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Synthesis and Decomposition of Alkane- and Arenesulfonyl Aryl Disulfides

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Pyridinium alkane- and arenethiolsulfonates were allowed to react with arenesulfenyl chlorides, ClSAr′, to yield sulfonyl disulfides in which R is *n*-dodecyl, benzyl, phenyl, or *p*-tolyl group, and Ar′ *o*-nitrophenyl or *o*-nitro-*p*-chlorophenyl. *p*-Toluenesulfonyl *p*-nitrophenyl disulfide was also prepared by this method. IR and UV spectra of these compounds were determined and compared with those of the corresponding thiolsulfonates. Decomposition of ^{35}S-labeled *p*-toluenesulfonyl *p*-nitrophenyl disulfide, *p*-$CH_3C_6H_4SO_2S^{35}SC_6H_4NO_2$-*p*, gave ^{35}S-labeled *p*-nitrophenyl *p*-toluenethiolsulfonate, *p*-$CH_3C_6H_4SO_2{}^{35}SC_6H_4NO_2$-*p*. Triphenylphosphine was found to attack two oxygen atoms and a sulfur atom of *p*-toluenesulfonyl *o*-nitrophenyl disulfide at the same rate. The reaction of triphenylphosphine with ^{35}S-labeled *p*-toluenesulfonyl *o*- and *p*-nitrophenyl disulfides revealed that the central sulfur atom of these sulfonyl disulfides was desulfurated. This result coincides with that of the decomposition mentioned above. The susceptibility of sulfonyl disulfides containing *p*-nitrophenyl group to the decomposition and the desulfuration of the central sulfur atom of sulfonyl disulfides in general are also discussed.

Very little work has been published on the synthesis and chemistry of organic sulfonyl disulfides (RSO_2SSR', sulfonyl sulfenyl thioanhydride in IUPAC) which are considered as partially oxidized compounds of organic trisulfides. Brooker *et al.*[1] reported synthesis of arenesulfonyl aryl disulfides by the reaction of finely powdered potassium arenethiolsulfonates with arenesulfenyl chlorides in ether. Uhlenbroek and Koopmans[2] examined fungitoxic activity of arenesulfonyl trichloromethyl disulfides which were prepared by the heterogeneous reaction of potassium arenethiolsulfonates in water with trichloromethanesulfenyl chloride.

$$ArSO_2SK + ClSAr' \rightarrow ArSO_2SSAr' + KCl$$

$$ArSO_2SK + ClSCCl_3 \rightarrow ArSO_2SSCCl_3 + KCl$$

In the present work we succeeded in the homogeneous synthetic reaction in organic solvents by using pyridinium alkane- or arenethiolsulfonates and arenesulfenyl chlorides. Since most sulfenyl chlorides are sensitive to hydrolysis, our method will promise synthesis of a variety of the entitled compounds.

Some types of organic sulfonyl disulfides including several novel compounds were successfully prepared by our method, but others were found to decompose during preparation process or recrystallization procedure to give the corresponding thiolsulfonates, RSO_2SAr'. So far as our experiments show, *p*-toluenesulfonyl *p*-nitrophenyl disulfide, was only one stable compound containing *p*-nitrophenyl group as Ar′ in RSO_2SSAr'. This compound specifically labeled with ^{35}S was utilized to confirm which sulfur atom was desulfurated on the spontaneous decomposition, $RSO_2SSAr' \rightarrow RSO_2SAr'$.

In order to obtain further knowledge on sulfonyl disulfides, we allowed nonlabeled and ^{35}S-labeled *p*-toluenesulfonyl *p*- or *o*-nitrophenyl disulfides to react with triphenylphosphine, which has been known to behave as both deoxygenating and desulfurating agents.

Results and Discussion

Synthesis of Alkane- and Arenesulfonyl Aryl Disulfides. A chloroform solution of arenesulfenyl chloride (9 mmol) was added to pyridinium alkane- or arene-

1) L. G. S. Brooker, R. Child, and S. Smiles, *J. Chem. Soc.*, **1927,** 1384.

2) J. H. Uhlenbroek and M. J. Koopmans, *Rec. Trav. Chim. Pays-Bas*, **76**, 660 (1957).

