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Reduction of Sulfonic Acids and Related Organosulfur Compounds with Triphenylphosphine-Iodine System

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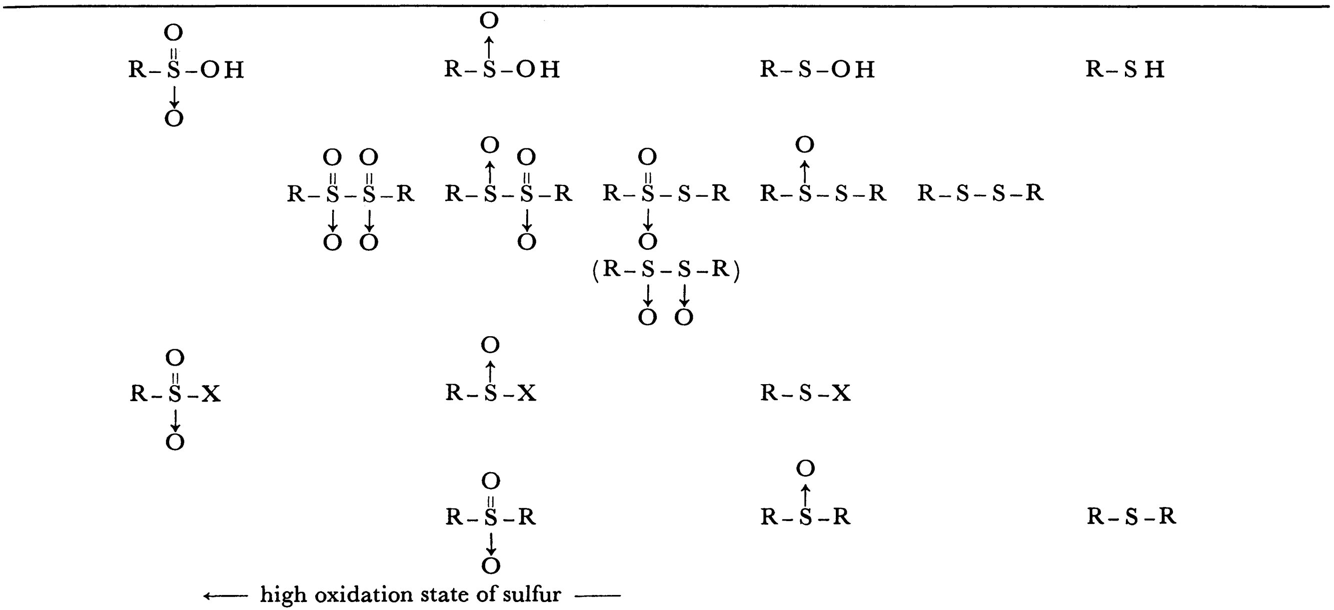
Arenesulfonic acids, their sodium salts, and alkyl arenesulfonates can be reduced readily to the corresponding arenethiols quantitatively by treatment with a mixture of triphenylphosphine and a catalytic amount of iodine, while alkanesulfonic acids, sulfinic acids, disulfides, thiosulfonic *S*-esters, and sulfonates are also readily reduced to the corresponding thiols similarly. Upon treatment with a mixture of triphenylphosphine and excess iodine, however, these aliphatic sulfur compounds are converted eventually to the corresponding alkyl iodides. The relative reactivities of these sulfonyl derivatives in the reaction with the triphenylphosphine–iodine system are the following. Aromatic series: $ArSO_2Cl$, $ArSO_2SAr' > ArSO_2H > ArSO_3R > ArSO_3^-HNBu_3^+$ (or PyH^+) $> ArSO_3H > ArSO_2SO_2Ar \gg ArSO_2CH_2C(CH_3)_3$, $ArSO_3Ar'$. Aliphatic series: RSO_2Cl, RSO_2SR', $RSO_2^-HNBu_3^+ > RSO_3^-HNBu_3^+ > RSSR$, $RSO_2H > RSO_3H > RSH > RSO_3R'$. In these reactions, the arenesulfonic acids bearing electron-donating substituents can be reduced more readily than those having electron-withdrawing substituents.

Organosulfur compounds can have several oxidative states, and the systematic representation of those compounds is shown in the Table 1 in which various sulfur compounds are arranged in order of the decrease of oxidation state from left to right hand side.$^{1)}$ Sulfur atom in the sulfonic acid is in the highest oxidation state. Since the disulfone is formally a dehydrated condensation product between the sulfonic acid and the sulfinic acid, it is placed at the position between these two compounds in the Table. The sulfinylsulfone occupies the same position as the sulfinic acid, since the sulfinylsulfone is formed by dehydration of the sulfinic acid. While the thiosulfonic *S*-ester and the α-disulfoxide are also placed in the same position, the thiosulfinic *S*-ester and the disulfide are assigned at the different oxidation states as shown in Table 1.

Among these compounds, the sulfonic acid is exceptionally stable and inert to most reducing agents hitherto known, and no good method has been found to reduce sulfonic acids in one step. Reduction of other oxidized sulfur compounds can be found in numerous literatures, most of which are, however, rather fragmentary works done only for synthetic interests. Thus no systematic investigation on the reduction of these organic sulfur compounds has been carried out. Meanwhile, sulfonation of hydrocarbon has been a very important industrial process to introduce a sulfur functional group into organic compounds. Meanwhile sulfonic acids are so widely used in general chemical industries and also in laboratory organic syntheses, and hence a good method to reduce sulfonic acids has long been invoked, since synthetic chemistry using organosulfur compounds has recently been developed extensively. The purpose of this work is to discover a new reducing system powerful enough to reduce even organic sulfonic acids and also to investigate systematically the modes of deoxygenation of all these common oxidized organic compounds with the same reducing agent.

TABLE 1. OXIDOREDUCTION TABLE FOR ORGANOSULFUR COMPOUNDS



X: Halogens, NR^1R^2, OR.

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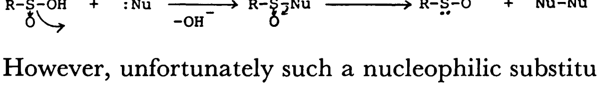
Direct electron transfer from alkali metal and related compounds to sulfonic acid has been known to lead mainly to reductive cleavage of C–S bond[2] (C–S bond dissociation energy: ≈293 kJ/mol[3]). Therefore, the deoxygenative reduction of the sulfonic acid would have to proceed stepwise *via* the initial nucleophilic displacement of OH group of the sulfonic acid by a good leaving group, followed by subsequent nucleophilic attack on the leaving group by the second nucleophile as shown in Eq. 1.

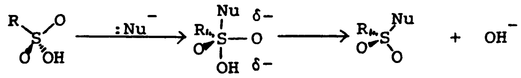


(1)

However, unfortunately such a nucleophilic substitution of OH^- group of the sulfonic acid does not readily proceed. Followings are some of the reasons why the sulfonic acid is so inert toward common reducing agents.

1) The sulfonic acid is so strong that it gives away proton to the nucleophilic reducing agent which upon protonation becomes no longer an effective nucleophile, while the deprotonated sulfonate anion possesses negatively charged three oxygen atoms which repel even strong nucleophiles to approach the central sulfur atom.

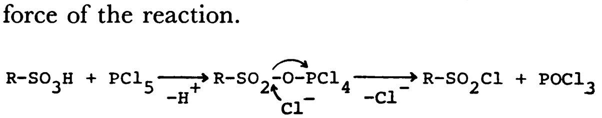
2) The reactivities of sulfonic acids and derivatives in nucleophilic displacements would be somewhat reduced since there would be unfavorable lone pair-lone pair repulsion between the nucleophile and two very electronegative oxygens at equatorial positions at the transition state of the trigonal bipyramide structure for the reaction. The sulfinic acid and its derivatives, having only one polarized oxygen atom on the sulfur and relatively weak S–O linkages, is more reactive in the nucleophilic displacement.



(2)

3) The poor leaving ability of OH group may also be partly responsible for the low reactivity of the sulfonic acid toward most nucleophiles.

However, the sulfonic acid can be made more reactive by replacing hydrogen by a suitable electron-withdrawing Y group to form RSO_2–OY upon treatment with a good condensing agent, XY. Indeed, nucleophilic displacement of OH group from the sulfur atom of sulfonic acid is very difficult, however, once RSO_2OY is formed, nucleophilic displacement of OY group in RSO_2OY by hard nucleophiles proceeds rather readily. Chlorination of sulfonic acids with PCl_5[4] or $SOCl_2$[5] is a good example (Eqs. 3 and 4) of transformation of sulfonic acids to RSO_2OY species. Obviously the formation of very stable phosphoryl chloride or SO_2 is the driving force of the reaction.



