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Reduction of Organic Sulfonic Acids, Sodium Sulfonates, and Sulfonic Esters to the Corresponding Disulfides with Polyphosphoric Acid Derivatives, Potassium Iodide and Tetrabutylammonium Iodide System

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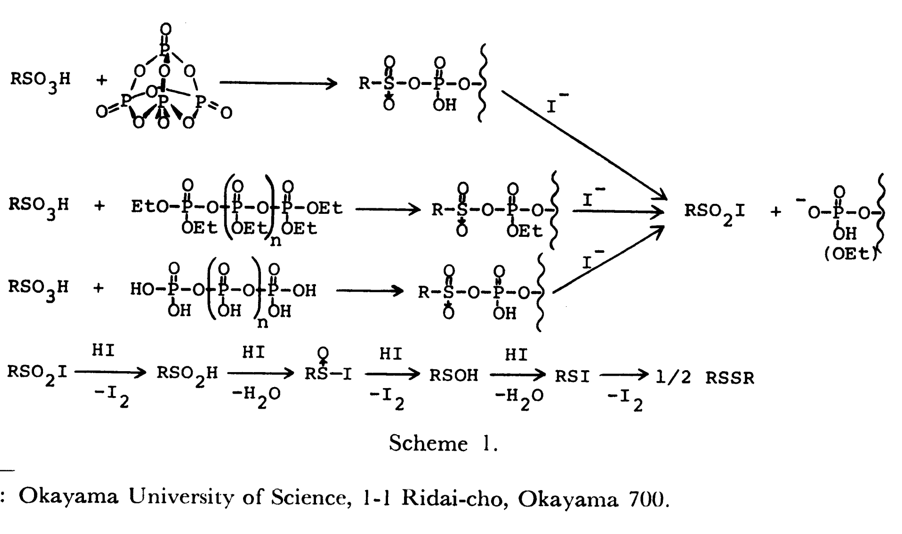
Organic sulfonic acids, sodium sulfonates, and alkyl sulfonates were readily reduced to the corresponding disulfides in moderate yields upon treatment with a mixture of a polyphosphoric acid derivative and iodide. In these reactions, formation of mixed anhydrides each having a P–O–S linkage is the key step, and subsequent attack of iodide on the sulfur atom gives the corresponding sulfonyl iodides which are reduced further exothermally to the disulfides with hydrogen iodide. Actually, *p*-toluenesulfonyl chloride was isolated in the reaction of *p*-toluenesulfonic acid and polyphosphoric acid derivatives with chloride ion. The competitive reduction of various aromatic sulfonic acids reveals that an aromatic sulfonic acid bearing an electron-donating para-substituent is more readily reduced to the disulfide than that which has an electron-withdrawing para-substituent.

The reduction of organic sulfonic acid which is in the highest oxidative state among all organosulfur compounds is one of the most challenging problems in organosulfur chemistry. Sulfonic acids, however, can be reduced in multi-step processes through initial conversion of sulfonic acids to the corresponding sulfonyl derivatives, *i.e.* sulfonyl halide,[1] sulfonic anhydride,[2] sulfonic ester,[3] and sulfonamide[4] and subsequent reduction of these derivatives with reducing agents to the corresponding thiols or thiol derivatives. Recently, there have appeared three procedures which can reduce sulfonic acids directly to the corresponding disulfides or thiols in one-pot process.[5–7] Each of these three procedures is epochal, and quite useful, since in a one-pot process reduction of various sulfonic acids and its derivatives to thiols or disulfides can be achieved. However, these reactions have some drawbacks, since the reagents used in these procedures, *i.e.* $(CF_3CO)_2/O(n\text{-}Bu)_4NI$,[5] Ph_3P/I_2 (catalyst),[6] $Ph_3P/(ArS)_2$(catalyst),[8] and BX_3-(X=Cl, Br, I)/KI[7] systems are either in large excess or by no means cheap. Another facile procedure to reduce both arene- and alkanesulfonic acids to the corresponding disulfides as the sole products has been found by us who used cheap reagents, such as polyphosphoric acid (PPA), ethyl polyphosphate (PPE), tetraphosphorus decaoxide (P_4O_{10}) and iodide ion, in organic media This paper gives a full account of this direct reduction of sulfonic acids.