Table 1. The Mp and analysis of the compounds

Compound No.	R	Ar′	Yield (%)	Mp (°C)	Anal, Found (Calcd) C	H	N	S
				RSO_2SAr'				
1	n-$C_{12}H_{25}$	o-$NO_2C_6H_4$	90.5	67— 68	51.49 (51.52)	7.21 (6.97)	3.53 (3.34)	23.2 (22.92)
2	$C_6H_5CH_2$	o-$NO_2C_6H_4$	87.7	132—135	45.87 (45.73)	3.28 (3.25)	4.05 (4.10)	28.1 (28.17)
3	C_6H_5	o-$NO_2C_6H_4$	98.5	151—153	44.31 (44.02)	2.74 (2.78)	4.19 (4.28)	29.2 (29.28)
4	p-$CH_3C_6H_4$	o-$NO_2C_6H_4$	91.4	140—141 (lit,[1] 141)				
5	n-$C_{12}H_{25}$	o-NO_2-p-ClC_6H_3	88.1	49— 51	47.71 (47.61)	6.51 (6.23)	2.71 (3.09)	
6	$C_6H_5CH_2$	o-NO_2-p-ClC_6H_3	85.7	133—134	41.52 (41.41)	2.46 (2.54)	3.62 (3.62)	
7	C_6H_5	o-NO_2-p-ClC_6H_3	93.5	131—134	39.86 (39.83)	2.20 (2.23)	3.73 (3.87)	
8	p-$CH_3C_6H_4$	o-NO_2-p-ClC_6H_3	96.2	110—113 (lit,[1] 114)				
9	p-$CH_3C_6H_4$	p-$NO_2C_6H_4$	66.6	105—106	45.94 (45.73)	3.15 (3.25)	4.28 (4.10)	27.5 (28.17)
				RSO_2SAr'				
1a	n-$C_{12}H_{25}$	o-$NO_2C_6H_4$	98.3	64— 66	55.54 (55.77)	7.48 (7.58)	3.58 (3.61)	16.5 (16.54)
2a	$C_6H_5CH_2$	o-$NO_2C_6H_4$	93.5	89— 91	50.43 (50.47)	3.49 (3.59)	4.47 (4.53)	20.8 (20.73)
3a	C_6H_5	o-$NO_2C_6H_4$	96.7	82— 83 (lit,[3] 84—85)				
4a	p-$CH_3C_6H_4$	o-$NO_2C_6H_4$	96.8	99—100	50.71 (50.47)	3.56 (3.58)	4.28 (4.53)	20.4 (20.73)
5a	n-$C_{12}H_{25}$	o-NO_2-p-ClC_6H_3	91.8	47— 49	50.59 (51.22)	6.77 (6.70)	3.32 (3.32)	
6a	$C_6H_5CH_2$	o-NO_2-p-ClC_6H_3	90.1	107—109	44.89 (45.41)	2.72 (2.94)	4.20 (4.07)	
7a	C_6H_5	o-NO_2-p-ClC_6H_3	93.9	100—102	43.52 (43.70)	2.28 (2.45)	4.41 (4.25)	
8a	p-$CH_3C_6H_4$	o-NO_2-p-ClC_6H_3	90.1	120—121	45.03 (45.41)	2.84 (2.94)	3.95 (4.07)	
9a	p-$CH_3C_6H_4$	p-$NO_2C_6H_4$	55.1	135—136 (lit,[3] 133—134)				

thiolsulfonate (10 mmol) in chloroform at room temperature. The mixture was allowed to stand overnight for completion of the reaction, and washed with water to remove the unchanged pyridinium thiolsulfonate and pyridinium hydrochloride produced. Our experience indicates that an excess

$$RSO_2S^-C_5H_5NH^+ + ClSAr' \rightarrow RSO_2SAr' + C_5H_5NH^+Cl^- \quad (1)$$

sulfenyl chloride should be avoided not to induce undesirable reaction between the sulfonyl disulfide produced and the excess sulfenyl chloride. The results are summarized in Table 1 together with the results of the corresponding thiolsulfonates for comparison. Table 1 clearly indicates that when Ar′ in RSO_2SAr' is o-nitrophenyl or o-nitro-p-chlorophenyl, the sulfonyl disulfides are stable enough to be isolated. With the exception of **9** in Table 1, synthesis of alkane- and arenesulfonyl p-nitrophenyl disulfides failed in spite of all our efforts.

