The Reaction of Elemental Sulfur with Organic Compounds. IV. The Reactions of *N*-Arenesulfonylsulfilimine and Sulfoximine with Sulfur and Diaryl Disulfide[1]

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(Received February 28, 1972)

The reactions of elemental sulfur and diaryl disulfide with the compounds bearing a semipolar S→N linkage were investigated. Elemental sulfur was found to react with *N*-arenesulfonylsulfilimine and sulfoximine affording the corresponding sulfide and the sulfoxide respectively. Diaryl disulfide also was found to undergo similar reactions with these compounds. In the reaction of diaryl disulfide with *N*-arenesulfonylsulfilimine, *N*,*N*-bis(arylthio)arenesulfonamide was obtained as a main product besides the corresponding sulfide. The mechanisms of these reactions are discussed.

In the course of our studies on the reactions of elemental sulfur and disulfide, we have shown that compounds bearing a semipolar linkage, such as sulfoxides,[2-4] sulfones,[2,4-6] and pyridine *N*-oxides,[7] are reduced to the corresponding sulfides or pyridines by treatment with either sulfur or diaryl disulfide. As an extension of these works we have investigated the reactions of *N*-arenesulfonylsulfilimine and sulfoximine, which are isoelectronic nitrogen analogs of sulfoxide and sulfone, respectively, with both elemental sulfur and diaryl disulfides. This paper will describe the reactions in detail.

Results and Discussion

Reactions of N-*arenesulfonylsulfilimine with Sulfur and Diaryl Disulfide.* When a mixture of one mole-equivalent diphenyl-*N*-*p*-tosylsulfilimine (I) and one atom-equivalent elemental sulfur was heated in refluxing chlorobenzene, diphenyl sulfide was obtained in *ca.* 50% yield. Similarly diphenyl disulfide also reduced I to afford diphenyl sulfide in an almost quantitative yield under a similar reaction condition. In the latter reaction, besides diphenyl sulfide, *N*,*N*-bis(phenylthio)-*p*-toluenesulfonamide (IIa) was isolated in 28% yield from the product mixture (Eq. (1)). The compound

$$\underset{\underset{\text{N-Ts}}{\downarrow}}{\text{PhSPh}} + \text{PhSSPh} \longrightarrow \text{PhSPh} + \underset{\underset{\text{Ts}}{|}}{\text{PhSNSPh}} \qquad (1)$$

I IIa

Ts = -$SO_2C_6H_4CH_3$-*p*

IIa gives the characteristic IR and NMR spectra and satisfactory analysis of carbon, hydrogen, and nitrogen. In Table 1 the results of the reactions of a few other sulfilimines with disulfides are shown. The relatively small yields of II were attributable to thermal instability of II. In fact, thermal decomposition of IIa took place readily at about 160°C to give diphenyl disulfide and dark colored substance (Eq. (2)).

$$\text{IIa} \longrightarrow \text{PhSSPh} + \text{dark colored substance} \qquad (2)$$

Reactions of Sulfoximine with Sulfur and Diaryl Disulfide. When a mixture of one mole-equivalent diphenyl sulfoximine (III) and one atom-equivalent elemental sulfur was heated at *ca.* 160°C, a dark red colored solution was obtained. From this solution diphenyl sulfoxide was separated in an almost quantitative yield through column chromatography. Diphenyl disulfide was found also to react with III to give diphenyl sulfoxide in *ca.* 86% yield. These results were tabulated in Table 2 together with the results of the reactions of methyl *p*-tolyl sulfoximine.

$$\underset{\underset{\text{NH}}{\downarrow}}{\overset{\overset{\text{O}}{\uparrow}}{\text{PhSPh}}} \xrightarrow[\text{PhSSPh}]{\text{S or}} \overset{\overset{\text{O}}{\uparrow}}{\text{PhSPh}} \qquad (3)$$

III

Mechanism of the Reactions of N-*arenesulfonylsulfilimine with Sulfur and Diaryl Disulfide.* *N*-Sulfonylsulfilimines are weak bases[8] and behave as effective nucleophiles,[9] while diaryl disulfide is susceptible to nucleophilic attack.[10] Therefore the initial step of the reaction (1) is considered to be the nucleophilic attack of the negatively charged nitrogen atom of the sulfilimine on the sulfur atom of the S–S bond, forming the sulfonium salt (IV). The subsequent step is presumed to be the homolytic cleavage of the N–S bond of IV to give radical cation of diphenyl sulfide and the amino radical (V) for the following two reasons, (A) and (B). (A) It is known that radical cations can be formed readily from such similar compounds as diaryl sulfide, thianthrene, and phenoxathiin.[11] Moreover, those sulfilimines which are presumed to give the stable radical cations such as thianthrene, phenoxathiin, and dibenzothiophene *N*-tosylsulfilimines actually were found to react with the disulfide very