Results and Discussion

Arene- and alkanesulfonic acids used in this investigation are listed in Tables 1, 2, and 3, while the sulfonic esters are summarized in Table 4. The condensing reagents used were tetraphosphorus decaoxide, polyphosphoric acid, and ethyl polyphosphate,[9] while acetonitrile and sulfolane are the choice solvents in the reduction with P_4O_{10}/I^- and PPA/I^- systems respectively because of the solubility of polyphosphoric acid derivatives, whereas acetonitrile, sulfolane, and chloroform were the choice solvents in the reduction with PPE/I^- system. Of the three systems, the reduction with P_4O_{10}/I^- or PPE/I^- gives the corresponding disulfides in higher yields than that with PPA/I^- system in the presence of $(n\text{-}Bu)_4NI$, whereas, in the absence of $(n\text{-}Bu)_4NI$ the yields of the disulfides are more satisfactory in the reduction with PPA/I^- than those with the former systems. It is worthy to note that *d*-camphor-10-sulfonic acid, which is a highly sterically hindered alkanesulfonic acid, was also reduced to the corresponding disulfide in a high yield, though the reaction was substantially slow. In this reduction, the sulfonyl iodide is considered to be the



Scheme 1.

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TABLE 1. REDUCTION OF SULFONIC ACID TO DISULFIDES USING TETRAPHOSPHORUS DECAOXIDE/POTASSIUM IODIDE/TETRABUTYLAMMONIUM IODIDE SYSTEM IN CH_3CN

Sulfonic acid	Amounts (mmol) of reagents used[a)] $RSO_3H/P_4O_{10}/KI/n\text{-}Bu_4NI$	Reaction conditions Time/h (Reflux)	Yield of disulfide/%[b)]
$p\text{-}CH_3C_6H_4SO_3H \cdot H_2O$	6.0/33.8/30.0/1.5	14	57
$p\text{-}ClC_6H_4SO_3H$	6.0/42.2/36.2/1.5	24	40
$2,4\text{-}(CH_3)_2C_6H_3SO_3H$	6.0/42.2/36.2/1.5	14	55
$p\text{-}CH_3C_6H_4SO_3Na$	6.0/42.2/36.2/1.5	34	60
$p\text{-}CH_3C_6H_4SO_3H \cdot H_2O$	6.0/33.8/30.0/0	14	33[c)]

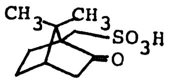
a) The molecular weight of P_4O_{10} was taken as 142. b) Yield of isolated product. c) Small amount of thiosulfonic *S*-ester was obtained as by-product.

TABLE 2. REDUCTION OF SULFONIC ACIDS TO DISULFIDES USING POLYPHOSPHORIC ACID/POTASSIUM IODIDE/TETRABUTYLAMMONIUM IODIDE SYSTEM IN SULFOLANE

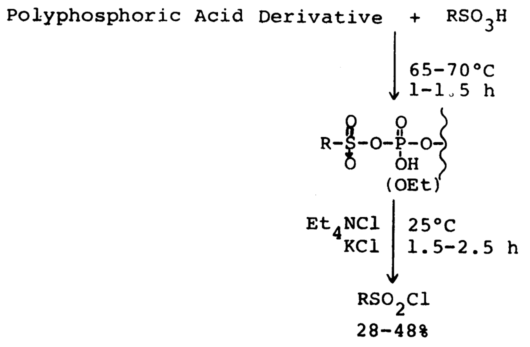
Sulfonic acid	Amounts(mmol) of reagents used[a)] $RSO_3H/PPA/KI/n\text{-}Bu_4NI$	Temp/°C	Time/h	Yield of disulfide/%[b)]
$p\text{-}CH_3C_6H_4SO_3H \cdot H_2O$	6.0/48.0/48.0/1.5	95—100	8	65
	6.0/48.0/48.0/0	95—100	8	75
$p\text{-}ClC_6H_4SO_3H$	6.0/48.0/60.0/1.5	95—100	10	47
	6.0/48.0/48.0/0	95—100	8	58
$2,4\text{-}(CH_3)_2C_6H_3SO_3H$	6.0/48.0/48.0/1.5	95—100	8	68
	6.0/48.0/48.0/0	95—100	8	70
$p\text{-}CH_3C_6H_4SO_3Na$	6.0/48.0/48.0/1.5	95—100	23	58
	6.0/48.0/48.0/0	95—100	21	55[c)]
$CH_3(CH_2)_7SO_3H \cdot H_2O$	6.0/48.0/48.0/1.5	80	5	66

a) The molecular weight of PPA was taken as 338. b) Yield of isolated product. c) Small amount of thiosulfonic *S*-ester was obtained as by-product.