Absorption Spectra of the Sulfonyl Disulfides. In Table 2 are summarized the spectral data of the sulfonyl disulfides together with those of the corresponding thiolsulfonates. As expected from the literatures on sulfones and thiolsulfonates,[4] IR bands of SO_2 group of the sulfonyl disulfides in Table 2 are in a range from 1117 to 1149 and a range from 1325 to 1338 cm^{-1}, respectively.

Leandri *et al.*[5] reported absorption spectra of some thiolsulfonates in near-UV range. The sulfonyl disulfides prepared by us are restricted to only the compounds containing nitro-aromatic rings attached to the thiol sulfur atom, because of the synthetic dif-

3) G. Leandri and A. Tundo, *Ann. Chim. Appl.*, **44**, 74 (1954).

4) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, New York (1954), pp. 297—299.

5) G. Leandri, A. Mangini, and A. Tundo, *J. Chem. Soc.*, **1957**, 52.

Table 2. The UV and IR spectra

Compound No.	UV $\lambda_{max}(m\mu)$[a]	UV log ε	IR ν_{SO_2} (cm^{-1})	Compound No.	UV $\lambda_{max}(m\mu)$[a]	UV log ε	IR ν_{SO_2} (cm^{-1})
1	223	4.14	1136	**1a**	228	4.26	1136
	252	4.04	1334		282[s]	3.52	1326
	278[s]	3.88					
	347	3.60					
2	225	4.32	1117	**2a**	233	4.20	1125
	250[s]	4.18	1334				1335
	345	3.61					
3	226[s]	4.32	1135	**3a**	232	4.30	1147
	265[s]	4.04	1332		278[s]	3.63	1335
	344	3.59					
4	233	4.36	1136	**4a**	234	4.36	1145
	269[s]	4.11	1335		279[s]	3.68	1334
	347	3.62					
5	235	4.20	1125	**5a**	234	4.28	1134
	250[s]	4.11	1325				1336
	355	3.51					
6	236	4.32	1125	**6a**	233	4.23	1134
	256[s]	4.20	1335				1335
	360	3.59					
7	238	4.18	1143	**7a**	235	4.32	1149
	263[s]	3.99	1332				1331
	359	3.48					
8	238	4.42	1145	**8a**	237	4.36	1144
	260[s]	4.23	1335				1338
	360	3.60					
9	239[s]	4.18	1149	**9a**	251	4.15	1151
	261[s]	4.15	1338		263	4.11	1350
	314[s]	3.86			304[s]	3.79	

