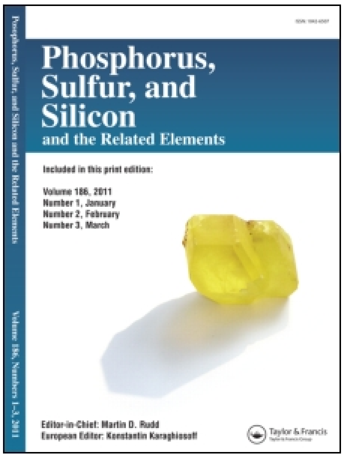

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SULFENAMIDES AND SULFINAMIDES II[1] INTERCHANGE REACTIONS OF AROMATIC SULFENAMIDES

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SULFENAMIDES AND SULFINAMIDES II[1]
INTERCHANGE REACTIONS OF AROMATIC SULFENAMIDES

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ABSTRACT

A study has been made of photocatalyzed interchange reactions of aromatic sulfenamides. The significance of the results in relation to the relative ease of S–N and S–S bond fission is discussed, together with possible mechanisms of interchange. Relevance to industrial processes is noted.

The sulfenamides ($R\,S \cdot N\,R'R''$) are a group of organosulfur compounds of interest in several different fields, but whose chemistry has been studied only intermittently. Aromatic derivatives were considered as intermediates for the preparation of medicinally important sulfonamides[2,3] and the capacity of the alkyl derivative, N,N-di-*n*-butyl hexylsulfenamide ($R = C_6H_{13}$; $R' = R'' = C_4H_9$) to inhibit the growth of *Staph. aureus* has been observed.[4]

However, sulfenamides have found their most abundant use as accelerators in the vulcanization of dry rubber, where their effect has been attributed to the activity of free radicals produced by the thermal dissociation of the S–N bond at high temperatures–above 140°.[5,6] Thus, it has been observed that butadiene-styrene copolymers acquire a vulcanized structure when heated to high temperatures in the presence of benzthiazyl sulfenamides (R = 2-benzthiazolesulfenyl) or dibenzthiazyl disulfide.[7] Considerable emphasis has been placed on the high temperature requirement.

A series of sulfenamides based on 2-mercaptobenzthiazole has shown that the kinetics of vulcanization may be regulated to a considerable degree by change in the substituents, R′R″ on the amide nitrogen. From this an attempt has been made to correlate the strength of the S–N bond and the rate of scission with initiator properties.[7]

Present work, by contrast, draws attention to the ease with which aromatic derivatives undergo photocatalyzed reactions. A particular point is that reactions occur at low temperature on exposure to diffused daylight. Exposure to direct sunlight is not required.

Results and Discussion

A qualitative demonstration of interchange of symmetrical phenyl and *p*-tolyl derivatives ($R = R' = C_6H_5$ or $CH_3C_6H_4$; $R'' = H$) photocatalyzed by diffused light at room temperature is given in Figure I. Both the forward and reverse reactions of the equation are illustrated:

$$CH_3C_6H_4S \cdot NHC_6H_4CH_3 + C_6H_5S \cdot NHC_6H_5 \rightleftharpoons$$
$$CH_3C_6H_4S \cdot NHC_6H_5 + C_6H_5S \cdot NHC_6H_4CH_3$$

It is shown that starting from a mixture of symmetrical derivatives (2) a mixture of unsymmetrical derivatives is obtained which appear on these chromatograms as one spot. Conversely, starting with the mixture of unsymmetrical derivatives (3) the two symmetrical derivatives are formed.

Similar results were obtained with an equivalent series of phenyl- and *p*-chlorophenyl derivatives.