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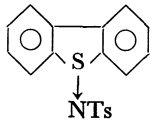
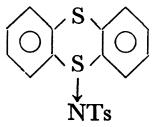
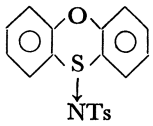
Table 1. Reactions of sulfilimines with sulfur and disulfide

Sulfilimine	Sulfur or Disulfide	Condition	Product
$Ph_2S(:NTs)$[a]	S_8	PhCl reflux, 24 hr	Ph_2S (50%)
$Ph_2S(:NTs)$	$(PhS)_2$	PhCl reflux, 35 min	Ph_2S (quantitative) $(PhS)_2NTs$ (IIa) (28%)
$Ph_2S(:NTs)$	$(p\text{-}CH_3C_6H_4S)_2$	PhCl reflux, 60 min	Ph_2S (20—30%) $(p\text{-}CH_3C_6H_4S)_2NTs$ (IIb) (14%)
$Ph_2S(:NTs)$	$(p\text{-}CH_3OC_6H_4S)_2$	PhCl reflux, 3 min	Ph_2S (quantitative) $(p\text{-}CH_3OC_6H_4S)_2NTs$ (IIc) (10%)
$Ph_2S(:NTs)$	$(p\text{-}ClC_6H_4S)_2$	PhCl reflux, 30 min	Ph_2S (quantitative) $(p\text{-}ClC_6H_4S)_2NTs$ (IId) (26%)
$Ph_2S(:NB)$[b]	$(PhS)_2$	PhCl reflux, 30 min	Ph_2S (quantitative) $(PhS)_2NB$ (IIe) (14%)
$Ph_2S(:NB)$	$(p\text{-}CH_3C_6H_4S)_2$	PhH reflux, 40 hr	Ph_2S (quantitative) $(p\text{-}CH_3C_6H_4S)_2NB$ (IIf) (21%)
	$(PhS)_2$	PhCl reflux, 20 min	IIa (16%)
	$(PhS)_2$	PhCl reflux, 15 min	IIa (21%)
	$(PhS)_2$	PhCl reflux, 13 min	IIa (36%)

a) Ts=$-SO_2C_6H_4CH_3$-*p* b) B=$-SO_2C_6H_5$

Table 2. Reactions of sulfoximines with sulfur and disulfide

Sulfoximine	Sulfur or disulfide	Condition	Product
$Ph_2S(:O)(:NH)$	S_8	neat 150—160°C, 15 min	$Ph_2S(:O)$ (quantitative)
$Ph_2S(:O)(:NH)$	$(PhS)_2$	*o*-$C_6H_4Cl_2$ reflux, 5 hr	$Ph_2S(:O)$ (86%)
p-$CH_3C_6H_4S(:O)(:NH)CH_3$	S_8	neat 150—160°C, 10 min	*p*-$CH_3C_6H_4S(:O)CH_3$ (quantitative)
p-$CH_3C_6H_4S(:O)(:NH)CH_3$	$(PhS)_2$	*o*-$C_6H_4Cl_2$ reflux, 17 hr	*p*-$CH_3C_6H_4S(:O)CH_3$ (82%)

readily (Table 1). However dialkyl or alkyl aryl sulfilimines, which would not give stable radical cation, did not react or reacted very little. These observations seem to suggest that a radical cation species is involved in the course of the reaction. (B) A strong ESR absorption was observed during the course of the reactions (1) and (2). The spectrum (Fig. 1) clearly indicates that the amino radical V was formed, and which may be considered to be a relatively stable radical species.

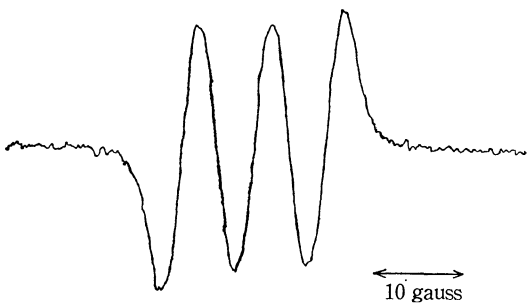
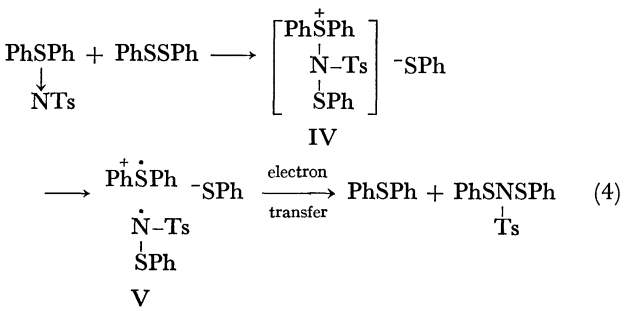


Fig. 1. ESR spectrum of ·N(SPh)$SO_2C_6H_4CH_3$-*p*.

