Facile Conversions of Aliphatic Sulfonic Acids, Sulfinic Acids, Thiols, Sulfonates, Thiolsulfonates, and Disulfides to the Corresponding Alkyl Iodides by Triphenylphosphine/Iodine

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Recently, we have shown that arenesulfonic acids can be readily reduced nearly quantitatively by treatment with a mixture of triphenylphosphine and iodine[1]. When this reducing system was applied to pentanesulfonic acid, unexpectedly pentyl iodide was found to be the sole product (Scheme A, R = n-C_5H_{11}). We now report that the sulfur functions in the title compounds can be readily replaced by iodine by simple treatment of any one of the title compounds with triphenylphosphine/iodine to afford the corresponding alkyl iodide quantitatively.

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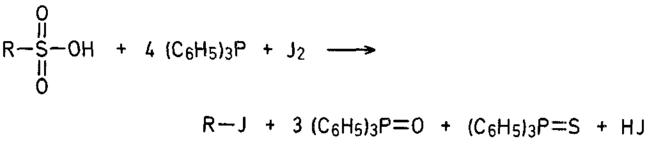
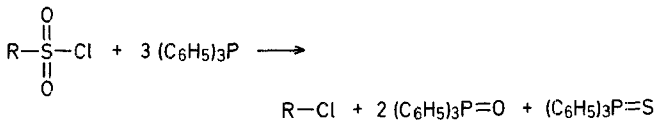


Scheme A

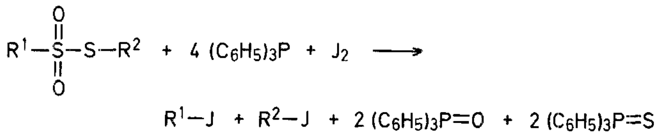
Pentanesulfonic acid is considered to be reduced at first to dipentyl disulfide or pentanethiol as in the case of the arenesulfonic acids. Then either the disulfide or the thiol, formed upon treatment with triphenylphosphine/iodine, is converted to the iodide as in the case of the reactions of organic disulfides[2,3,4,5] and alcohols[6] with phosphorus trihalides. In a separate experiment, both pentanethiol and dipentyl disulfide were found to be converted to pentyl iodide quantitatively on treatment with triphenylphosphine/iodine. Actually, the intervention of pentanethiol was detected during the reaction. It is worth noting that even the sterically-hindered D-camphor-10-sulfonic acid is successfully converted to the corresponding iodide (Table 1).

Pentanesulfinic acid reacted more readily with triphenylphosphine/iodine than pentanesulfonic acid affording pentyl iodide. Octanesulfonyl chloride also reacted to give a mixture of octyl iodide (major) and octyl chloride (minor), while the reaction of the same compound with triphenylphosphine alone also proceeded smoothly at room temperature in benzene to give octyl chloride[7] in 80% yield (Scheme **B**).

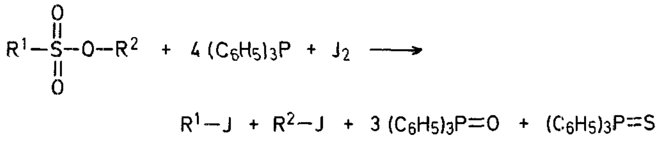
Alkyl alkanethiolsulfonates (Scheme **C**) and alkyl alkanesulfonates (Scheme **D**) also react to give alkyl iodide quantitatively on treatment with triphenylphosphine/iodine (Table 2).



Scheme **B**



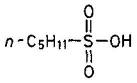
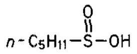
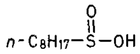
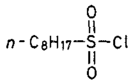
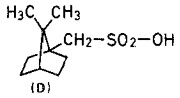
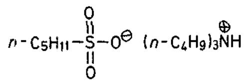
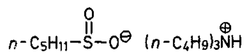
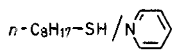
Scheme **C**



Scheme **D**

The reactions of aliphatic thiols, sulfinic acids, and sulfonic acids are presumed to be initiated by the nucleophilic attack of the conjugate bases of these acidic organosulfur compounds on the iodotriphenylphosphonium ion[1], formed upon treatment of triphenylphosphine with iodine. This assumption seems to be supported by the observation that these reactions were markedly accelerated by the presence of a base, i.e., tri-*n*-butylamine, pyridine, etc. (Table 1). However, the reductions of other aprotic substrates were not assisted by the addition of base, as was to be expected.

Table 1. Reaction of Aliphatic Sulfur Compounds with Triphenylphosphine/Iodine (Scheme **A** and **B**)