a) s: shoulder

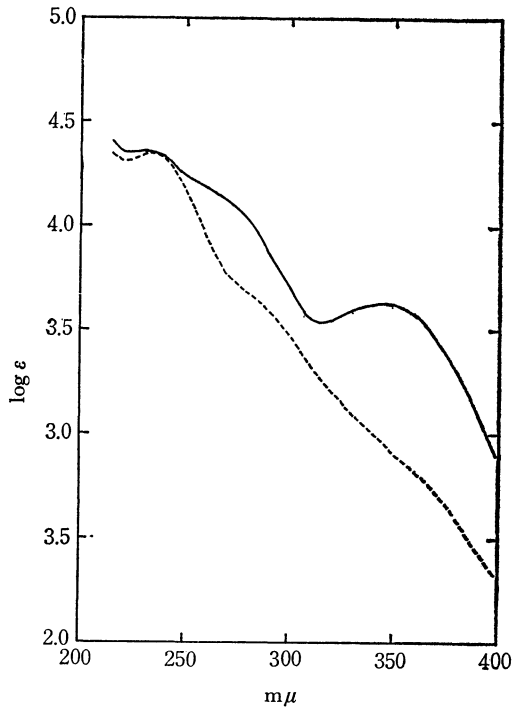


Fig. 1. The UV spectra of **4** and **4a**.
—— **4**, ---- **4a**

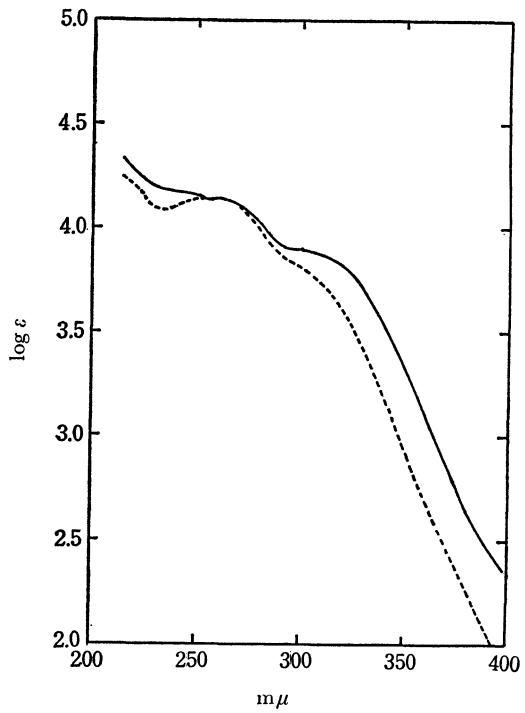
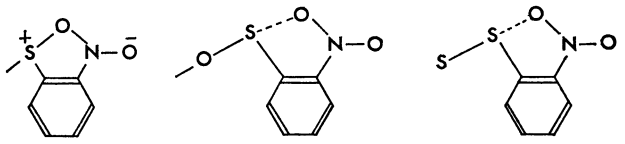


Fig. 2. The UV spectra of **9** and **9a**.
—— **9**, ---- **9a**

ficulty. Therefore, the discussion should be confined to only a limited type of the compounds. As to the UV spectra of thiolsulfonates, Leandri[5] noticed that substituent effects in benzene ring attached to sulfonyl group are comparatively small to affect the general character of the spectra. The same effect as Leandri noticed is observed in the UV spectra of the sulfonyl disulfides in Table 2. (Compare **3** with **4**, and **7** with **8** in Table 2.) Moreover, when the spectra of alkanesulfonyl aryl disulfides (**1**, **2**, **5**, and **6**) were compared with those of arenesulfonyl aryl disulfides (**3**, **4**, **7**, and **8**), prominent difference was not observed. However, the effect of a nitro-substituent in thiol-containing benzene ring is eminent depending on whether the nitro group is in *ortho* or *para* position.

Figure 1 shows UV spectra of **4** and **4a**, and Fig. 2 those of **9** and **9a**. A band at 233 mμ and a shoulder at 269 mμ of **4** in Fig. 1 are attributed to the excitations of benzene ring attached to sulfonyl group as Leandri has assigned for thiolsulfonates. (Refer to those of **4a** in Fig. 1.) However, the broad but well defined band at 347 mμ is considered specific for **4**, because **4a** exhibits only smooth running in this range.[6] We[7] reported already that di-*o*-nitrophenyl sulfide and disulfide have a maximum near 350 mμ and that structure I might contribute to the excitation of these compounds. The specific band at 347 mμ of **4** may be rationalized by the contribution of the structure I,



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in which N, O, and S atoms are coplanar with benzene ring. The similar specific bands are observed in UV spectra of **1**—**3** (sulfonyl *o*-nitrophenyl disulfides), and slight bathochromic shifts are also observed in **5**—**8** (sulfonyl *o*-nitro-*p*-chlorophenyl disulfides). The smooth running down of the spectrum of thiolsulfonate **4a** in this range suggests that coplanarity in structure I disappeared because of steric effect of adjacent SO_2 group or that the electrons of sulfur atom attached to nitrobenzene ring are intensively withdrawn by SO_2 group.

A shoulder near 310 mμ of **9** in Fig. 2 may be assigned to the excited structure of *p*-nitrobenzenesulfenyl group, because di-*p*-nitrophenyl disulfide was reported[8] to exhibit a maximum at 316 mμ. The similar shoulder of **9a** is shifted to shorter wavelength. This suggests that the excited state of *p*-nitrobenzenesulfenyl group is disturbed to some extent by the intensive electron-withdrawing effect of adjacent SO_2 group, while in **9** this effect is weakened to a greater extent by the intervening sulfur atom.