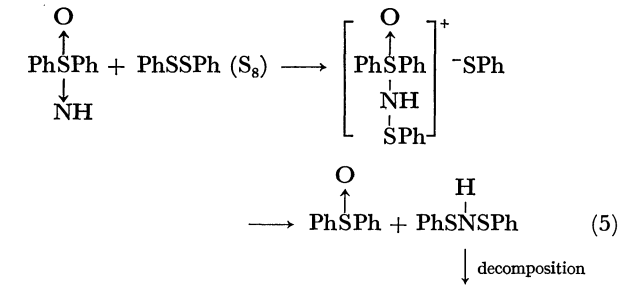
In the following scheme the most likely reaction pathway is shown.

The reaction of the sulfilimine with elemental sulfur is considered to proceed through a similar route.

Mechanism of the Reactions of Sulfoximine with Sulfur and Diphenyl Disulfide. Sulfoximine is known to be basic,[12] therefore the following ionic pathway involving the nucleophilic attack of the sulfoximine on sulfur atom of diphenyl disulfide seems to be the most conceivable (Eq. (5)).



(4)



(5)

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Experimental

Materials. Diaryl disulfides were prepared from the corresponding aryl mercaptans by iodine or nitric acid ((p-$ClC_6H_4S)_2$) oxidation. $(C_6H_5S)_2$ mp 61°C (lit, 61.5°C[13]), (p-$CH_3C_6H_4S)_2$ mp 46°C (lit, 45.5°C[14]), (p-$CH_3OC_6H_4S)_2$ mp 43—44°C (lit, 44—45°C[15]), (p-$ClC_6H_4S)_2$ mp 70—71°C (lit, 73°C[16]).

N-p-Tosylsulfilimines were prepared from the corresponding sulfides and chloramine-T according to the usual procedure.[17] *N*-Benzenesulfonylsulfilimine was prepared similarly from the corresponding sulfide and chloramine-B. (Ts=-$SO_2C_6H_4CH_3$-p, B=-$SO_2C_6H_5$). $(CH_3)_2S$(:NTs) mp 157°C (lit, 157—157.5°C,[17]) PhS(:NTs)CH_3 mp 129—130°C (lit, 129—130°C[17]), Ph_2S(:NTs) mp 112°C (lit, 111—112°C[17]), Ph_2S(:NB) mp 120°C, dibenzothiophene(:NTs) mp 169°C (Found: C, 64.06; H, 4.33; N, 3.81%. Calcd for $C_{19}H_{15}NO_2S_2$: C, 64.59; H, 4.25; N, 3.97%), thianthrene(:NTs) mp 166—167°C (Found: C, 59.58; H, 4.04; N, 3.46%. Calcd for $C_{19}H_{15}NO_2S_3$: C, 59.22; H, 3.90; N, 3.64%), phenoxathiin(:NTs) mp 169°C (Found: C, 61.38; H, 4.04; N, 3.74%. Calcd for $C_{19}H_{15}NO_3S_2$: C, 61.79; H, 4.06; N, 3.79%).

Sulfoximines were prepared by the hydrolysis of corresponding *N-p*-tosylsulfoximines with conc. sulfuric acid according to the method used by Bentley and Whitehead.[18] $Ph_2S(:O)(:NH)$ mp 102.5°C (lit, 102—102.5°C[12]), p-$CH_3C_6H_4S(:O)(:NH)CH_3$ mp 71°C (lit, 71—72°C[12]).

*The Reaction of Elemental Sulfur with Diphenyl-*N-p-*tosylsulfilimine.* Diphenyl-*N-p*-tosylsulfilimine (I), 0.71 g (0.002 mol) and 0.064 g (0.002 g atom) of sulfur was dissolved in 5 m*l* of chlorobenzene and the mixture was refluxed for about 24 hr. The product obtained was analyzed by thin layer and gas liquid chromatographies, and diphenyl sulfide was obtained as the main product. The yield of the sulfide was determined by gas liquid chromatography as *ca.* 50%.