TABLE 3. REDUCTION OF SULFONIC ACIDS TO DISULFIDES USING ETHYL POLYPHOSPHATE/POTASSIUM IODIDE/TETRABUTYLAMMONIUM IODIDE SYSTEM IN CHLOROFORM

Sulfonic acid	Amounts(mmol) of reagents used[a)] $RSO_3H/PPE/KI/n\text{-}Bu_4NI$	Reaction conditions Time/h (Reflux)	Yield of disulfide/%[b)]
$p\text{-}CH_3C_6H_4SO_3H \cdot H_2O$	6.0/35.6/48.0/1.5	1.5	60
	6.0/35.6/48.0/0	2	12
$CH_5SO_3H \cdot H_2O$	6.0/47.4/48.0/1.5	2	43
$p\text{-}CH_3C_6H_4SO_3Na$	6.0/35.6/48.0/1.5	6	43
$CH_3(CH_2)_7SO_3HH_2O$	6.0/47.4/48.0/1.5	2	47
	6.0/47.4/48.0/1.5	5	74

a) The molecular weight of PPE was taken as 500. b) Yield of isolated product.



Scheme 2.

key intermediate which is stepwisely reduced further very readily to the corresponding sulfinyl and sulfenyl iodides which are eventually reduced to the symmetrical disulfide[10)] as shown in Scheme 1. Indeed, *p*-toluenesulfonyl chloride was obtained in 48 and 28% yields respectively when potassium chloride, which has no reducing ability at all, and tetraethylammonium chloride were added into the mixture of either P_4O_{10} or PPE and *p*-toluenesulfonic acid in acetonitrile. Meanwhile, *p*-toluenesulfonyl iodide, which was prepared from the reaction of sodium *p*-toluenesulfinate and iodine in a mixture of benzene and water, was found to be reduced exothermically to the corresponding disulfide by hydroiodic acid in a high yield in dioxane.

Competitive reduction of an equimolar mixture of para-substituted benzenesulfonic acids, *i.e.* *p*-chlorobenzene-, benzene-, and *p*-methylbenzenesulfonic acids, with the PPA/KI/(*n*-Bu)$_4$NI (catalyst) system was carried out. Since the mixture of $C_6H_5SSC_6H_5$, $C_6H_5SSC_6H_4\text{-}p\text{-}$ $C_6H_5SSC_6H_4Cl\text{-}p$, $p\text{-}CH_3C_6H_4SSC_6H_4CH_3\text{-}p$, $p\text{-}CH_3C_6H_4SSC_6H_4Cl\text{-}p$, and $p\text{-}ClC_6H_4SSC_6H_4Cl\text{-}p$ was not readily separated or determined, the mixture of these disul-

Table 4. Reduction of sulfonate with polyphosphoric acid derivative/potassium iodide/tetrabutylammonium iodide

Sulfonate RSO_3R'	Polyphosphoric acid derivative	Reaction conditionse			Products/%	
		Solvent	Temp/°C	Time/h	RSSR	R′I
p-$CH_3C_6H_4SO_3C_6H_5$	PPA[a)]	Sulfolane	93	7	No reaction[c)]	
$C_6H_5SO_3CH_2CH_3$	PPA[b)]	Sulfolane	93	8	50	b)
	P_4O_{10}[b)]	Acetonitrile	81	33	70	d)
p-$CH_3C_6H_4SO_3(CH_2)_4CH_3$	PPA[b)]	Sulfolane	93	12	54	89[e)]
$CH_3(CH_2)_7SO_3(CH_2)_4CH_3$	PPA[b)]	Sulfolane	100	7	45	81[e)]

a, b) Amounts (mmol) of reagents used of sulfonate/polyphosphoric acid derivative/potassium iodide/tetrabutylammonium iodide: a=2/16/16/0; b=2/16/16/0.2. c) Starting material was recovered in 91% yield. d) Not determined. e) The yield was after 15 min.

fides was converted to the corresponding arenethiols upon treatment of the mixture with triphenylphosphine and water at room temperature. Thus, the amounts of arenethiols formed in the reduction were estimated as shown below.

p-$CH_3C_6H_4SH$	C_6H_5SH	p-ClC_6H_4SH
71%	60%	34%

These data reveal clearly that, in the reduction of para-substituted benzenesulfonic acids, benzenesulfonic acid bearing an electron-donating substituent such as methyl group is more readily reduced than that has an electro-withdrawing group such as chloro group. Apparently, the rate-determining step is the formation of a mixed anhydride bearing $-\overset{\|}{\underset{|}{P}}-O-\overset{\|}{\underset{\|}{S}}-$ bond which is formed by nucleophilic attack of sulfonic acid on the polyphosphoric acid derivative.