(3)

(4)

Thus, the key step of the reduction of the sulfonic acid represented by Eq. 5 is the activation of leaving OH group by the introduction of Y group on the sulfonyl oxygen, while Y should be an electron-withdrawing group and hence YO^- ought to be an excellent leaving group in the subsequent nucleophilic displacement. Once the intermediate (I) is formed, subsequent reactions are quite facile.

$$\mathrm{R\text{-}SO_3H + XY} \xrightarrow[\text{-HX}]{} \mathrm{R\text{-}SO_2\text{-}OY}$$

$$\xrightarrow{:\mathrm{Nu}^-} \underset{\text{(I)}}{\mathrm{R\text{-}SO_2Nu}} + \mathrm{YO}^- \qquad (5)$$

For example, sulfonyl chloride,[6] sulfonamide,[7] sulfonate,[8] thiosulfonic *S*-ester,[9] and sulfonic anhydride[10] (Nu=Cl, NRR′, OR, SR, and OSO_2R, respectively) are all intermediates of this type (I) which can be reduced to the corresponding thiols by common reducing agents. Thus, the success of the reduction of the sulfonic acids depends entirely upon a choice of XY and Nu^- to promote the reaction shown in Eq. 5. The first example of one pot reduction of sulfonic acids to thiols was recently reported from this laboratory, by using $(CF_3CO)_2O/(n\text{-}Bu)_4N^+I^-$, $X=CF_3CO_2^-$, $Y=CF_3CO$, $Nu^-=I^-$ shown in Eq. 5. This method is the first break through in the direct deoxygenative reduction of sulfonic acids, however, it not only requires a large excess of expensive reagents but also affords a mixture of reduction products, *i.e.* thiols and thiol trifluoroacetate.[11] More recently, G. A. Olah *et al.* reported the reduction of sulfonic acids to the corresponding disulfides with BX_3(X=Cl, Br, I)/KI.[12]

A series of extensive investigations on these basic problems have provided us a few other useful one-pot procedures to reduce sulfonic acids. Among those, the reducing system consisted of triphenylphosphine and iodine is quite convenient for reducing arenesulfonic acids to the corresponding arenethiols and also for reductive conversion of alkanesulfonic acids and related compounds to the corresponding alkyl iodides in one-pot reaction. This paper gives detailed accounts of these reductions.

Although triphenylphosphine is known to be a relatively strong reducing agent, it does not react directly with sulfonic acids. Triphenylphosphine has a strong oxygen affinity and hence if Ph_3P^+ group is introduced as Y in Eq. 5, even a weak nucleophile may attack the sulfonyl sulfur atom because of the excellent leaving ability of triphenylphosphine oxide. Meanwhile, the mixture of triphenylphosphine with halogen[13] and that of triphenylphosphine and disulfide[14] 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 phosphine and halogen,[15] the desulfurization of disulfides to the corresponding sulfides with phosphine,[14,16–18] the condensation of carboxylic acids and alcohols or amines to the corresponding esters or amides[19] by treatment with a mixture of phosphine and diaryl disulfide,[20–22] diselenide,[23] or halogen and also the conversion of alcohols to sulfides with a mixture of phosphine and disulfide.[24] Thus a mixture of triphenylphosphine and a catalytic amount of iodine was our choice system for the reduction, (Eq. 5), in which not only RSO_2–OY ($Y=Ph_3P^+$) is easily generated from the reaction be-

TABLE 2. THE REACTION OF ARENESULFONIC ACIDS WITH TRIPHENYLPHOSPHINE/IODINE IN BENZENE UNDER REFLUX CONDITIONS

$ArSO_3H$	$ArSO_3/I_2/Ph_3P$	Time/h	Products yields/%[a)]	
			ArSH	Ph_3PO
$p\text{-}CH_3C_6H_4SO_3H$	2/1/10	2.5	89	(128)[b)]
$p\text{-}ClC_6H_4SO_3H$	2/1/10	4.0	98	(95)[b)]
$C_6H_5SO_3H$	2/1/10	2.0	90	(116)[b)]
$2\text{-}C_{10}H_7SO_3H$	2/1/10	2.0	85(67)[b)]	—
$p\text{-}CH_3C_6H_4SO_3H$	2/0.2/8	5.5	88	—
	2/0/10	2.5	0	0
	$2/1/10(Bu_3P)$	2.0	33	—
	$2/1(Br_2)/10$	3.0	13	—
$2\text{-}C_{10}H_7SO_3H$	$2/1/8/2(Bu_3N)$[c)]	0.5	70	—
$p\text{-}CH_3C_6H_4SO_3H$	$2/1/8/2(Bu_3N)$[c)]	0.5	95	—
$C_6H_5SO_3^-(CH_3CH_2)_4N^+$	2/1/8	10 min	94	—

a) Yields of Products were calculated based on the stoichiometry as shown in Eq. 6. b) Isolated yield. c) Amine was added into this system.

tween the reagent and the sulfonic acid but also iodide is a relatively strong reducing agent enough to reduce the sulfonyl derivatives.[10,11,25)]

Results and Discussion

Reduction of Arenesulfonic Acids, Their Sodium Salts, and Alkyl Arenesulfonates with Triphenylphosphine and Iodine.[26)] Triphenylphosphine is known to react with iodine to afford iodotriphenylphosphonium iodide[13,27)] which would behave as a halogenating agent of sulfonic acids like phosphorus pentachloride (Eq. 3), while hydrogen iodide formed may act as a reducing agent. Based on this assumption, the reaction between sulfonic acids and Ph_3P/I_2 was investigated. Meanwhile, the successful conversion of alcohols and thiols to the corresponding halides with halotriphenylphosphonium halide has also prompted us to examine this reduction. As soon as triphenylphosphine was dissolved into a benzene solution which contained iodine, iodine color disappeared immediately giving a pale yellow solution of iodotriphenylphosphonium iodide. Upon treatment of *p*-toluenesulfonic acid with this reagent in refluxing benzene, the expected reduction of the sulfonic acid proceeded smoothly and *p*-toluenethiol was obtained nearly quantitatively. Even when the amount of iodine was reduced, the yield of the thiol was not reduced but the reaction required a prolonged period to complete, suggesting that iodine catalyzes the reduction of the sulfonic acid with triphenylphosphine. Thus, the whole reaction between arenesulfonic acids and triphenylphosphine in the presence of iodine can be expressed by Eq. 6.

$$\mathrm{ArSO_3H + 3\,Ph_3P \xrightarrow{I_2} Ar\text{-}SH + 3\,Ph_3PO} \qquad (6)$$

Since the reagent readily reacts with water, eventually affording triphenylphosphine oxide and hydrogen iodide, the sulfonic acid was carefully dehydrated by azeotropic distillation with benzene just before subjecting to the reduction in refluxing benzene. The results are summarized in Table 2. Neither triphenylphosphine alone nor iodide anion reacts with the arenesulfonic acid at all. The initial reaction is undoubtedly the reaction of the arenesulfonic acid with iodotriphenylphosphonium iodide to generate the (arylsulfonyloxy)triphenylphosphonium iodide as an incipient intermediate which receives subsequently nucleophilic attack of gegen ion, I^-, at the sulfonyl sulfur atom to form the arenesulfonyl iodide as shown in Eqs. 7—9.