Circular paper chromatography was employed as a means of providing fast development of chromatograms,

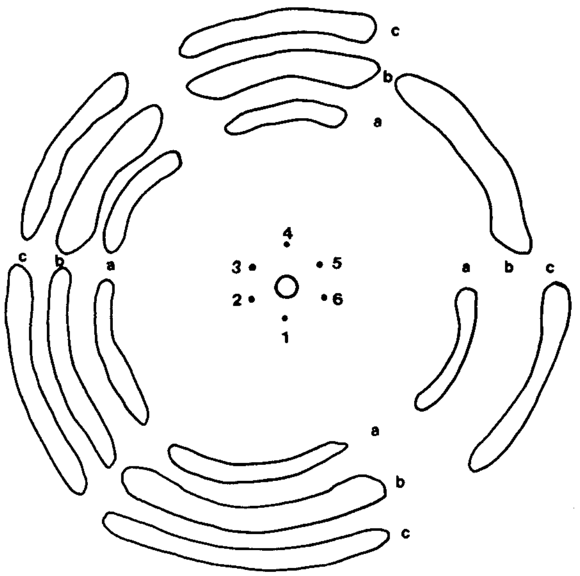


FIGURE I

Chromatography of interchange products of sulfenamides (RS·NHR′)

(*a*) R = $CH_3C_6H_4$, R′ = $H_4C_6CH_3$; (*b*) mixture of R = $CH_3C_6H_4$, R′ = C_6H_5 and R = C_6H_5, R′ = $H_4C_6CH_3$;
(*c*) R = C_6H_5, R′ = C_6H_5
1 and 4 = control mixture of (*a*) (*b*) and (*c*) prepared for chromatography.
2 = mixture of (*a*) and (*c*) exposed to light, (*b*) appear as products.
3 = mixture (*b*) exposed to light, (*a*) and (*c*) appear as products.
5 = mixture (*b*) stored in the dark.
6 = mixture (*a*) and (*c*) stored in the dark.

to a point where separation of derivatives was sufficient for areas to be cut out, for solvent extraction and spectrophotometric estimation of products.

The separations were standardized against N-phenyl benzenesulfenamide as internal standard; R_ϕ values for the derivatives are given in Table I.

It is important to note that the technique employed easily separates other materials such as disulfides from sulfenamides. The consistent R_ϕ values, color reactions with bromine and agreement of absorption spectra of leached products with reference compounds, leave no doubt about the identity of interchange products.

In addition to the ease of interchange a noteworthy feature of the reactons is that the near quantitative recovery of products indicates little loss by way of side reactions in the early stages (Table II).

It has been shown previously that photocatalyzed exchanges between aromatic disulfides in diffused light requires hot solutions.[8] No detectable products were obtained after seven days at room temperature. The easier scission of the S–N bond under similar conditions is now demonstrated, with products from the sulfenamides detectable after four hours.

This result is interesting in view of results of interchange at high temperature between benzthiazyl sulfenamides (R = 2-benzthiazylsulfenyl) and dibenzthiazyl disulfide.[7] The extent of interchange in three hours at temperatures in the range 130–140° then varied from 100% in the case of the N-cyclohexyl derivative (R′ = C_6H_{11}; R″ = H) to no interchange with the phenyl derivative (R′ = C_6H_5; R″ = H). With derivatives giving intermediate extent of exchange, 40–70%, results were then generally in accordance with activity in vulcanization processes. Interpretation of the results placed emphasis on the capacity of sulfenyl radicals derived from scission of the disulfide to act as displacing agents on the sulfenamides.

Mechanism of the Photo Reaction

If emphasis is placed on the photocatalysis, an immediate possibility is that homolysis of the S–N bond gives free radicals, the random recombination of which leads to the interchange products. The same process would account for the reversibility of the reacton and for the extent of redistribution of starting materials as mixed derivatives.

$$\begin{tikzcd}
RS\cdot NHR \arrow[r, shift left, "h\nu"] & R\dot{S} + \dot{N}HR \arrow[l, shift left] \\
R'S\cdot NHR' \arrow[r, shift left] & R'\dot{N}H + \dot{S}R' \arrow[l, shift left] \arrow[d, shift left] \\
 & RS\cdot NHR' + R'S\cdot NHR \arrow[u, shift left]
\end{tikzcd}$$

However, recombination would not be restricted to these sequences, and the probability exists for formation of disulfides, symmetrical and unsymmetrical, as well as for the formation of equivalent hydrazobenzenes from recombinations of anilino and substituted anilino radicals. In addition the formation of aminosulfides is possible.

$$R\dot{S} + \dot{N}HR \rightarrow NH_2RSR$$

Results of the chromatography show that these secondary processes do not occur in the early stages. Products were not detected, and loss of sulfenamides from the overall equilibria would also occur. The quantitative results also show that this does not happen.