The stability of the sulfonyl disulfides containing *o*-nitrophenyl or *o*-nitro-*p*-chlorophenyl group (compounds **1**—**8**) may be explained as follows. Hamilton and La Placa[9] attributed the stability of *o*-nitrobenzenesulfenate to a resonance stability originated from the coplanarity as indicated in II and a specific nonbonding interaction of S and O atoms of sulfenic acid group with almost linear O—S···O configuration. The stability of the compounds **1**—**8** may be rationalized by the same argument mentioned above (III).

The Decomposition of ^{35}S*-labeled* p-*Toluenesulfonyl* p-*Nitrophenyl Disulfide (labeled* **9***).* As stated above, **9** was obtained as only one stable compound among sulfonyl *p*-nitrophenyl disulfides. We examined the decomposition of the ^{35}S-labeled **9** by submitting to several recrystallizations from a polar solvent. This labeled compound was prepared as shown below.

$$p\text{-}NO_2C_6H_4{}^{35}S{}^{35}SC_6H_4NO_2\text{-}p + Cl_2 \rightarrow 2\,p\text{-}NO_2C_6H_4{}^{35}SCl$$

$$p\text{-}CH_3C_6H_4SO_2S^-C_5H_5NH^+ + p\text{-}NO_2C_6H_4{}^{35}SCl \rightarrow p\text{-}CH_3C_6H_4SO_2S{}^{35}SC_6H_4NO_2\text{-}p$$

(labeled **9**)

This compound, after recrystallizations of more than ten times, was found to be converted into *p*-nitrophenyl *p*-toluenethiolsulfonate (labeled **9a**), of which specific activity was determined as 1,395 dpm/mg. The standard labeled **9a** for radioassay was prepared from the same *p*-nitrobenzenesulfenyl chloride as for the labeled **9**. The specific activity of the standard **9a** was found 1,427 dpm/mg and coincided with that (1,395 dpm/mg) of the decomposition product from the labeled **9** within experimental error. Therefore, we can conclude that the central sulfur atom of **9** is desulfurated on the spontaneous decomposition. This conclusion does not contradict with the explanation on the stability of compounds **1**—**8** mentioned above. The failure to synthesize other compounds than **9** which contain *p*-nitrophenyl as Ar′ in RSO_2SSAr' may be ascribed to the extreme susceptibility to spontaneous decomposition.[10]

$$p\text{-}CH_3C_6H_4SO_2S{}^{35}SC_6H_4NO_2\text{-}p \rightarrow p\text{-}CH_3C_6H_4SO_2{}^{35}SC_6H_4NO_2\text{-}p \quad (2)$$

(labeled **9**) (labeled **9a**)

The Reaction of Triphenylphosphine with p-*Toluenesulfonyl* o-*Nitrophenyl Disulfide (***4***).* Hayashi *et al.*[11] subjected thiolsulfonates and disulfonyl sulfides

6) Leandri *et al.*[5] reported that UV spectra of phenyl *o*- and *p*-nitrobenzenethiolsulfonates, when determined in ethanol, have each maximum at 400 and 340 mμ respectively, besides those determined in cyclohexane. They ascribed these additional bands to specific interaction between alcohol and the nitrobenzenethio-group. However, as shown in Figs. 1 and 2 (**4a** and **9a**), we could not observe such additional bands as they reported.

7) T. Nakabayashi and J. Tsurugi, *J. Org. Chem.*, **26**, 2482 (1961).

8) E. Campaigne, J. Tsurugi, and W. W. Meyer, *ibid.* **26**, 2486 (1961).

9) W. C. Hamilton and S. J. La Placa, *J. Amer. Chem. Soc.*, **86**, 2289 (1964).

10) We attempted to prepare also alkanesulfonyl alkyl disulfides like $C_6H_5CH_2SO_2SSCH_2C_6H_5$ and arenesulfonyl aryl disulfides such as $C_6H_5SO_2SSC_6H_5$, but failed in spite of all our efforts. The order of the susceptibility of sulfonyl disulfide to the decomposition to thiolsulfonate is estimated by the numbers of times of recrystallization (from ethanol) to be converted to the corresponding thiolsulfonate. The order is: alkanesulfonyl alkyl> arenesulfonyl aryl>arenesulfonyl *p*-nitrophenyl.