$$\mathrm{Ph_3P + I_2 \rightleftarrows Ph_3\overset{+}{P}\text{-}I\ I^-} \qquad (7)$$

$$\mathrm{ArSO_3H + Ph_3\overset{+}{P}\text{-}I\ I^- \rightleftarrows ArSO_3^-\ Ph_3\overset{+}{P}\text{-}I + HI} \qquad (8)$$

$$\mathrm{ArSO_3^-\ Ph_3\overset{+}{P}\text{-}I \rightleftarrows ArSO_2\text{-}O\text{-}\overset{+}{P}Ph_3\ I^-} \qquad (8')$$

$$\mathrm{ArSO_2\text{-}O\text{-}\overset{+}{P}Ph_3\ I^- \longrightarrow ArSO_2I + Ph_3PO} \qquad (9)$$

$$\mathrm{ArSO_2I + HI \longrightarrow ArSO_2H + I_2} \qquad (10)$$

$$\mathrm{ArSO_2H + Ph_3\overset{+}{P}\text{-}I\ I^- \longrightarrow ArSO\text{-}O\text{-}\overset{+}{P}Ph_3\ I^-} \qquad (11)$$

$$\mathrm{ArSO\text{-}O\text{-}\overset{+}{P}Ph_3\ I^- \longrightarrow ArSO\text{-}I + Ph_3PO} \qquad (12)$$

$$\mathrm{ArSOI + HI \longrightarrow ArSOH + I_2} \qquad (13)$$

$$\mathrm{ArSOH + Ph_3\overset{+}{P}\text{-}I\ I^- \longrightarrow ArS\text{-}O\text{-}\overset{+}{P}Ph_3\ I^- + HI} \qquad (14)$$

$$\mathrm{ArS\text{-}O\text{-}\overset{+}{P}Ph_3\ I^- \longrightarrow ArSI + Ph_3PO} \qquad (15)$$

$$\mathrm{ArSI + Ph_3\overset{+}{P}\text{-}I\ I^- \longrightarrow ArS\text{-}\overset{+}{P}Ph_3\ I^- + I_2} \qquad (16)$$

$$\mathrm{ArS\text{-}\overset{+}{P}Ph_3\ I^- + HI \longrightarrow ArSH + Ph_3\overset{+}{P}\text{-}I\ I^-} \qquad (17)$$

$$\mathrm{ArSO_2I + Ph_3P \longrightarrow ArSO_2^-\ Ph_3\overset{+}{P}\text{-}I \longrightarrow ArSO\text{-}O\text{-}\overset{+}{P}Ph_3\ I^- \longrightarrow ArSOI + Ph_3PO} \qquad (18)$$

$$\mathrm{ArSOI + Ph_3P \longrightarrow ArSO^-\ Ph_3\overset{+}{P}\text{-}I \longrightarrow ArS\text{-}O\text{-}\overset{+}{P}Ph_3\ I^- \longrightarrow ArSI + Ph_3PO} \qquad (19)$$

The arenesulfonyl halide is known to be reduced with hydrogen iodide[28)] to afford the diaryl disulfide, and also can be reduced by triphenylphosphine alone to give a mixture of the diaryl disulfide and the arenethiol.[29)] Thus, two paths are conceivable for the reduction of the arenesulfonyl iodide. One path involves the initial nucleophilic attack of iodide anion on the arenesulfonyl iodide to afford iodine and the sulfinic acid which is eventually reduced to the diaryl disulfide *via* the arenesulfenic acid by the same reaction cycles through

Table 3. The reaction of sulfinic acid and sodium sulfinate with triphenylphosphine/iodine in benzene

$ArSO_2H(Na)$	$ArSO_2H(Na)/I_2/Ph_3P$	Temp/°C	Time/h	Products/%[a)]	
				ArSH	Ph_3PO
p-$CH_3C_6H_4SO_2H$	2/1/6.6	25	0.5	92	(118)[b)]
p-$ClC_6H_4SO_2H$	2/1/6.6	25	0.5	87	—
$C_6H_5SO_2H$	2/1/6.6	25	0.5	90	(111)[b)]
p-$CH_3C_6H_4SO_2Na$	2/1/6.6	Reflux[c)]	2	92 (88)[b)]	—[d)]
$C_6H_5SO_2Na$	2/1/6.6	Reflux[c)]	2	87	—[d)]
$C_6H_5SO_2H$	2/0/6.6	25	2	50[e)]	—

a) Yields of products were calculated based on the stoichiometry as shown in the following equation $ArSO_2H + 2\ Ph_3P \longrightarrow ArSH + 2\ Ph_3PO$. b) Isolated yield. c) The mixture of 3 ml of benzene and 5 ml of dioxane was used as a solvent. d) After this reaction, the mixture of about 200 mg of water and 1 ml of dioxane was added and refluxed for 0.5—1 h. e) Diphenyl disulfide was obtained in 24% yield as a by-product.

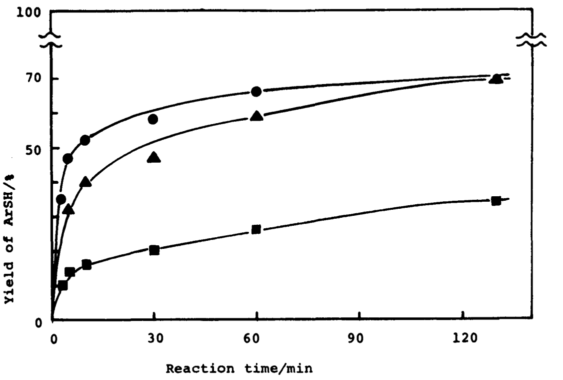


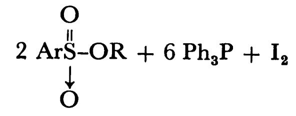
Fig. 1. Reaction of $ArSO_3H$ with Ph_3P/I_2 in Benzene at 72 °C to 73 °C.
■: p-$ClC_6H_4SO_3H$, ▲: $C_6H_5SO_3H$, ●: p-$CH_3C_6H_4SO_3H$ [p-$CH_3C_6H_4SO_3H/C_6H_5SO_3H/p$-$ClC_6H_4SO_3H/Ph_3P/I_2$= 1/1/1/12/1(mmol)].

which the arenesulfonic acid is converted to the arenesulfonyl iodide as shown in Eqs. 7—9. Another conceivable process involves nucleophilic attack of triphenylphosphine on the arenesulfonyl iodide to result in the formation of the same reaction intermediate, the (arylsulfinyloxy)triphenylphosphonium iodide, obtained in the former path, as shown in Eqs. 18 and 19. In order to clarify which nucleophilic reagent, iodide anion or triphenylphosphine initiated the reduction of the arenesulfonyl iodide, the sulfonyl iodide was treated with either triphenylphosphine alone or hydriodic acid respectively. However, since the reduction was found to proceed in both systems readily, it could not be concluded which process predominates over the other. Probably both processes are participating concurrently. The extremely fast reduction of the arenesulfonyl iodide is clearly evidenced by the fact that no probable intermediate can be detected during the reactions of the arenesulfonic acid with Ph_3P/I_2 system, since the initial conversion of sulfonic acid to the sulfonyl iodide is undoubtedly one of the slowest steps of this multi-step reduction of the sulfonic acid to the thiol. One interesting observation is that the reduction is accelerated considerably by the presence of such an amine as tributylamine (Table 2), which can readily dissociate the arenesulfonic acid to the corresponding sulfonate anion to facilitate the reduction. Therefore, tetraethylammonium benzenesulfonate, which is soluble in benzene under our reaction conditions, can be readily reduced to benzenethiol in a high yield. The effect of polar substituent on aromatic ring observed in the reduction of the arenesulfonic acid also indicates that the sulfonic acid bearing an electron-donating substituent was found to be reduced more readily than the one having an electron-withdrawing substituent as shown in Fig. 1. This also suggests that the reaction shown by Eq. 8′ is the rate-determining step of the reduction.

Though the arenesulfinic acid can be reduced very slowly with triphenylphosphine alone, the addition of iodine accelerates this reduction remarkably to give the corresponding arenethiol quantitatively (Table 3). While sodium arenesulfinate cannot be reduced at all with triphenylphosphine alone, the triphenylphosphine/iodine system can reduce the sulfinate readily to the arenethiol and diaryl disulfide even in the absence of any phase-transfer catalyst.

The arenesulfonyl chloride and the S-aryl arenethiosulfonate can be readily reduced with triphenylphosphine alone, or better with the mixture of triphenylphosphine and iodine (Table 4).