Other rearrangements of sulfenamides occur under conditions to be contrasted with the mildness of those presently employed. Thus N-phenyl-*o*-nitrobenzenesulfenamide, in boiling alcoholic alkali, gives 2-mercapto-2′-nitrodiphenylamine, and in boiling aniline, 2-amino-2′-nitrodiphenylsulfide.[9]

TABLE I

Photocatalyzed Interchanges of Sulfenamides in Chloroform Solution at Room Temperature—Qualitative results

Sulfenamides—RS · NHR′				Chromatography				Color Test	
Reactants		Products		Reaction mixture		Controls		Product of	
R	R′	R	R′	Distance cm	R_ϕ*	Distance cm	R_ϕ	reaction**	Control
		C_6H_5	C_6H_5	5.9	—	5.8	—	Blue-mauve	Blue-mauve
$CH_3C_6H_4$ C_6H_5	C_6H_5 $CH_3C_6H_4$			4.7	0.80	4.7	0.81	Mauve-blue	Mauve-blue
		$CH_3C_6H_4$	$CH_3C_6H_4$	3.7	0.62	3.4	0.59	Pink-brown	Pink-brown
C_6H_5	C_6H_5			6.3	—	6.3	—	Blue-mauve	Blue-mauve
		$CH_3C_6H_4$ C_6H_5	C_6H_5 $CH_3C_6H_4$	5.3	0.84	5.3	0.84	Mauve-blue	Mauve-blue
$CH_3C_6H_4$	$CH_3C_6H_4$			4.0	0.64	4.2	0.67	Pink-brown	Pink-brown
		C_6H_5	C_6H_5	6.7	—	6.4	—	Blue-mauve	Blue-mauve
ClC_6H_4 C_6H_5	C_6H_5 ClC_6H_4			5.7	0.85	5.3	0.83	Blue-mauve	Blue-mauve
		ClC_6H_4	ClC_6H_4	5.1	0.76	4.7	0.73	Brownish-mauve	Brownish-mauve
C_6H_5	C_6H_5			6.1	—	6.4	—	Blue-mauve	Blue-mauve
		ClC_6H_4 C_6H_5	C_6H_5 ClC_6H_4	5.1	0.84	5.3	0.83	Blue-mauve	Blue-mauve
ClC_6H_4	ClC_6H_4			4.5	0.74	4.7	0.73	Brownish-mauve	Brownish-mauve

* Ratio of distance travelled by compound compared to distance travelled by N-phenyl benzenesulfenamide.

** Absorption spectra of products of reaction and of controls had a single peak maximum identical in all cases.

TABLE II

Rate of Interchange of Sulfenamide (RS · NHR′) in Diffused Light

Time of exposure (hrs)		0	4	8	10	50
Reactant mixture A						
(i) R = $CH_3C_6H_4$;	R′ = C_6H_5	50	68	55	47	45
(ii) R = C_6H_5;	R′ = $C_6H_4CH_3$	50				
Product mixture						
(i) R = $CH_3C_6H_4$;	R′ = $C_6H_4CH_3$	—	14	23	23	25
(ii) R = C_6H_5;	R′ = C_6H_5	—	14	22	24	25
Total recovery of sulfenamides (%)			96	100	95	95
Reactant mixture B						
(i) R = $CH_3C_6H_4$;	R′ = $C_6H_4CH_3$	50	—	35	28	25
(ii) R = C_6H_5;	R′ = C_6H_5	50	—	38	31	26
Product mixture						
(i) R = $CH_3C_6H_4$;	R′ = C_6H_5	—	—	23	33	42
(ii) R = C_6H_5;	R′ = $C_6H_4CH_3$	—	—			
Total recovery of sulfenamides (%)				96	92	93

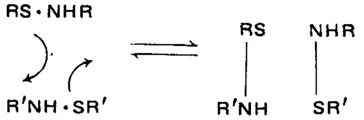
Similar results were obtained for the various mixtures of phenyl- and *p*-chlorophenyl derivatives.