The Reaction of Diaryl Disulfide with N-*Sulfonylsulfilimine.* Diphenyl disulfide, 0.436 g (0.002 mol) and 0.71 g (0.002 mol) of I was dissolved in 5 m*l* of chlorobenzene and refluxed for about 40 min until the color of the solution turned to dark red. After the solvent was evaporated a dark red tarry product mixture was obtained. The product was separated by column elusion chromatography through silica gel packed column, and diphenyl sulfide was obtained quantitatively with *n*-hexane as eluent, and subsequently *N,N*-bis(phenylthio)-*p*-toluenesulfonamide (IIa) was obtained with toluene as eluent. The crude IIa was recrystallized from absolute ethanol and colorless needles (mp 97.5—98°C) were obtained (0.276 g, 28%). This was the general procedure applied also for the other runs. The yields of II are shown in Table 1 while mp, IR, NMR, and CH analysis data are shown below. IIa mp 97.5—98°C. Found: C, 58.97; H, 4.49; N, 3.75%. Calcd for $C_{19}H_{17}NO_2S_3$: C, 58.91; H, 4.39; N, 3.62%. IR (cm^{-1}, KBr): ν_{SO_2} 1345 and 1160, ν_{S-N} 875. NMR ($CDCl_3$): 2.40 (s, 3H), 7.00—8.00 (m, 14H). IIb mp 94.5°C. Found: C, 60.43; H, 5.10; N, 3.33%. Calcd for $C_{21}H_{21}NO_2S_3$: C, 60.72; H, 5.06; N, 3.37%. IR (cm^{-1}, KBr): ν_{SO_2} 1345 and 1170, ν_{S-N} 835. NMR ($CDCl_3$): 2.52 (s, 6H), 2.59 (s, 3H), 7.30—8.30 (m, 12H). IIc mp 92.5°C. Found: C, 56.56; H, 4.63; N, 3.15%. Calcd for $C_{21}H_{21}NO_4S_3$: C, 56.38; H, 4.70; N, 3.13%. IR (cm^{-1}, KBr): ν_{SO_2} 1340 and 1160, ν_{S-N} 850. NMR ($CDCl_3$): 2.45 (s, 3H), 3.87 (s, 6H), 6.70—8.00 (m, 12H). IId mp 111—112°C. Found: C, 50.05; H, 3.38; N, 3.10%. Calcd for $C_{19}H_{15}Cl_2NO_2S_3$: C, 50.00; H, 3.29; N, 3.07%. IR (cm^{-1}, KBr): ν_{SO_2} 1350 and 1170, ν_{S-N} 850. NMR ($CDCl_3$): 2.55 (s, 3H), 7.20—8.10 (m, 12H), IIe mp 80.5°C. Found: C, 57.58; H, 4.05; N, 3.78%. Calcd for $C_{18}H_{15}NO_2S_3$: C, 57.91; H, 4.02; N, 3.75%. IR (cm^{-1}, KBr): ν_{SO_2} 1350 and 1170, ν_{S-N} 880. NMR ($CDCl_3$): 7.20—8.20 (m, 15H). IIf mp 92°C. Found: C, 59.51; H, 4.89; N, 3.37%. Calcd for $C_{20}H_{19}NO_2S_3$: C, 59.85; H, 4.74; N, 3.49%. IR (cm^{-1}, KBr): ν_{SO_2} 1350 and 1165, ν_{S-N} 880. NMR ($CDCl_3$): 2.31 (s, 6H), 7.00—8.00 (m, 13H).

The Reaction of Elemental Sulfur with Sulfoximine. Diphenyl sulfoximine (III), 0.217 g (0.001 mol) and 0.032 g (0.001 g atom) of sulfur was placed in a glass tube, and was heated in an oil bath maintained at *ca.* 160°C for 15 min. The red colored product was treated with column chromatography on silica gel. As a main product diphenyl sulfoxide (0.200 g) was obtained in an almost quantitative yield. The same procedure was found to be applied to the reactions of methyl *p*-tolyl sulfoximine with elemental sulfur.

The Reaction of Diphenyl Disulfide with Sulfoximine. Diphenyl disulfide, 0.218 g (0.001 mol), and diphenyl sulfoximine, 0.217 g (0.001 mol) was dissolved in 5 m*l* of *o*-dichlorobenzene and refluxed for about 5 hr. As a main product diphenyl sulfoxide was obtained in *ca.* 86% yield (0.174 g) by column elusion chromatography on silica gel. The same procedure could be applied to the reaction of methyl *p*-tolyl sulfoximine with diphenyl disulfide.

The Reaction of Diphenyl Disulfide with Dimethyl or Methyl Phenyl N-p-*Tosylsulfilimines.* The reaction of dimethyl-*N-p*-tosylsulfilimine with diphenyl disulfide did not proceed after 15 hr heating in refluxing chlorobenzene and the reactants were recovered. Methyl phenyl *N-p*-tosylsulfilimine was also treated with the disulfide under the same condition, however the reaction proceeded very little.

Thermal Decomposition of IIa. *o*-Dichlorobenzene solution of IIa was heated for *ca.* 1 hr at 160°C. From the dark colored product mixture diphenyl disulfide was obtained as a purely separable substance by chromatography through a silica gel column.

ESR Measurement. In a quartz sample tube 1 mm in diameter was placed the *o*-dichlorobenzene solution of IIa. The spectrum was recorded at 160°C with JES-ME-3X spectrometer. An identical spectrum was observed in the course of the reaction of I with diphenyl disulfide.

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