativity of Ar′ group and any electron-withdrawing substituent on Ar group should accelerate the nucleophilic displacement on the sulfonyl sulfur. The retardation of the rate of the reaction, Eq. 3, by addition of any base can be rationalized in terms of our postulate that the rate-determining step is the reaction shown by Eq. 4. If the reaction shown by Eq. 5 would be the rate-determining step, the addition of a base would have to accelerate the reaction, since the base ionizes the thiol, generating the thiolate anion which is a much stronger nucleophile than the thiol, toward the sulfonyl sulfur. Once the thiosulfonic *S*-ester is formed, this can be very readily reduced by either triphenylphosphine[3] or thiol.

Alkyl arenesulfonate, sodium arenesulfonate, and tetraethylammonium benzenesulfonate, however, could not be reduced to the corresponding thiols even with triphenylphosphine/dipyridyl disulfide which was the best catalyst.

Experimental

Preparation of Disulfide. Disulfides, which are not commercially available, were synthesized by a known method.[12] To a benzene solution (150 ml) of a thiol (0.05 mol) and pyridine (0.055 mol), was added dropwise iodine (0.025 mol) dissolved in benzene (50 ml). When the color of the solution changed to brown by excess iodine, the addition was stopped. The reaction mixture was washed with water, 5% HCl solution, $Na_2S_2O_3$ solution, and then water again, and the organic layer was dried over $MgSO_4$. After evaporation of benzene, the residual disulfide was purified by recrystallization usually from hexane. Yields were nearly quantitative. Di-*p*-tolyl disulfide mp 44—45 °C (lit,[13] 46 °C). Bis(*p*-chorophenyl) disulfide mp 70—71 °C (lit,[14] 73 °C). 1,2-Dithiaacenaphthene was prepared according to the method of Zweig and Hoffmann, starting with commercial 8-amino-1-naphthalenesulfonic acid *via* initial formation of yellow crystals of 1,8-naphthalenedithiol[7.1%, NMR ($CDCl_3$) $\delta=$ 4.11 (2H, s), 7.0—7.8 (6H, m)] and subsequent autoxidation of the dithiol (84%). The product was recrystallized from ethanol. Mp 116—117 °C (lit,[15] 116 °C).

Competitive Reduction of p-*Substituted Benzenesulfonic Acids with $Ph_3P/(PyS)_2$ System.* A mixture of 190.2 mg (1 mmol) of *p*-toluenesulfonic acid, 176 mg (1 mmol) of benzenesulfonic acid, and 192.5 mg (1 mmol) of *p*-chlorobenzenesulfonic acid was dissolved in 5 ml of benzene, and the mixture was refluxed in a reactor which was equipped with a condenser and a calcium chloride tube. These sulfonic acids were dehydrated to nearly completely dry prior to the reaction by way of azeotropic distillation with benzene. After 3406 mg (13 mmol) of triphenylphosphine and 154 mg (1 mmol) of biphenyl (standard) were added to the mixture of these sulfonic acids, this reactor was equipped with another condenser and a nitrogen balloon and then substituted with this inert gas with a vacuum pump. Then, 330 mg (1.5 mmol) of di-2-pyridyl disulfide which was dissolved in 5 ml of dry benzene was added into the mixture which was stirred at 75 °C. A small portion, 0.1 ml, of the reaction mixture was picked up by a microsyringe and quenched with a mixture of water–dioxane–benzene ($v=1/1/2$) at every fixed time (2, 6, 15, 30, 60, and 120 min from initial reaction time respectively).

The yields of three thiols obtained by this method were determined by comparison of the GLC curve with the predetermined calibration curve by gas chromatography (SE-30, using biphenyl as the standard).

Relative Catalytic Effects of Various $(Ar'S)_2$ Catalysts in the Reduction of p-*Toluenesulfonic Acid with $Ph_3P/(Ar'S)_2$ System.* *p*-Toluenesulfonic acid monohydrate 381 mg (2 mmol) was dissolved in 5 ml of benzene, refluxed, and dehydrated to nearly completely dry by the same procedure. After 2100 mg (8 mmol) of triphenylphosphine and 300 mg (2 mmol) of biphenyl were added to this dried sulfonic acid, this reactor was equipped with another condenser and a nitrogen balloon, and was substituted with this inert gas with a vacuum pump. Then, 3 ml of dry benzene was added to this mixture and 1 mmol of a chosen diaryl disulfide (di-2-pyridyl disulfide, bis(2,4,5-trichlorophenyl) disulfide, or bis(*p*-chlorophenyl) disulfide) which was dissolved in 5 ml of dry benzene was added to this mixture (total benzene 8 ml) and the whole mixture was stirred, and refluxed (bath temperature 112 °C). A small portion, 0.1 ml, of reaction mixture was picked up by a microsyringe and quenched with a mixture of water–dioxane–benzene ($v=1/1/2$) at fixed time intervals. The yields of thiols obtained by this procedure were determined by comparison of the GLC curve with the predetermined calibration curve by gas chromatography (SE-30, using biphenyl as the standard).