Alkyl arenesulfonates were found to react smoothly with Ph_3P/I_2 in benzene forming alkyl iodides and diaryl disulfides. The disulfides were converted ultimately to the arenethiols upon treatment with triphenylphosphine and water (Table 5).



$$2\ Ar\overset{\overset{O}{\|}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}OR + 6\ Ph_3P + I_2 \longrightarrow (ArS)_2 + 2\ RI + 6\ Ph_3PO \tag{20}$$

$$(ArS)_2 + Ph_3P + H_2O \longrightarrow 2\ ArSH + Ph_3PO \qquad (21)^{30)}$$

On the other hand, both aryl arenesulfonates and neopentyl arenesulfonates were found to be quite inert in this reducing system even under prolonged reaction times as shown in Table 5. Obviously the reaction of Eq. 20 is initiated by the nucleophilic displacement (S_N2) at the alkyl carbon with iodide anion to form the alkyl iodide and arenesulfonate anion which is further reduced to arenethiol by Ph_3P/I_2. Due to the lack of reactivity at aromatic carbon and steric hindrance of neopentyl group, both aryl arenesulfonates and neopentyl arenesulfonates resist the nucleophilic attack of iodide

TABLE 4. THE REACTION OF $ArSO_2X$ WITH TRIPHENYLPHOSPHINE/IODINE IN BENZENE[a)]

$ArSO_2X$	$ArSO_2X/I_2/Ph_3P$	Temp/°C	Time/min	ArSH/%[b)]
$p\text{-}ClC_6H_4SO_2Cl$	2/1/8	25	30	100
$p\text{-}CH_3C_6H_4SO_2Cl$	2/0/8	25	30	92
$C_6H_5SO_2SC_6H_5$	1/1/4	25	10	89
$C_6H_5SO_2SC_6H_5$	1/0/4	25	10—15	83

a) After this reaction, the mixture of about 200 mg of water and 1 ml of dioxane was added and refluxed for 0.5—1.0 h.
b) GLC yields (20% OV-1, 10 m glass column).

TABLE 5. THE REACTION OF ARENESULFONATES WITH TRIPHENYLPHOSPHINE/IODINE IN BENZENE UNDER ARGON ATMOSPHERE

$ArSO_3R(Ar')$	$ArSO_3R(Ar')/I_2/Ph_3P$	Time (Reflux)	Products/%[a)]	
			ArSH	RI
$p\text{-}CH_3C_6H_4SO_3CH_2C(CH_3)_3$	2/1.5/8	5 h	no reaction[b)]	
$p\text{-}CH_3C_6H_4SO_3C_6H_5$	2/1/10	45 h	no reaction[c)]	
$C_6H_5SO_3CH_2CH_3$	2/1.5/8	10 min	88	—
$p\text{-}CH_3C_6H_4SO_3(CH_2)_4CH_3$	2/1.5/8	10 min	95	90
$C_6H_5SO_3(CH_2)_4CH_3$	2/1.5/8	10 min	90	96
$C_6H_5SO_3CH_2CH_3$	2/0/10	2 h	no reaction	

a) Yields of products were calculated based on the stoichiometry as shown in the Eqs. 20 and 21. After this reaction, the mixture of about 200 mg of water and 1 ml of dioxane was added and refluxed for 0.5—1.0 h. b) Starting material was recovered in 85% yield. c) Starting material was recovered in 86% yield.

anion and no reaction appears to start even after a prolonged treatment with Ph_3P/I_2. Interestingly, pentyl benzenesulfonate, an alkyl arenesulfonate, reacted readily with tetrabutylammonium iodide in benzene affording tetrabutylammonium benzenesulfonate and pentyl iodide, whereas, under similar conditions phenyl benzenesulfonate did not react with tetrabutylammonium iodide.

$$C_6H_5SO_3CH_2(CH_2)_3CH_3 + Bu_4N^+I^- \xrightarrow[\text{benzene reflux}]{\text{10 min}}$$

$$Bu_4N^+\,C_6H_5SO_3^- + CH_3(CH_2)_4I \quad 100\% \tag{22}$$

$$p\text{-}CH_3C_6H_4SO_3C_6H_5 + Bu_4N^+I^- \xrightarrow[\text{benzen reflux}]{\text{15 min}}$$

$$\text{no reaction} \tag{23}$$

When bromine was used instead of iodine as the catalyst in the reduction of *p*-toluenesulfonic acid with triphenylphosphine, the yield of the thiol was found to be low (Table 2). Although tributylphosphine is a stronger nucleophile than triphenylphosphine, only 33% of *p*-toluenethiol was obtained along with unidentified side products upon treatment of the sulfonic acid with Bu_3P/I_2 (Table 2).

Phosphorus trichloride and phosphonic acid also gave only small amounts of diaryl disulfides and arenethiols, respectively, upon treatment of arenesulfonic acids in the presence of iodine.

$$p\text{-}CH_3C_6H_4SO_3H\cdot H_2O \xrightarrow[\text{neat 3 h reflux}]{I_2/PCl_3} \underset{18\%}{(p\text{-}CH_3C_6H_4S)_2}$$

$$p\text{-}CH_3C_6H_4SO_3H\cdot H_2O \xrightarrow[\text{CH}_3\text{CN 4.5 h reflux}]{I_2/H_3PO_3} \underset{25\%}{p\text{-}CH_3C_6H_4SH}$$

Inspection of data in Tables 2 and 5 reveals that the reduction of arenesulfonic acids takes place more slowly than alkyl arenesulfonates. This may mean that arenesulfonate anions are more reactive than arenesulfonic acids in the reaction with the reducing system, Ph_3P/I_2. The treatment of alkyl arenesulfonates with iodide ion involves the initial facile nucleophilic attack of iodide ion on alkyl group, eventually affording arenesulfonate anions as primary intermediates. Similarly, tertiary amine have already been found to accelerate the reduction of arenesulfonic acids with Ph_3P/I_2. All these observations, *i.e.* the higher reactivities of arenesulfonic acids bearing electron-donating substituents in the reduction, the acceleration of the reduction by addition of amine, and the facile rates of reduction of both arenesulfonates and tetraethylammonium arenesulfonates suggest clearly that the rate-determining step is the nucleophilic substitution of the sulfonate anion, which is a gegen anion, on the central phosphorus atom of iodotriphenylphosphonium cation to form (arylsulfonyloxy)triphenylphosphonium iodide which has a P–O–S linkage (Eq. 8′).

Sodium arenesulfonate did not react with Ph_3P/I_2 in benzene at all because of its insolubility, however, it was smoothly reduced to the thiol in the presence of such a phasetransfer catalyst as 18-crown-6. The rate of the reaction was found to depend on the amount of the phase transfer catalyst (Table 6). Thus, this reducing procedure is quite useful, since sulfonic acids are usually available in the form of sodium salts in industry. However *p*-aminobenzenesulfonic acid, arenesulfonamides, and sulfones were not reduced by our systems even at high temperatures and under prolonged heating in other common solvents. The unsuccessful reduction of *p*-aminobenzenesulfonic acid and arenesulfonamide is believed to be due to the lack of solubilities of these compounds in such solvents as benzene, acetonitrile and dioxane, which were used in the actual reduction.

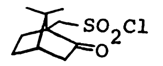
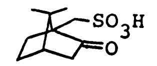
Diphenyl disulfone of which the central sulfur is highly sterically hindered, is very inert to triphenylphosphine or

Table 6. The reaction of sodium arenesulfonate with Ph_3P/I_2/18-crown-6 in benzene under argon atmosphere[a)]

$ArSO_3Na$	$ArSO_3Na/I_2/Ph_3P$/18-Crown-6	Time/h (Reflux)	ArSH/%[b)]
p-$CH_3C_6H_4SO_3Na$	2/1/10/0[d)]	24	Trace
	2/2/10/1	5	51 (50)[c)]
	2/2/10/1	31	85
$C_6H_5SO_3Na$	2/2/10/1	35	83
2-$C_{10}H_7SO_3Na$	2/2/10/1	24	67 (50)[c)]
	2/2/10/1	36	96 (93)[c)]
p-$CH_3C_6H_4SO_3Na$	2/2/8/0.02	79	80
2,4-$(CH_3)_2C_6H_3SO_3Na$	2/2/10/0.5	41	(63)[c)]
1-$C_{10}H_7SO_3Na$	2/2/10/0.5	35	70

a) Yields of product were calculated based on the stoichiometry as shown in the following equation $2ArSO_3Na + 7Ph_3P \xrightarrow[2)\ H_2O]{1)\ I_2} 2ArSH + 7Ph_3PO$. After this reaction, the mixture of about 200 mg of water and 2 ml of dioxane was added, and refluxed for 0.5—1 h. b) GLC yield (OV-1 20%, 1 m glass column). c) Isolated yield. d) The mixture of 3 ml of benzene and 5 ml of dioxane was used as a solvent.