The contrast in conditions must be extended to the displacement reactions with aromatic amines for which a S_N2 transition state has been proposed[10] and to other thermal rearrangements in both of which high temperatures are involved.[11,12]

The present photocatalyzed interchange results are accelerated by heat. Thus, the rate in carbon tetrachloride, requiring four hours for positive results at room temperature, was enhanced in boiling solvent to shorten the detection time to 1½ hour. Similar results were obtained with benzene as solvent.

The facility with which the S–N bond undergoes ionic scission has been used in reforming the amino group, protected as the sulfenamide derivative during peptide synthesis,[13-15] and in reaction with thiosulfate used for the estimation of sulfenamides.[10]

Following upon the deficiencies of the simple theory of radical recombination two other mechanisms may be suggested for the interchange process. The first, involving a four-point reaction would account for interchange without appearance of decomposition products, might contribute to the accelerated rate in boiling solvent.



The second, and possibly more attractive at this stage, reverts to the role of free radicals in a chain-displacement reaction, with the advantage of allowing a very gradual appearance of decomposition products. Exchanges of the following type may be proposed:

$$RS\cdot NHR \overset{h\nu}{\rightleftharpoons} R\dot{S} + \dot{N}HR$$

$$R\dot{S} + R'S\cdot NHR' \rightleftharpoons RS\cdot NHR' + R'\dot{S}$$

$$R'\dot{S} + RS\cdot NHR \rightleftharpoons R'S\cdot NHR + R\dot{S}$$

$$R'\dot{S} + \dot{N}HR \rightleftharpoons R'S\cdot NHR$$

It is of interest to note that N-cyclohexylbenzthiazole-2-sulfenamide, heated to 143° for 135 minutes, gave no electron spin resonance signal.[17] After an induction period a weak signal was obtained which gradually increased in intensity. Products such as N,N'-dicycylohexylhydrazine and 2,2'-dibenzthiazyl disulfide indicated the appearance of radical intermediates in the decomposition.

Experimental Section

Sulfenamides were prepared by condensation of the sulfenyl chloride (1 *M*) with the appropriate amine (2 *M*) in ether solution. Materials were purified to satisfactory mp and elemental analysis.

Photocatalyzed Interchange

A solution of N-phenyl benzenesulfenamide (5 mg) and N-*p*-tolyl-*p*-tolylsulfenamide (5 mg) in chloroform (1 ml) was exposed to diffused daylight. At intervals aliquots (0.01 ml) were withdrawn for analysis.

Other mixtures were similarly treated and in all cases control samples, stored in the dark, showed no evidence of interchange.

Analytical procedures

(*a*) *Qualitative*

Samples were spotted on to Whatman No. 4 paper prepared for circular chromatography. Sheets were previously impregnated with liquid paraffin by drawing through a solution (3% v/v) in light petroleum (bp 40–60°) and allowing solvent to evaporate from the suspended paper.

Chromatograms were developed using methanol/water, 2:1–time required was generally about 60–75 min. Sulfenamides were located by exposure to bromine vapour[18] and identity established by reference to standards on the same chromatogram.

(*b*) *Quantitative*

Chromatograms from measured aliquots were developed on zinc carbonate-fluorescein papers[19] further treated as above. Derivatives, located as mauve bands under ultraviolet light were removed from the cut section of the paper by extraction with spectroscopic ethanol (4 ml) and estimated by measuring absorbance at 247.5 nm or other peak wave length. Solutions obey Beer's Law over the range 1–10 μg/ml.

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