(RSO_2SSO_2R') to deoxygenation and desulfuration with triphenylphosphine and concluded as summarized below. It seems interesting to examine whether or

$$RSO_2SR' \xrightarrow[\text{reflux}]{Ph_3P} RSOSR' \xrightarrow[\text{reflux}]{Ph_3P} RSSR'$$

$$RSO_2SSO_2R' \xrightarrow[\text{reflux}]{4\ Ph_3P} RSSSR' \xrightarrow[\text{reflux}]{Ph_3P} RSSR'$$

not sulfonyl disulfide behaves similarly to thiolsulfonate or disulfonyl sulfide. Benzene solution of **4** (1 mmol) was added to equimolar amount of triphenylphosphine in ethanol. After the mixture was allowed to stand for one hour at room temperature, glc analysis indicated that 0.67 mmol of triphenylphosphine oxide and 0.33 mmol of triphenylphosphine sulfide were produced. This result shows that under these conditions two oxygen atoms of sulfonyl group and a sulfur atom were eliminated with triphenylphosphine, and makes a clear contrast to the stepwise deoxygenation and desulfuration of thiolsulfonate and disulfonyl sulfide.

The Reaction of Triphenylphosphine with ^{35}S-Labeled p-*Toluenesulfonyl* o- *and* p-*Nitrophenyl Disulfides (Labeled* ***4*** *and* ***9***). In order to confirm which sulfur atom of sulfonyl disulfide is desulfurated, we utilized ^{35}S-labeled **4**, which was prepared as shown below. The specific activity of the labeled **4** recrystallized from

$$p\text{-}CH_3C_6H_4SO_2^-C_5H_5NH^+ + {}^{35}S \rightarrow p\text{-}CH_3C_6H_4SO_2{}^{35}S^-C_5H_5NH^+$$

$$p\text{-}CH_3C_6H_4SO_2{}^{35}S^-C_5H_5NH^+ + o\text{-}NO_2C_6H_4SCl \rightarrow p\text{-}CH_3C_6H_4SO_2{}^{35}SSC_6H_4NO_2\text{-}o$$

(labeled **4**)

carbon tetrachloride was 25,634 dpm/mg. One mmol of the labeled **4** in benzene was allowed to react with three mmol of triphenylphosphine in ethanol at room temperature for one hour. An aliquot of the reaction mixture, when determined by GLC, showed 2 : 1 molar ratio of phosphine oxide and sulfide produced. Triphenylphosphine sulfide was separated from the mixture by recrystallization from ethanol. Specific activity of the sulfide obtained was 29,855 dpm/mg. The standard triphenylphosphine sulfide for radioassay was prepared from triphenylphosphine and the same radioactive sulfur as used for the labeled **4**. The specific activity of this standard was found 29,867 dpm/mg and coincided with that (29,855) of the desulfuration product from the labeled **4**. Therefore,

$$p\text{-}CH_3C_6H_4SO_2{}^{35}SSC_6H_4NO_2\text{-}o + 3(C_6H_5)_3P \rightarrow 2(C_6H_5)_3PO + (C_6H_5)_3P{}^{35}S + p\text{-}CH_3C_6H_4SSC_6H_4NO_2\text{-}o \quad (3)$$

The ^{35}S-labeled **9**, $p\text{-}CH_3C_6H_4SO_2S^{35}SC_6H_4NO_2\text{-}p$, which was utilized for the decomposition of sulfonyl disulfide as shown above, was also allowed to react with triphenylphosphine. Triphenylphosphine sulfide separated similarly to the case for the labeled **4** was found nonradioactive.

$$p\text{-}CH_3C_6H_4SO_2S^{35}SC_6H_4NO_2\text{-}p + 3(C_6H_5)_3P \rightarrow 2(C_6H_5)_3PO + (C_6H_5)_3PS + p\text{-}CH_3C_6H_4S^{35}SC_6H_4NO_2\text{-}p \quad (4)$$