Reductive Conversion of Alkanesulfonic Acid with $Ph_3P/(PyS)_2$ System. 1-Pentanesulfonic acid, 304 mg (2 mmol) of which was dried completely by a vacuum pump and 2620 mg (10 mmol) of triphenylphosphine were added into a reactor which was equipped with a condenser and a nitrogen balloon. Then, 440 mg (2 mmol) of di-2-pyridyl disulfide which was dissolved in 5 ml of dry benzene was added to this mixture which was then stirred for 3.5 h at room temperature; the reaction was monitored by GLC. After the reaction, the yields of triphenylphosphine sulfide, pentyl 2-pyridyl sulfide were determined by GLC (SE-30). Pentyl 2-pyridyl sulfide 60% IR (NaCl) 750, 1120, 1400, 1440, 1570 cm^{-3}. GC-MS: *m/e* 181, TLC (benzene) $R_f=0.4$, bp 104—106 °C/5.5 mmHg (1 mmHg $=$ 133.322 Pa). Found: C, 66.33; H, 8.35; N, 7.77. Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.33; N, 7.72. NMR (CCl_4) $\delta=8.3$ (m, 1H), 6.7—7.5 (m, 3H), 0.9 (t, 3H, $J=6$ Hz), 1.1—2.9 (m, 6H), 3.15 (t, 2H, $J=6$ Hz).

Triphenyphosphine sulfide 83%. The yield of triphenylphosphine oxide was determined through a silica-gel column chromatography with benzene as eluent (85%).

Preparation of Diphenyl Diselenide. Diphenyl diselenide was prepared according to a known procedure[16,17] by autoxidation of benzeneselenol which was prepared by treating phenyl Grignard reagent with black selenium in an excellent yield. Mp 57—58 °C (lit,[17] 61—63 °C).

Reduction of Arenesulfonic Acid with $Ph_3P/(PyS)_2$/Amine System. To a carefully dehydrated mixture of 352 mg (2 mmol) of benzenesulfonic acid and 371 mg (2 mmol) of tributylamine, 2360 mg (9 mmol) of triphenylphosphine was added into a reactor which was equipped with a condenser and a nitrogen balloon and substitued thoroughly with this inert gas with a vacuum pump. Then, 220 mg (2 mmol) of di-2-pyridyl disulfide which was dissolved in 5 ml of dry benzene was added to this mixture. The reaction mixture was stirred and refluxed for 2 h, following the reaction by GLC. Then a mixture of 3 ml of water and 3 ml of dioxane was added to this reaction mixture which was refluxed for 0.5 h. Benzenethiol was obtained in 18% yield by GLC.

References

1) T. Numata, H. Awano, and S. Oae, *Tetrahedron Lett.*, **21**, 1235 (1980).

2) G. A. Olah, S. C. Narang, L. D. Field, and R. Karpeles, *J. Org. Chem.*, **46**, 2408 (1981).

3) S. Oae and H. Togo, *Bull. Chem. Soc. Jpn.*, **56**, 3802 (1983).

4) A. D. Beveridge, G. S. Harris, and F. Inglis, *J. Chem. Soc., Perkin Trans. 1* , **1966**, 520; L. Horner and H. Nickel, *Ann. Chim. (Paris)*, **597**, 20 (1955).

5) D. N. Harpp, J. G. Gleason, *J. Am. Chem. Soc.*, **93**, 2437 (1971).

6) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964); G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Lett.*, **1964**, 2509; R. Michinek and W. Liittke, *Synthesis*, **1975**, 255.

7) D. N. Harpp and J. G. Gleason, *J. Org. Chem.*, **35**, 3259 (1970); D. N. Harpp, J. G. Gleason, and J. P. Snyder, *J. Am. Chem. Soc.*, **90**, 4181 (1968); I. L. Knunyants, *Dokl. Chem.*, **224**, 521 (1975); D. N. Harpp and J. G. Gleason, *J. Org. Chem.*, **36**, 73 (1971); D. N. Harpp and J. G. Gleason, *J. Am. Chem. Soc.*, **93**, 2437 (1971).

8) S. Kobayashi, T. Iimori, T. Izawa, and M. Ohno, *J. Am. Chem. Soc.*, **103**, 2406 (1981); R. Matsueda, H. Maruyama, M. Ueki, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **44**, 1373 (1971); T. Endo, S. Ikenaga, and T. Mukaiyama, *ibid.*, **43**, 2632 (1970); T. Mukaiyama, K. Goto, R. Matsueda, and T. Ueki, *Tetrahedron Lett.*, **1970**, 5293; E. J. Corey and D. J. Brunelle, *ibid.*, **1976**, 3409; T. Mukaiyama, M. Ueki, H. Maruyama, and R. Matsueda, *J. Am. Chem. Soc.*, **90**, 4490 (1968); T. Takaku and Y. Shimada, *Chem. Lett.*, **1975**, 873; T. Mukaiyama and M. Hashimoto, *J. Am. Chem. Soc.*, **94**, 8528 (1972).

9) H. Takaku, T. Konishi, and H. Hata., *Chem. Lett.*, **1977**, 655.

10) I. Nakagawa and T. Hata., *Tetrahedron Lett.*, **1975**, 1409.

11) D. N. Harpp, J. G. Gleason, and J. P. Snyder, *J. Am. Chem. Soc.*, **90**, 4181 (1968); D. N. Harpp and J. G. Gleason, *J. Org. Chem.*, **36**, 73 (1971).

12) D. T. McAllen, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3629 (1951).

13) L. Field, *J. Am. Chem. Soc.*, **74**, 394 (1954).
14) M. B. Sparke, J. L. Cameron, and N. Kharasch, *J. Am. Chem. Soc.*, **75**, 4907 (1953).
15) A. Zweig and A. K. Hoffmann, *J. Org. Chem.*, **30**, 3997 (1965).
16) E. C. Horning, *Org. Synth.*, Coll. Vol. III, 771 (1965).
17) Aldrich Chemical Co.