Table 7. Reaction of aliphatic sulfur compounds with triphenylphosphine/iodine in benzene under nitrogen atmosphere

Substrate	Substrate/I_2/Ph_3P/Amine	Temp/°C	Time	Yield of RI/%
$CH_3(CH_2)_4SO_3H$	2/3/10/0	25	26 h	81
	2/3/10/0	Reflux	0.5 h	63
$CH_3(CH_2)_4SO_2H$	2/1/6.6/0	25	30 min	71[b)]
	2/3/6.6/0	25	2 h	95
$CH_3(CH_2)_7SO_2H$	2/3/6.6/0	25	2 h	85
$CH_3(CH_2)_7SO_2Cl$	2/3/8/0	25	10 min	75[c)]
	2/0/8/0	25	20 min	80[$CH_3(CH_2)_7Cl$]
	2/4/8/0	Reflux	8 h	(87)[d)]
$CH_3(CH_2)_7SH$	2/3/3/0	Reflux	1 h	98
$CH_3(CH_2)_4SH$	2/2/2.5/0	Reflux	1.5 h	90
$CH_3(CH_2)_4SO_3Na$	2/3/8[e)]	Reflux	26 h	40
$CH_3(CH_2)_4SO_3H$	2/3/10/2(Bu_3N)[f)]	25	25 min	79
$CH_3(CH_2)_4SO_2H$	2/3/6.6/2(Bu_3N)	25	10 min	100
$CH_3(CH_2)_7SH$	2/3/3/2(pyridine)	25	20 min	88
$CH_3(CH_2)_4SH$	2/3/3/2(Bu_3N)	25	20 min	100
	2/6/10/0	Reflux	9 h	87 (67)[d)]

a) GLC yield (20% OV-1, 1 m glass column). b) 1-Pentanethiol obtained as by-product (10% yield). c) 1-Chlorooctane obtained as by-product (12% yield). d) Isolated yield. e) 18-Crown-6 was used as a phase-transfer catalyst. f) The mixture of benzene and acetonitrile was uesd as a solvent.

triphenylphosphine/iodine system at room temperature. Diphenyl disulfone can hardly be reduced by triphenylphosphine alone even in refluxing benzene or acetonitrile, however it can be reduced by triphenylphosphine/iodine system in a quantitative yield under similar conditions.

$$C_6H_5SO_2SO_2C_6H_5 \xrightarrow[\substack{CH_3CN/C_6H_6\ \text{reflux}\ 24\ \text{h}\\ 2)\ H_2O}]{1)\ Ph_3P} \underset{26\ \%}{C_6H_5SH} + \underset{20\ \%}{\text{recovered disulfone}}$$

$$C_6H_5SO_2SO_2C_6H_5 \xrightarrow[\substack{CH_3CN/C_6H_6\ \text{reflux}\ 20\ \text{h}\\ 2)\ H_2O}]{1)\ Ph_3P/I_2} \underset{91\ \%}{C_6H_5SH}$$

This reaction proceeds by the initial nucleophilic attack of iodide anion, which is formed by the reaction of triphenylphosphine and iodine, on the central sulfur atom of diphenyl disulfone to give benzenesulfonyl iodide and benzenesulfinate which can be readily reduced by triphenylphosphine/iodine system.

Finally, since triphenylphosphine/carbon tetrachloride system was known to form phosphonium salt,[31)] arenesulfonic acids were treated with this Ph_3P/CCl_4 system. Actually, the corresponding diaryl disulfides were obtained, but the yields were in general only 40% to 50% [arenesulfonic acid/Ph_3P=2/8(mmol)] when the reduction was carried out in the mixture of 1 ml of carbon tetrachloride and 5 ml of benzene under refluxing conditions for 1.5 h.

Reductive Conversion of Alkanelfonic Acids, Sulfinic Acids, Thiols, Disulfides, Thiosulfonic S-*Esters, and Sulfonates to the Corresponding Alkyl Iodides with Triphenylphosphine/Iodine.*[32] When this reducing system was applied for the reduction of 1-pentanesulfonic acid, 1-pentanethiol which was the expected product, was not obtained, but pentyl iodide was the sole product obtained, when one equivalent amount of iodine was used.

$$\mathrm{RSO_3H + 4\,Ph_3P + I_2 \longrightarrow RI + 3\,Ph_3PO + Ph_3PS + HI} \qquad (24)$$

1-Pentanesulfonic acid is considered to be reduced at first to dipentyl disulfide or 1-pentanethiol as in the case of arenesulfonic acids. The subsequent multi-step reaction of either the disulfide or the thiol with Ph_3P/I_2 would afford eventually the iodide. In separate experiments, both 1-pentanethiol and dipentyl disulfide were found to be converted to pentyl iodide quantitatively upon treatment with Ph_3P/I_2.

$$\mathrm{RSSR + 2\,Ph_3\overset{+}{P}\text{-}I\ I^- \longrightarrow 2\,R\text{-}S\text{-}\overset{+}{P}Ph_3\ I^- \longrightarrow 2\,RI + 2\,Ph_3PS} \qquad (25)$$

$$\mathrm{RSH + Ph_3\overset{+}{P}\text{-}I\ I^- \longrightarrow R\text{-}S\text{-}\overset{+}{P}Ph_3\ I^- + HI \longrightarrow RI + Ph_3PS} \qquad (26)$$

It is worthy to note that even sterically-hindered *d*-camphor-10-sulfonic acid was successfully converted to the corresponding optically active 10-iodo-*d*-camphor. The formation of the corresponding thiol as the intermediate is shown in Fig. 2. 1-Pentanethiol was not detected in the direct conversion of 1-pentanesulfonic acid to pentyl iodide in the reduction with Ph_3P/I_2, since sterically unhindered 1-pentanethiol is so reactive, whereas *d*-camphor-10-thiol was actually isolated in a maximum yield of about 15% in the conversion of *d*-camphor-10-sulfonic acid to 10-iodo-*d*-camphor with Ph_3P/I_2. Since the *d*-camphor-10-thiol has a neopentyl structure, further desulfurization (S_N2) reaction is rather slow. Therefore, we can detect *d*-camphor-10-thiol during the reductive conversion of *d*-camphor-10-sulfonic acid to the corresponding iodide. 1-Pentanesulfinic acid reacted more readily with Ph_3P/I_2 than 1-pentanesulfonic acid, both affording pentyl iodide. 1-Octanesufonyl chloride gave a mixture of octyl iodide (major) and octyl chloride (minor), while the reaction of the same compound with triphenylphosphine alone proceeded also smoothly at room temperature in benzene to give octyl chloride in 80% yield (Eq. 27). Results of all these reactions are summarized in Table 7. *d*-Camphor-10-sulfonyl chloride can also be converted to the corresponding iodide upon heating with Ph_3P/I_2.

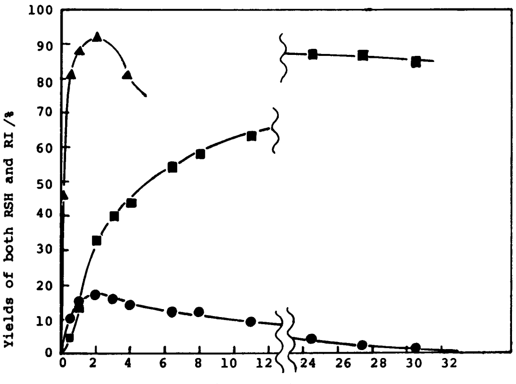
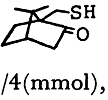
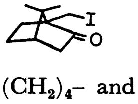
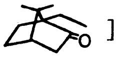


Fig. 2. Reaction of RSO_3H with Ph_3P/I_2 in Benzene under Reflux Conditions.