Although Eqs. (3) and (4) predict the formation of the nonlabeled *p*-tolyl *o*-nitrophenyl disulfide and labeled *p*-tolyl *p*-nitrophenyl disulfide respectively, their isolation was not carried out, because our intention is to isolate and assay the radioactivity of phosphine sulfide produced. The formation of radioactive phosphine sulfide in Eq. (3) clearly indicates that the central sulfur atom of the sulfonyl disulfide is desulfurated. Eq. (4) also supports this conclusion. In the present paper we noticed that unstable sulfonyl disulfide decomposes into thiolsulfonate by recrystallization from ethanol. The decomposition results in the release of the central sulfur atom. (See Eq. (2).) This analogy suggests that the decomposition may arise from a nucleophilic attack by ethanol.

Experimental

All melting points are uncorrected. Infrared spectra were recorded on a JASCO IR-S spectrometer by KBr disk method and UV spectra were recorded on a Shimadzu RS-27 spectrometer in 99.5% ethanol. Triphenylphosphine oxide and sulfide were identified by comparison of their retention times with those of authentic specimens, and estimated by use of triphenylphosphorothionate as an internal standard, with a Yanagimoto GCG-5DH gas chromatograph using Silicone DC 200 column. Specific activities of all the labeled compounds, which were recrystallized until the respective constant specific activities attained, were counted with a Packard Tri-Carb Liquid Scintillation Spectrometer, Model 314, using a mixture of POPOP and PPO (0.1 g and 4 g in 1 *l* of toluene) as a scintillator.

Materials. Benzene- and *p*-toluenesulfinic acids were prepared by acidification of commercial sodium salts. *n*-Dodecanesulfinic acid was prepared from *n*-dodecylmagnesium bromide and sulfur dioxide.[12] *ω*-Toluenesulfinic acid was prepared from *ω*-toluenesulfonyl chloride by reduction with sodium sulfite.[13]

Pyridinium salts of alkane- and arenethiolsulfonic acids were prepared from the corresponding sulfinic acids and elemental sulfur in pyridine.[14] Mp and analysis of the compounds are summarized in Table 3.

Table 3. The Mp and analysis of the pyridinium thiolsulfonates

Pyridinium thiolsulfonate[b]	Mp (°C)	Anal, Found (Calcd)			
		C	H	N	S
n-Dodecane	65— 70	58.76 (59.07)	9.08 (9.06)	3.75 (4.05)	18.4 (18.56)
p-Toluene	88— 94	54.06 (53.91)	5.20 (4.90)	5.23 (5.24)	23.9 (23.98)
w-Toluene	129—131	53.69 (53.91)	4.85 (4.90)	5.08 (5.24)	24.13 (23.98)

b) Since benzenethiolsulfonate was obtained as an oily material, it was used for the succeeding synthesis without isolation.

11) S. Hayashi, M. Furukawa, J. Yamamoto, and K. Hamamura, *Chem. Pharm. Bull.*, **15**, 1310 (1967).
12) C. S. Marvel and R. S. Johnson, *J. Org. Chem.*, **13**, 822 (1948).
13) S. Smiles and C. M. Bere, "Organic Syntheses," Coll. Vol. 1, p. 7.
14) F. Kurzer and J. R. Powell, *J. Chem. Soc.*, **1952**, 3733.

Arenesulfenyl chlorides were prepared from the corresponding disulfides by chlorination.[15,16]

Thiolsulfonates. Compounds **1a**—**8a** were prepared from the arenesulfenyl chlorides and a slight excess of the sulfinic acids both in chloroform. Compound **9a** was prepared from pyridinium sulfinate by the same method as for **1a**—**8a**. Crude products were recrystallized from ethanol.

Alkane- and Arenesulfonyl Aryl Disulfides. To a solution of the pyridinium alkane- or arenethiolsulfonate (10 mmol) in 30 m*l* of chloroform, was added a solution of the arenesulfenyl chloride (9 mmol) in 30 m*l* of chloroform dropwise at room temperature. The mixture was allowed to stand overnight at the same temperature. The reaction mixture was thoroughly washed with water and then dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, the crude sulfonyl disulfide was recrystallized from ethanol. Only **9** was recrystallized from carbon tetrachloride for prevention of the decomposition.