Substrate	Amounts (mmol) used Substrate/J_2/$(C_6H_5)_3P$/Base	Reaction Conditions Temperature [°C]/Time	Yield [%][a] of R—J	b.p. [°C]/torr or m.p. [°C] observed	reported	Purity [%] by G.L.C.[b]
 $n\text{-}C_5H_{11}\text{-}SO_2\text{-}OH$	5/7.5/25/—	r.t./26 h	81	157°/760	157°/760[8]	>99
 $n\text{-}C_5H_{11}\text{-}S(O)\text{-}OH$	5/7.5/16.5/—	r.t./2 h	95	157°/760	157°/760[8]	>99
	5/2.5/16.5/—	r.t./30 min	71[c]		—	>99
 $n\text{-}C_8H_{17}\text{-}S(O)\text{-}OH$	5/7.5/16.5/—	r.t./2 h	85	110°/23	226°/760[9]	>99
 $n\text{-}C_8H_{17}\text{-}SO_2\text{-}Cl$	5/7.5/20/—	r.t./10 min	75[d]	—	—	>99
$n\text{-}C_8H_{17}\text{-}SH$	5/7.5/7.5/—	reflux/1 h	98	110°/23	226°/760[9]	>99
$n\text{-}C_5H_{11}\text{-}SH$	5/5/6.25/—	reflux/1.5 h	90	157°/760	157°/760[8]	>99
	5/10/25/—	reflux/8 h	67	71°	—	100
 $n\text{-}C_5H_{11}\text{-}SO_2\text{-}O^{\ominus}\ (n\text{-}C_4H_9)_3\overset{\oplus}{N}H$	5/7.5/25/5 $(C_4H_9)_3N$	r.t./1.5 h	85	157°/760	157°/760[8]	>99
 $n\text{-}C_5H_{11}\text{-}S(O)\text{-}O^{\ominus}\ (n\text{-}C_4H_9)_3\overset{\oplus}{N}H$	5/7.5/16.5/5 $(C_4H_9)_3N$	r.t./10 min	100	157°/760	157°/760[8]	>99
	5/7.5/7.5/5 pyridine	r.t./20 min	88	110°/23	226°/760[9]	>99
$n\text{-}C_5H_{11}\text{-}SH$ / $(n\text{-}C_4H_9)_3N$	5/7.5/7.5/5 $(C_4H_9)_3N$	r.t./20 min	100	157°/760	157°/760[8]	>99

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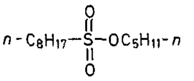
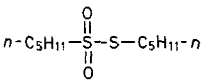
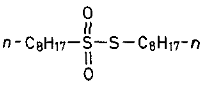
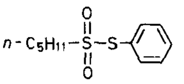
[a] Yield of isolated product.

[b] Conditions: 1 m glass column, 20% OV-1, Hitachi 163 gas chromatograph, injector temperature 250 °C, initial temperature 50 °C, final temperature 250 °C.

[c] *n*-Pentanethiol[7] obtained as by-product (10% yield).

[d] 1-Chlorooctane[7] obtained as by-product (12% yield).

Table 2. Reaction of Aliphatic Sulfur Compounds with Triphenylphosphine/Iodine (Scheme C and D)

Substrate $R^1—S—R^2$	Amounts (mmol) used Substrate/J_2/$(C_6H_5)_3P$	Reaction Conditions Temperature/Time	Yield [%][a] of $R^1—J$	$R^2—J$	Purity [%] by G.L.C.[b]	
 $n\text{-}C_8H_{17}—S(=O)_2—OC_5H_{11}\text{-}n$	5/17.5/27.5	reflux/5 h	95	95	>99	>99
 $n\text{-}C_5H_{11}—S(=O)_2—S—C_5H_{11}\text{-}n$	2.5/6.25/12.5	r.t./10 min	200		>99	
 $n\text{-}C_8H_{17}—S(=O)_2—S—C_8H_{17}\text{-}n$	2.5/6.25/12.5	r.t./10–15 min	184		>99	
	2.5/6.25/12.5	r.t./10 min	92	—[c]	>99	—
$n\text{-}C_5H_{11}—S—S—C_5H_{11}\text{-}n$	2.5/5/7.5[d]	r.t./1.5 h	200		>99	
$n\text{-}C_8H_{17}—S—S—C_8H_{17}\text{-}n$	2.5/5/7.5[d]	r.t./2 h	200		>99	

[a] Yield of isolated product.

[b] Conditions: see Table 1, footnote[b].

[c] After the reaction, water (0.5 ml)/dioxan (2.5 ml) is added and benzenethiol is obtained (yield: 89%).

[d] Reaction solvent is 1:1 benzene/dichloromethane.

D-10-Iodocamphor from D-Camphor-10-Sulfonic Acid; Typical Procedure:

The reaction is carried out under a dry nitrogen atmosphere in a two-necked flask equipped with a reflux condenser. To a dry benzene (20 ml) solution of a mixture of D-camphor-10-sulfonic acid (1.16 g, 5 mmol) and triphenylphosphine (6.55 g, 25 mmol) is added solid iodine (2.54 g, 10 mmol) at room temperature. Then the mixture is heated under reflux for 8 h in a nitrogen atmosphere. Benzene (100 ml) is added to the resultant mixture which is then washed with water (3 × 50 ml). The organic layer is dried with magnesium sulfate and the solvent evaporated. The residue is subjected to column chromatography on silica gel (eluent: benzene) in order to separate *triphenylphosphine sulfide* [R_F: 0.5; yield: 0.88 g (60%); m.p. 162–163 °C (Lit.[7], m.p. 162–164 °C), *D-10-iodocamphor* [R_F: 0.4], and *triphenylphosphine oxide* [R_F: 0.1; yield: 4.97 g (90%); m.p. 154–155 °C (Lit.[7], m.p. 154–157 °C)].

D-10-Iodocamphor; yield: 0.94 g (67%); m.p. 71°; $[\alpha]_D^{25}$: −20.6° (c 1.0 g/100 ml, $CHCl_3$).

$C_{10}H_{17}J$	calc.	C 43.18	H 5.43	J 45.62
(264.1)	found	43.29	5.38	45.75

I.R. (KBr): ν=1735; 1375; 1390 cm^{-1}.

^{1}H-N.M.R. (CCl_4): δ=0.90 (s, 3H); 1.10 (s, 3H); 3.05 (d, 1H, J=10.5 Hz); 3.35 (d, 1H, J=10.5 Hz); 1.0–2.4 ppm (m, 7H).

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