▲: $CH_3(CH_2)_4I$, ●:  , ■: 

[$RSO_3H/Ph_3P/I_2$=2/10/4(mmol), R=$CH_3(CH_2)_4$– and ].

$$\mathrm{RSO_2Cl + 3\,Ph_3P \longrightarrow RCl + 2\,Ph_3PO + Ph_3PS} \qquad (27)$$

Reaction of both alkyl alkanesulfonates and *S*-alkyl alkanethiosulfonates with Ph_3P/I_2 proceeded smoothly to give alkyl iodides quantitatively upon treatment with Ph_3P/I_2 (Table 8).

$$\mathrm{RSO_2SR' + 4\,Ph_3P + I_2 \longrightarrow RI + R'I + 2\,Ph_3PO + 2\,Ph_3PS} \qquad (28)$$

$$\mathrm{RSO_2OR' + 4\,Ph_3P + I_2 \longrightarrow RI + R'I + 3\,Ph_3PO + Ph_3PS} \qquad (29)$$

$$\mathrm{RSO_2SAr + 3\,Ph_3P + I_2} \qquad \mathrm{RI + ArSH + 2\,Ph_3PO + Ph_3PS + HI} \qquad (30)$$

Nucleophilic substitution on alkyl group, R′, by iodide ion is undoubtedly involved in the initial step of the reaction of the sulfonate (Eq. 29), while there are two possible paths to initiate the reaction of *S*-alkyl alkanethiosulfonate (Eq. 28), *i.e.* nucleophilic substitution on the sulfenyl sulfur and that on alkyl carbon. The *S*-aryl alkanethiosulfonate reacts with Ph_3P/I_2 quite readily to form the alkyl iodide and the arenethiol. This reaction should also be initiated by the nucleophilic displacement on the sulfenyl sulfur of the substrate with either triphenylphosphine or iodide anion. Since the reactions of both *S*-alkyl alkanethiosulfonate and *S*-aryl alkanethiosulfonate with Ph_3P/I_2 proceed much more readily than the reaction of alkyl alkanesulfonate under the same conditions, the reactions of the former two thiosulfonic *S*-esters are undoubtedly initiated by nucleophilic substitution on the divalent sulfur. Both iodide anion and triphenylphosphine being just as strong nucleophiles for divalent sulfur, it is hard to conclude which nucleophile plays an important key role in initiating of the reaction. The rate-determining step of the reaction of alkanethiols, sulfinic acids, and sulfonic acids are presumed to be the nucleophilic attack of conjugate bases of these organosulfur compounds on the phosphorus atom of iodotriphenylphosphonium ion,[33,34] as discussed in the former section which deals with the reduction of arenesulfonic acids. In accordance with this assumption, these reactions were markedly accelerated by the presence of amines (Table 7) while the reduction of the other aprotic derivatives were not affected by the addition of base. The reaction is quite useful in conversion of alkanesulfonic acids, thiosulfonic *S*-esters, sulfonates, disulfides, thiols, and sulfonyl chlorides to the corresponding alkyl iodides quantitively under mild conditions in one-pot treatment.

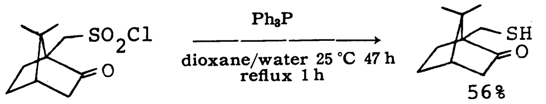
Table 8. Reaction of aliphatic sulfur compounds with triphenylphosphine/iodine in benzene under nitrogen atmosphere

Substrate R^1– –R^2	Substrate/I_2/Ph_3P	Temp/°C	Time / min	Products/%[a)] R^1I	R^2I
$CH_3(CH_2)_7SO_2O(CH_2)_4CH_3$	2/7/11	Reflux	5 h	95	95
$CH_3(CH_2)_4SO_2S(CH_2)_4CH_3$	1/2.5/5	25	10	200(R^1=R^2)	
$CH_3(CH_2)_7SO_2S(CH_2)_7CH_3$	1/2.5/5	25	10—15	184(R^1=R^2)	
$CH_3(CH_2)_4SS(CH_2)_4CH_3$[b)]	1/2/3	25	90	200(R^1=R^2)	
$CH_3(CH_2)_7SS(CH_2)_7CH_3$[b)]	1/2/3	25	120	200(R^1=R^2)	
$CH_3(CH_2)_4SO_2SC_6H_5$	1/2.5/5	25	10	92	c)

a) GLC yields (20 % OV-1, 10 m glass column). b) The mixture of benzene and dichloromethane was used as a solvent. c) After this reaction, the mixture of 0.5 ml of water and 2.5 ml of dioxane was added. Benzenethiol was obtained in 89% yield.

Finally, various alkanesulfonyl chlorides were found to be converted to the corresponding iodides by Ph_3P/I_2 system, however these sulfonyl chlorides were able to be converted to the corresponding chlorides with Ph_3P alone. Meanwhile, in an interesting and useful reaction, the corresponding thiols can be obtained in the reduction of alkanesulfonyl chlorides with Ph_3P/H_2O systems as shown by the following examples.

$$CH_3(CH_2)_7SO_2Cl \xrightarrow[\text{dioxane/water 25 °C 24 h, reflux 1 h}]{Ph_3P} \underset{75\ \%}{CH_3(CH_2)_7SH}$$



Experimental

Conversion of Sodium Sulfonate to the Corresponding Sulfonic Acid. The cation exchange resin which was converted to the protonated form by flowing 1 mol dm^{-3} aqueous HCl solution packed in a column [Dowex 50w-x8 200—400 mesh, H-form, Muromachi Kagaku Co.] was used.

GLC. Hitachi-163 Gas Chromatograph (20% OV-1 1m glass column) was used.

Reduction of Arenesulfonic Acid with Ph_3P/I_2 System. A mixture of 380 mg (2 mmol) of *p*-toluenesulfonic acid monohydrate and 5 ml of benzene was added into a reactor which was equipped with a cooler and a calcium chloride tube and then refluxed. The sulfonic acid was carefully dehydrated to completely dry prior to the reaction by way of azeotropic distillation with benzene. After 2620 mg (10 mmol) of triphenylphosphine was added to this dried sulfonic acid, the reactor was equipped with another cooler and an argon or nitrogen balloon, and substituted with this inert gas with a vacuum pump for 20 to 30 min at room temperature. Then, 5 ml of dry benzene and 254 mg (1 mmol) of iodine were added into this mixture and the whole mixture was stirred and refluxed (bath temperature 90—100 °C) for 2.5 h. The reaction was followed by GLC. After the reaction was complete, a mixture of 3 ml of water and 3 ml of dioxane was added to this reaction mixture which was refluxed for 1.0—0.5 h to decompose a small excess of triphenylphosphine–iodine complex to triphenylphosphine oxide and hydrogen iodide. The solution was poured into benzene and the benzene solution was washed with water for three times, and then dried ($MgSO_4$). *p*-Toluenethiol was obtained by GLC in 89% yield. After benzene was evaporated, the residue was separated through silica-gel column chromatography (Kieselgel-60, 70—230 mesh, MERCK, eluent: $CHCl_3$). A mixture of *p*-toluenethiol and a small excess of triphenylphosphine was obtained from fraction-1, and 2133 mg (128%) of triphenylphosphine oxide was obtained from fraction-2. Fraction-1 was separated further through silica-gel column chromatography (eluent: benzene/hexane = 1/5 = v/v) to give *p*-toluenethiol (R_f = 0.5) in 54% yield. This was identical with commercially available authentic compound. The low yield of *p*-toluenethiol isolated as compared with that of GLC yield is believed to be due to the high volatility of the thiol. Ph_3PO mp 154—155 °C (lit,[35] 154—157 °C).

Reduction of Arenesulfonic Acid with Ph_3P/I_2/Amine System. Triphenylphosphine (2100 mg, 8 mmol) was added into the carefully dehydrated 380 mg (2 mmol) of *p*-toluenesulfonic acid of which reactor was equipped with a cooler and an argon or nitrogen balloon and substituted thoroughly with this inert gas with a vacuum pump. Then, after 5 ml of dry benzene and 254 mg (1 mmol) of iodine was added to this mixture, 371 mg (2 mmol) of tributylamine was finally added to this mixture This reaction mixture was stirred and refluxed for 20 min, 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 5 min. *p*-Toluenethiol was obtained in 95% yield by GLC.

Reduction of Sodium Arenesulfonate with Ph_3P/I_2/18-Crown-6 System. After 460 mg (2 mmol) of sodium 2-naphthalenesulfonate was dissolved in 5 ml of benzene, the mixture was refluxed and dehydrated to nearly completely dry by the same method. Triphenylphosphine 2620 mg (10 mmol) and 264 mg (1 mmol) of 18-crown-6 were added to this sodium salt. The reactor was equipped with a cooler and an argon or nitrogen balloon. After substitution with the inert gas by vacuum pumping, 5 ml of dry benzene and 508 mg of iodine were added to this mixture which was stirred and refluxed for 36 h. After the reaction, a mixture of 2-naphthalenethiol and di-2-naphthyl disulfide were detected by GLC. Di-2-naphthyl disulfide was converted to the 2-naphthalenethiol by addition of a mixture of 200 mg of water and 2 ml of dioxane and the reaction mixture was refluxed for 1 h. The reaction mixture was then treated in a similar way as in the case of arenesulfonic acids. 2-Naphthalenethiol was obtained in 95% yield and isolated in 93% yield, however the amount of triphenylphosphine oxide was not determined.