The same reduction procedure has been found to be successfully applied for the reduction of sulfonic esters (Table 4). Alkyl arene- and alkanesulfonates were found to react with these systems under similar conditions to give the corresponding alkyl iodides and disulfides. Alkyl iodide was usually obtained quantitatively by this reaction after about 15 minutes; however, the yield of the corresponding disulfide was very poor in the early stage of the reaction. These observations suggest that the initial step is the S_N2 attack of iodide on the α-carbon of alkyl sulfonates to form the alkyl iodides and the sulfonate anions which are then reduced further to the corresponding disulfides in a slow reaction with the polyphosphoric acid derivative/iodide system. Thus, the initial S_N2 reaction by the attack of iodide on the alkyl group is quite fast; however, the reduction of the sulfonate anion formed is relatively slow. Actually, benzenesulfonate was found to react readily with tetrabutylammonium iodide in benzene to afford tetrabutylammonium benzenesulfonate and pentyl iodide, whereas phenyl p-toluenesulfonate was not found to react with tetrabutylammonium iodide at all. On the other hand, phenyl p-toluenesulfonate, an aryl arenesulfonate was found to be quite inert in the same treatment with these reducing systems even under much harder conditions. In the case of phenyl p-toluenesulfonate, an aryl arenesulfonate, the initial nucleophilic attack of iodide on aromatic ipso carbon is so sluggish that the reduction does not proceed.

Experimental

Materials. PPA, potassium iodide, tetraphosphorus decaoxide, p-toluenesulfonic acid, sodium p-toluenesulfonate potassium chloride, sodium benzenesulfonate, sodium 2,4-dimethylbenzenesulfonate, p-toluenesulfonyl chloride, and d-camphor-10-sulfonic acid were all from Wako Chemicals Co. Tetrabutylammonium iodide, p-chlorobenzenesulfonic acid, benzenesulfonic acid, sodium 1-octanesulfonate, tetraethylammonium chloride, and ethyl benzenesulfonate were from Tokyo Kasei Co.

Conversion of Sodium Sulfonate to the Corresponding Sulfonic Acid. The cation exchange resin which was converted to the protonated from by flowing 1 mol dm^{-3} aqueous HCl solution through a column (Dowex, 50w-x8, 200—400 mesh H-form, Muromachi Kagaku Co.) was used to convert sodium sulfonate to the corresponding sulfonic acid.

Preparation of Ethyl Polyphosphate. Ethyl polyphosphate, PPE, was prepared according to the known method[9)] using tetraphosphorus decaoxide and dry diethyl ether. A colorless syrupy (hard) ester which is very sensitive to moisture, was obtained.

General Procedure for Reduction of the Sulfonic Acid to the Corresponding Disulfide. Potassium iodide, 8 g, (48 mmol) and tetrabutylammonium iodide 583 mg (1.5 mmol) were added into a mixture of PPE 24 g (48 mmol) and a sulfonic acid, *e.g.*, d-camphor-10-sulfonic acid 1.39 g (6 mmol). Then, into this mixture, 20 ml of dry chloroform was added. The whole mixture was stirred and refluxed for 5 h under nitrogen atmosphere. Then 10 ml of water was added to this mixture and the mixture was refluxed for 1 h. The reaction mixture was poured into benzene (100 ml), and washed with water for 3 times. The benzene solution was washed with 0.5 mol dm^{-3} sodium thiosulfate solution and dried ($MgSO_4$). The solvent was evaporated and the crude product, *i.e.* the disulfide was chromatographed on a silica-gel column with benzene (R_f= 0.2, eluent; benzene). Removal of the solvent afforded 10,10′-dithiobis(d-camphor) as colorless crystals in 74% yield (817 mg). Mp 236—238 °C; $[\alpha]_D^{25}$ $-103.66°$ (c 1, $CHCl_3$); IR (KBr) 1730 cm^{-1} (C=O); NMR ($CDCl_3$) δ=0.90 (3H, s), 1.05 (3H, s), 2.75 (1H, d, J=13.5 Hz), 3.20 (1H, d, J=13.5 Hz), and 2.5—1.1 (7H, m); Found: C, 65.33; H, 8.25; S, 17.27%. Calcd for $C_{20}H_{30}S_2O_2$: C, 65.53; H, 8.24; S, 17.49%. Reduction of other sulfonic acids to the corresponding disulfides with the polyphosphoric acid derivative/iodide system were conducted in the same manner.