Specifically ^{35}S*-Labeled* p-*Toluenesulfonyl* o-*Nitrophenyl Disulfide (**4**).* Radioactive sulfur (5 mCi) in benzene was diluted with 18 g of nonactive sulfur in 200 m*l* of carbon disulfide. After removal of the solvent under reduced pressure, crystals of elementary sulfur were recrystallized from benzene. The crystals had an appropriate specific activity for the further synthesis. To a solution of *p*-toluenesulfinic acid (7.1 g) in pyridine (50 m*l*) was added 1.5 g of the radioactive sulfur. The mixture was treated by the same method as for nonactive one to yield 8.2 g of pyridinium *p*-toluenethiolsulfonate. The radioactive sulfonyl disulfide was prepared from this compound and *o*-nitrobenzenesulfenyl chloride by the same method as for nonactive compound and recrystallized from carbon tetrachloride (25,634 dpm/mg).

Specifically ^{35}S*-Labeled* p-*Nitrophenyl Disulfide (**9**).* Radioactive sulfur (1 mCi) in benzene was diluted with 10 g of nonactive sulfur in 100 m*l* of carbon disulfide. The solvent was removed under reduced pressure. From the active sulfur was prepared radioactive sodium disulfide, which was allowed to react with *p*-nitrochlorobenzene to give radioactive *p,p'*-dinitrodiphenyl disulfide (12.7 g, mp 182—183°C). The latter compound (1.6 g) was converted to radioactive *p*-nitrobenzenesulfenyl chloride by chlorination. Radioactive **9** was prepared from the radioactive sulfenyl chloride and pyridinium *p*-toluenethiolsulfonate (2.7 g) as for nonlabeled **9**, and recrystallized from carbon tetrachloride (mp 105—106°C, 1,287 dpm/mg).

Specifically ^{35}S*-Labeled* p-*Nitrophenyl* p-*Toluenethiolsulfonate (**9a**).* Radioactive *p*-nitrobenzenesulfenyl chloride which was used for the preparation of the labeled **9** and pyridinium *p*-toluenesulfinate (2.64 g) in chloroform (100 m*l*) was allowed to stand overnight. The mixture was washed with water three times and dried over anhydrous sodium sulfate. Removal of chloroform by a rotary evaporator yielded crystals. After five recrystallizations from ethanol, constant specific activity (1,427 dpm/mg) was obtained.

Standard ^{35}S*-Labeled Triphenylphosphine Sulfide.* To a solution of radioactive sulfur (0.32 g) which was used for the preparation of labeled **4** in benzene was added triphenylphosphine (2.62 g) in ethanol. The mixture was allowed to stand for one hour at room temperature. The solvent was removed under reduced pressure. After four recrystallizations from ethanol, constant specific activity (29,867 dpm/mg) was obtained.

Reaction of p-*Toluenesulfonyl* p-*Nitrophenyl Disulfide (**4**) with Triphenylphosphine.* To a solution of nonactive sulfonyl disulfide (1 mmol) in 10 m*l* of benzene, was added a solution of triphenylphosphine (1 mmol) in 5 m*l* of ethanol.

*Reaction of the Labeled **4** with Triphenylphosphine.* To a solution of radioactive sulfonyl disulfide (1 mmol) in 20 m*l* of benzene, was added a solution of triphenylphosphine (3 mmol) in 15 m*l* of ethanol at room temperature. The mixture was allowed to stand for one hour. An aliquot was analyzed by GLC. The solvent of the remaining portion of the solution was evaporated under reduced pressure, the solid was washed with cold ethanol and then recrystallized from ethanol to constant mp (162.5—163°C) and specific activity (29,855 dpm/mg).

*Reaction of the Labeled **9** with Triphenylphosphine.* Reaction was carried out by the same method as for labeled **4**. Pure triphenylphosphine sulfide obtained indicated no radioactivity.

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15) M. T. Bogert and A. Stull, "Organic Syntheses" Coll. Vol. 1, p. 220.
16) M. H. Hubacher, *ibid.*, Coll. Vol. 2, p. 455.