Competitive Reduction of para-Substituted Benzenesulfonic Acids with Ph_3P/I_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 in a reactor which was equipped with a cooler and a $CaCl_2$ tube, and the whole mixture was refluxed. All these sulfonic acids were dehydrated nearly completely dry prior to the reaction by way of azeotropic distillation with benzene. After 3144 mg (12 mmol) of triphenylphosphine and 154 mg (1 mmol) of biphenyl (standard compound) were added to this dry sulfonic acids, the reactor was equipped with a cooler and a nitrogen balloon, and substituted with this inert gas. Then, 254 mg (1 mmol) of iodine and 6 ml of dry benzene were added to this mixture which was then stirred at 72—73 °C. A small portion (0.1 ml) of the reaction mixture was picked up by a microsyring and quenched with a mixture of water–dioxane–benzene (v=1/1/2) every fixed time interval (3, 5, 10, 30, 60, and 120 min from the initial time, respectively). The yields of three thiols obtained in every case, were determined by comparison of GLC curve with the predetermined calibration curve.

Reduction of Arenesulfonate with Ph_3P/I_2 System. Pentyl *p*-toluenesulfonate (484 mg, 2 mmol) and 2100 mg (8 mmol) of triphenylphosphine were added into a reactor which was equipped with a cooler and an argon or nitrogen balloon and substituted with this inert gas with a vacuum pump. Then, 5 ml of dry benzene and 381 mg (1 mmol) of iodine were added into this mixture which was refluxed and stirred for 10 min. The starting ester was no longer present by this time upon analysis with GLC and TLC (silica gel $R_f=0.3$ eluent: benzene), and *p*-toluethiol, di-*p*-tolyl disulfide, and pentyl iodide were resulted. After the reaction, the mixture was treated in the same manner as in the case of the reduction of arenesulfonic acid. The yields of the reaction products were determined by GLC (20% OV-1). *p*-Toluenethiol 95%. Pentyl iodide 90%. Authentic pently iodide was obtained by the known method. Pentyl iodide bp 157 °C/760 Torr (lit,[36] 157 °C/760 Torr, 1 Torr=133.322 Pa).

Synthesis of p-*Toluenesulfonyl Iodide.* *p*-Toluenesulfonyl iodide was obtained by a known method. Rock-crystals of mp 85—86 °C (decomp) were obtained (lit,[37] 84—85 °C).

Reductive Conversion of d-*Camphor-10-sulfonic Acid with Ph_3P/I_2 System.* The reaction was carried out under dry nitrogen atmosphere in a two-necked flask with a reflux condenser. To 8 ml of dry benzene solution of a mixture of *d*-camphor-10-sulfonic acid, 464 mg (2 mmol), and triphenylphosphine (2620 mg, 10 mmol), was added solid iodine 1524 mg (6 mmol) at room temperature. Then the mixture was refluxed for 9 h in nitrogen atmosphere. Benzene was added to the resultant mixture which was then washed with water. The organic layer was dried ($MgSO_4$) and the solvent was evaporated. The residue was then subjected to column chromatography on silica gel (eluent: benzene) in order to separate triphenylphosphine sulfide [$R_f=0.5$, yield 60%, mp 162—163 °C (lit,[38] 162—164 °C)], 10-iodo-*d*-camphor ($R_f=0.4$), and triphenylphosphine oxide [$R_f=0.1$, yield 90%, mp 154—155 °C (lit,[35] 154—157 °C)]. 10-Iodo-*d*-camphor was obtained in 87% (GLC) yield and was isolated in 67% yield: mp 71 °C; $[\alpha]^{25}$ −20.6 (*c* 1, $CHCl_3$); IR (KBr) 1735 (C=O), 1375, and 1390 cm^{-1}; NMR (CCl_4) $\delta=0.9$ (3H, s), 1.1 (3H, s), 3.05 (1H, d, $J=10.5$ Hz), 3.35 (1H, d, $J=10.5$ Hz), and 1.0—2.4 (7H, m); Found: C, 43.29; H, 5.38; I, 45.74%. Calcd for $C_{10}H_{15}OI$: C, 43.18; H, 5.43; I, 45.62%.

Reductive Conversion of Alkanesulfonate with Ph_3P/I_2 System. Pentyl 1-octanesulfonate (529 mg, 2 mmol) and 2882 mg (11 mmol) of triphenylphosphine were added to a reactor which was equipped with a condenser and a nitrogen balloon and substituted with dry inert gas with a vacuum pump. Then, 8 ml of dry benzene and 1778 mg (7 mmol) of iodine were added to this mixture which was refluxed and stirred for 5 h. After the reaction, a mixture of 200 mg of water and 1 ml of dioxane was added into this mixture. The yields of reaction products were determined by GLC. Octyl iodide 95% bp 110 °C/23 Torr (lit,[39] 226 °C/760 Torr). Pentyl iodide 95%.

Preparation of d-*Camphor-10-thiol.* *d*-Camphor-10-sulfonic acid (10 g, 42 mmol) was dissolved in 15 ml of chloroform and then 18 g (86 mmol) of phosphorus pentachloride was added slowly. After this mixture was refluxed for 2 h, it was poured into 100 ml of chloroform which was then washed with water for 4 times, dried ($MgSO_4$) and evaporated to give *d*-camphor-10-sulfonyl chloride in 69% yield. Mp 65—67 °C (lit,[40] 67—68 °C). *d*-Camphor-10-sulfonyl chloride, 3 g (12 mmol) and 12.6 g (48 mmol) of triphenylphosphine were dissolved into a mixture of 40 ml of dioxane and 10 ml of water and the whole mixture was stirred for 47 h at room temperature, and then refluxed for 1 h. After the reaction, the mixture was separated through silica-gel column chromatography using benzene as eluent to give *d*-camphor-10-thiol in 56% yield. Mp 65—66 °C; TLC (eluent: benzene) $R_f=0.2$—0.3; IR (KBr) 1375, 1385, 1730 (C=O), and 2560 cm^{-1} (SH); NMR (CCl_4) $\delta=0.95$ (3H, s), 1.05 (3H, s), 1.2—2.6 (8H, m), 2.73 (1H, d, $J=6$ Hz), and 2.95 (1H, d, $J=6$ Hz); Found: C, 65.24; H, 8.72; S, 17.24%. Calcd for $C_{10}H_{16}OS$; C, 65.17; H, 8.75; S, 17.40%.

Monitoring the Reaction of Alkanesulfonic Acid with Ph_3P/I_2. *d*-Camphor-10-sulfonic acid (464 mg, 2 mmol), 2620 mg (10 mmol) of triphenylphosphine, and 308 mg (2 mmol) of biphenyl (standard) were dissolved in 10 ml of dry benzene, into which 1016 mg (4 mmol) of iodine was then added and the solution was refluxed under nitrogen atmosphere. At fixed time intervals, 0.1 ml of the reaction mixture was picked up by a microsyringe and quenched with a mixture of water and benzene (v/v=1/1). The yields of the thiol and the iodide obtained in every case were determined by comparison of the GLC (SE-30) curve with the predetermined calibration curve. In the case of 1-pentanesulfonic acid, the corresponding thiol was not present in any sample under these conditions.

Preparation of Thiosulfonic S-*Esters.* Thiosulfonic *S*-esters were prepared by a known method[41,42] which is the reaction of arenesulfenyl chloride, that was prepared by treating a thiol or a disulfide with gaseous Cl_2 in CCl_4 at 0 °C, with sulfinic acid in the presence of pyridine in CCl_4 at 0 °C in 80—90% yield. *S*-Phenyl benzenethiosulfonate mp 44—45 °C (lit,[41] 44—45 °C). *S*-*p*-Tolyl *p*-toluenethiosulfonate mp 72—74 °C (lit,[42] 76 °C).

Preparation of Sulfonates. Sulfonates were prepared by a known method,[43—46] which is the reaction of sulfonyl chloride with alcohol in a mixture of benzene and acetonitrile in the presence of pyridine at room temperature, in 50—60% yields.

Phenyl *p*-toluenesulfonate mp 92—93 °C (lit,[43] 93 °C).

neo-Pentyl *p*-toluenesulfonate mp 46—47 °C (lit,[44] 48 °C).

Pentyl benzenesulfonate bp 138—140 °C/1 Torr (lit,[45] 136—138 °C/1 Torr).

Pentyl *p*-toluenesulfonate bp 167—168 °C/3 Torr (lit,[46] 169—170 °C/3 Torr).