Di-p-tolyl disulfide mp 44—45 °C (lit,[11)] 46 °C).

Bis(p-chlorophenyl) disulfide mp 70—71 °C (lit,[12)] 73. °C)

Bis (2,4-dimethylphenyl) disulfide bp 180—186 °C/2—2.5 Torr (1 Torr=133.322 Pa) IR (NaCl) 540 and 800 cm^{-1};

NMR (CCl_4) δ=2.24 (3H, s), 2.33 (3H, s), and 3.4—2.6 (3H, m); Found: C, 69.69; H, 6.65; S, 23.58%. Calcd for $C_{16}H_{18}S_2$: C, 70.02; H, 6.61; S, 23.36%.

Dioctyl disulfide and diphenyl disulfide were identical to the authentic commercial samples.

Trapping Experiment of Sulfonyl Function. Tetraphosphorus decaoxide (1600 mg, 11.27 mmol) and 381 mg (2 mmol) of *p*-toluenesulfonic acid were dissolved in 5 ml of dry acetonitrile and the reaction mixture was heated (60—65 °C) for 1.5 h under nitrogen. Then, 33 mg (0.2 mmol) of tetraethylammonium chloride, 746 mg (10 mmol) of potassium chloride and 5 ml of dry acetonitrile were added to this reaction mixture at 0 °C and the mixture was kept standing for 3 h at room temperature. Then, the mixture was poured into 100 ml of benzene and the benzene solution was washed with water for three times, and then dried ($MgSO_4$). When the solvent was evaporated, *p*-toluenesulfonyl chloride was obtained in 48% yield (GLC); the isolated yield was 43%. The sulfonyl chloride was identical to the authentic sample of *p*-toluenesulfonyl chloride both in GLC and TLC. In the reduction with the PPE system, PPE, 6 g and 381 mg (2 mmol) of *p*-toluenesulfonic acid were dissolved in 5 ml of dry acetonitrile and the mixture was heated for 1 h at about 70 °C under nitrogen. Then, at 0 °C 33 mg of tetraethylammonium chloride and 746 mg (10 mmol) of potassium chloride were added to the reaction mixture which was kept standing for 2.5 h at room temperature. After the reaction, a similar treatment as that with P_4O_{10}, gave *p*-toluenesulfonyl chloride in 28% yield (GLC).

Preparation of p-*Toluenesulfonyl Iodide.* Treatment of sodium *p*-toluenesulfinate dihydrate with iodine according to a known method gave *p*-toluenesulfonyl iodide nearly quantitatively. Mp 85—86 °C (decomp) (lit,[13] 84—85 °C).

Reduction of p-*Toluenesulfonyl Iodide with Hydriodic Acid to Di*-p-*tolyl Disulfide.* *p*-Toluenesulfonyl iodide (300 mg, 1.06 mmol) was dissolved in 3 ml of dioxane and then 4 ml of hydriodic acid (57%) was slowly added to this mixture at room temperature. An exothermic reaction occurred affording di-*p*-tolyl disulfide. After 1 h the mixture was poured into benzene and the benzene solution was washed with water twice, 0.5 mol dm^{-3} $Na_2S_2O_3$ solution, and dried ($MgSO_4$). ($MgSO_4$). Only di-*p*-tolyl disulfide was obtained in 79% yield (GLC).