Pentyl 1-octanesulfonate TLC (eluent: benzene) $R_f=0.4$—0.5; IR (NaCl) 1340 (SO) and 1160 cm^{-1} (SO); NMR (CCl_4) $\delta=4.1$ (2H, t, $J=6$ Hz), 3.0 (2H, t, $J=6.7$ Hz), and 2.1—0.7 (24H, m); Found: C, 59.13; H, 10.55; S, 11.94%. Calcd for $C_{13}H_{28}SO_3$: C, 59.05; H, 10.67; S, 12.12%.

Preparation of Sulfinic Acids. *p*-Chlorobenzenesulfonyl chloride (5 g, 23.7 mmol) and 18 g (71.1 mmol) of sodium sulfite heptahydrate were added into 100 ml of water. The reaction mixture was kept at a temperature ranging 70—80 °C for 5 h. After the reaction, this water solution was washed with chloroform twice, acidified with excess concd HCl solution, cooled and filtered. The white precipitate was recrystallized from water yielding *p*-chlorobenzenesulfinic acid in a high yield (79%).

p-Chlorobenzenesulfinic acid mp 95—97 °C (lit,[47] 98—99 °C).

1-Octanesulfinic acid can also be obtained from 1-octanesulfonyl chloride by the similar procedure and identified as methyl octyl sulfone in 57% yield.

Methyl octyl sulfone mp 62—63 °C (lit,[48] 62 °C).

p-Toluenesulfinic acid and benzenesulfinic acid were obtained by acidification of the corresponding sodium arenesulfinates which were obtained as commercial samples. The white precipitates were recrystallized from water yielding the corresponding arenesulfinic acids.

Benzenesulfinic acid mp 78—80 °C (lit,[47] 81.5—83 °C).

p-Toluenesulfinic acid mp 84—85 °C (lit,[47] 84—85 °C).

1-Pentanesulfinic acid was prepared by a well known hydrolysis of 1-pentanesulfinyl chloride, which was prepared by treating dipentyl disulfide with chlorine in acetic anhydride in a mixture of ether and water at 0 °C in the presence of pyridine at the range of -20 °C to -10 °C in 77% yield. 1-Pentanesulfinic acid was identified as pentyl 2,4-dinitrophenyl sulfone by treating with 2,4-dinitrochlorobenzene.

Pentyl 2,4-dinitrophenyl sulfone (quantitative yield) mp 84 °C (lit,[49] 83 °C).

Preparation of S-Alkyl Thiosulfonates. *S*-Octyl 1-octanethiosulfonate and *S*-pentyl 1-pentanethiosulfonate were prepared by treating the corresponding disulfide with hydrogen peroxide in acetic acid at room temperature in nearly quantitative yields.

S-Pentyl 1-pentanethiosulfonate TLC (eluent: benzene) $R_f=0.5$; IR (NaCl) 1120 (SO) and 1320 cm^{-1} (SO); NMR (CCl$_4$) $\delta=0.7$—2.2 (18H, m), and 2.9—3.4 (4H, m); Found: C, 50.49; H, 9.34%. Calcd for $C_{10}H_{22}O_2S_2$: C, 50.38; H, 9.30%.

S-Octyl 1-octanethiosulfonate TLC (eluent: benzene) $R_f=0.5$; IR (NaCl) 1120 (SO) and 1320 cm^{-1} (SO); NMR (CCl$_4$) $\delta=0.7$—2.2 (30H, m), and 2.9—3.4 (4H, m); Found: C, 59.77; H, 10.68%. Calcd for $C_{16}H_{34}O_2S_2$: C, 59.57; H, 10.62%.

S-Phenyl 1-pentanethiosulfonate was prepared by treating benzenesulfenyl chloride with 1-pentanesulfinic acid in CCl$_4$ at 0 °C in the presence of pyridine. *S*-Phenyl 1-pentanethiosulfonate was obtained in a quantitative yield.

S-Phenyl 1-pentanethiosulfonate TLC (eluent: benzene) $R_f=0.4$; IR (NaCl) 1120 (SO) and 1320 cm^{-1} (SO); NMR (CCl$_4$) $\delta=0.7$—2.2 (9H, m), 2.9—3.3 (2H, t, $J=7.5$ Hz), and 7.2—7.7 (5H, m); Found: C, 54.07; H, 6.58%. Calcd for $C_{11}H_{16}O_2S_2$: C, 54.16; H, 6.59%.

Reaction of Alkanesulfinic Acid with Ph_3P/I_2. 1-Pentanesulfinic acid, 272 mg (2 mmol), was dissolved in a mixture of 5 ml of dry benzene and 5 ml of dichloromethane. Then, 1730 mg (6.6 mmol) of triphenylphosphine and 762 mg (3 mmol) of iodine were added to this mixture. The reaction was carried out for 2 h at room temperature. After the reaction, 1-pentyl iodide formed was obtained in 95% yield by GLC.

Reaction of Alkanesulfonyl Chloride with Ph_3P. 1-Octanesulfonyl chloride, 425 mg (2 mmol), was dissolved in 5 ml of benzene and then 2100 mg (8 mmol) of triphenylphosphine was slowly added. The reaction was carried out at room temperature for 20 min. 1-Octyl chloride was obtained in 80% yield (GLC).

Reaction of Arenesulfonic Acid with Ph_3P/CCl_4. Triphenylphosphine, 2100 mg (8 mmol), was added into the carefully dehydrated 380 mg (2 mmol) of *p*-toluenesulfonic acid in a reactor which was equipped with a cooler and a nitrogen balloon, and substituted thoroughly with this gas. Then, 1 ml of carbon tetrachloride, which was dissolved in 5 ml of benzene, was added to this mixture. The mixture was refluxed for 1.5 h. After the reaction, triphenylphosphine was not present. Di-*p*-tolyl disulfide was obtained in 57% yield by GLC. The yields of triphenylphosphine oxide and other minor unknown products were not determined.

Reaction of Sulfonic Acid with PCl_3/I_2. *p*-Toluenesulfonic acid monohydrate, 380.4 mg (2 mmol), and 762 mg (3 mmol) of iodine were added into a reactor which was equipped with a cooler and a calcium chloride tube. Then, 7850 mg (57.3 mmol) of phosphorus trichloride was added to this mixture, which was refluxed for 3 h. After the reaction, di-*p*-tolyl disulfide was obtained in 18% yield by GLC.

Reaction of Sulfonic Acid with H_3PO_3/I_2. *p*-Toluenesulfonic acid monohydrate, 381 mg (2 mmol), was dissolved in 10 ml of acetonitrile, and then 1016 mg (4 mmol) of iodine and 2000 mg (24.4 mmol) of phosphonic acid were added to the mixture which was refluxed for 4.5 h under nitrogen atmosphere. After the reaction, *p*-toluenethiol was obtained in 25% yield by GLC.

Reaction of Diphenyl Disulfone with Ph_3P/I_2. Diphenyl disulfone, 200 mg (0.71 mmol), was dissolved in a mixture of 3 ml of dry acetonitrile and 10 ml of dry benzene and then 1300 mg (5 mmol) of triphenylphosphine and 179 mg (0.71 mmol) of iodine were added into this mixture. The reaction mixture was refluxed for 20 h under nitrogen atmosphere. The reaction was followed by GLC (eluent: benzene $C_6H_5SO_2SO_2C_6H_5$, $R_f=0.3$). After the reaction, a mixture of 1 ml of water and 2 ml of dioxane was added and the mixture was heated for 1 h. Benzenethiol was obtained in 91% yield (GLC). Diphenyl disulfone was prepared by a known method, which is the oxidation of benzenesulfinic acid by KMnO$_4$ in acetic acid, in 5% yield.

Diphenyl disulfone mp 196—197 °C (lit,[52] 196—196.5 °C).

Other Compounds. 1-Naphthalenethiol 160—165 °C/35 Torr (lit,[50] 142—142.5 °C/7 Torr, 85—88 °C/0.27 Torr). NMR (CCl$_4$) $\delta=3.4$ (1H, s), and 7.05—8.30 (7H, m). 2,4-Dimethylbenzenethiol 74—76 °C/4 Torr (lit,[51] 80.5 °C/9 Torr, 93 °C/12 Torr) NMR (CCl$_4$) $\delta=2.2$ (6H, s), 2.9 (1H, s), and 6.5—7.0 (4H, m).

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