*Competitive Reaction of Arenesulfonic Acids with PPA/KI/*n-*Bu_4NI(Catalyst).* *p*-Toluenesulfonic acid, 190.2 mg (1 mmol), 176 mg (1 mmol) of benzenesulfonic acid, and 192.2 mg (1 mmol) of *p*-chlorobenzenesulfonic acid were dissolved in 10 ml of sulfolane, then 8100 mg of PPA, 3984 mg (24 mmol) of potassium iodide, 184 mg (0.5 mmol) of tetrabutylammonium iodide and 154 mg (1 mmol) of biphenyl were added to this mixture and the whole mixture was stirred (95—100 °C) for 4 h. The reaction was followed by GLC. After the reaction, 5 ml of water was added into the mixture which was then heated for 0.5 h. The solution was poured into benzene and the benzene solution was washed with water for 3 times, then with 0.5 mol dm^{-3} solution of $Na_2S_2O_3$ and dried ($MgSO_4$). The solution was found to contain only the mixture of disulfides *i.e.* $C_6H_5SSC_6H_5$, $C_6H_5SSC_6H_4CH_3$-*p*, $C_6H_5SSC_6H_4Cl$-*p*, *p*-$CH_3C_6H_4SSC_6H_4CH_3$-*p*, *p*-$CH_3C_6H_4SSC_6H_4Cl$-*p*, *p*-$ClC_6H_4SSC_6H_4Cl$-*p* which are converted to the corresponding thiols by treating with a mixture of triphenylphosphine or tributylphosphine (2 mmol) and water in a mixture solvent of benzene and dioxane over night at room temperature. The yields of the mixture of three thiols were determined with GLC. *p*-Toluenethiol, 71%; benzenethiol, 60%; *p*-chlorobenzenethiol, 34%.

In the reduction with the P_4O_{10} system, a mixture of three different para-substituted benzenesulfonic acids each with 1 mmol was dissolved in 20 ml of dry acetonitrile, and then 3000 mg (21 mmol) of P_4O_{10}, 3984 mg (24 mmol) of potassium iodide, and 184 mg (0.5 mmol) of tetrabutylammonium iodide were added to this mixture which was then refluxed for 7 h. After the reaction, a similar work-up procedure afforded a mixture of three para-substituted benzenethiols. The yields of these thiols were determined by GLC (SE-30, 1 m glass column) to be the following: *p*-toluenethiol, 50%; benzenethiol 50%; *p*-chlorobenzenethiol, 26%.

Preparation of Sulfonates. Treatment of organic sulfonyl chlorides with a choice alcohol according to a known procedure[14] gave various organic sulfonates. The yields of sulfonates are usually 50—60%.

Pentyl benzenesulfonate: 138—140 °C/1 Torr (lit,[14] 136—138 °C/1 Torr).

Pentyl *p*-toluenesulfonate: Mp 167—168 °C/3 Torr (lit,[15] 169—170 °C/3 Torr).

Phenyl *p*-toluenesulfonate: Mp 92—93 °C (lit,[17] 93 °C).

Pentyl 1-octanesulfonate: TLC (eluent: benzene) R_f=0.4—0.5; IR (NaCl) 1340 (SO_2) and 1160 cm^{-1} (SO_2); NMR-(CCl_4) δ=4.1 (2H, t, J=6.0 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 $C_{13}H_{28}O_3S$: C, 59.05; H, 10.67; S, 12.12%.

Reduction of Sulfonate with Polyphosphoric Acid Derivative/Potassium Iodide/Tetrabutylammonium Iodide System. PPA, 5408 mg (16 mmol), 2656 mg (16 mmol) of potassium iodide, and 484 mg (2 mmol) of pentyl *p*-toluenesulfonate were dissolved in 10 ml of sulfolane, and then 74 mg (0.2 mmol) of tetrabutylammonium iodide and 308 mg (2 mmol) of biphenyl (standard material) were added to this mixture, which was then heated (≈93 °C) with stirring under nitrogen. After 15 min, the starting ester was found to have disappeared upon GLC analysis and pentyl iodide was formed in 89% yield upon determination with GLC, but the yield of disulfide was still very poor during this period. After 12 h, 10 ml of water was added to this mixture and heated for 0.5 h. The mixture was poured into benzene which was then washed with water for three times, again with 0.5 mol dm^{-3} $Na_2S_2O_3$ solution and dried ($MgSO_4$). Thus, di-*p*-tolyl disulfide was obtained in 54% yield (GLC), and the yield of pentyl iodide was found to remain unchanged as compared with that, estimated after 15 min. Pentyl iodide 157 °C/760 Torr (lit,[16] 157 °C/760 Torr).

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