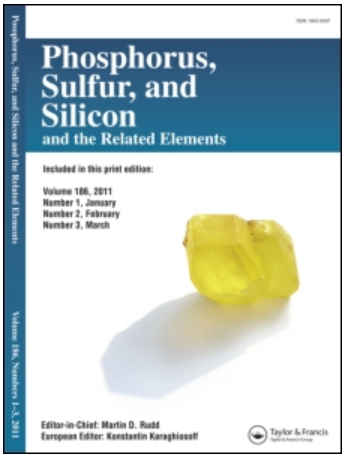

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Sulfenamides and Sulfinamides IX Exchange Reactions of Aryl Sulfinamides

Victor Clarke[a]; Edward R. Cole[a]
[a] School of Chemistry, The University of New South Wales, Kensington, N.S.W., Australia

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SULFENAMIDES AND SULFINAMIDES IX EXCHANGE REACTIONS OF ARYL SULFINAMIDES

VICTOR CLARKE and EDWARD R. COLE
School of Chemistry, The University of New South Wales, P.O. Box 1, Kensington-N.S.W., 2033 Australia

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A polar mechanism, associated with hydrogen bonding and emphasizing the ease of fission of the S—N bond, is proposed for the exchange reactions of aryl sulfinamides at ambient temperature. The mechanism starting with simple mixtures of sulfinamides extends to unlike combinations of sulfinamides with sulfenamides or amines. Results have bearing on the racemization of optically active sulfinamides.

Key words: Sulfinamides; sulfenamides; nucleophiles; racemization; exchange reactions; sulfur-nitrogen bond fission.

INTRODUCTION

Previous discussions on interchanges of aryl sulfenamides noted the ease of fission of the S—N bond.[1] Irrespective of whether an initial mixture of two symmetrical derivatives, RS—NHR/R'S—NHR', or of two unsymmetrical derivatives, RS—NHR'/R'S—NHR was employed, at low temperature the systems came to an equilibrium mixture containing four derivatives, two symmetrical and two unsymmetrical products, without diversion to other products such as disulfides or (hydr)azobenzenes that might have been expected from recombinations of a free radical mechanism. However although a four center mechanism was favored a radical chain process was not ruled out. The present discussion examines the role of the more polar sulfinyl group in similar exchange reactions of sulfinamides.

RESULTS AND DISCUSSION

Protonation of the sulfinyl group thereby rendering the sulfur atom more open to nucleophilic attack has been accepted as a contributing factor to several reactions of sulfoxides.[2,3] It is now suggested that interchanges of sulfinamides are prompted in a similar manner.

Exchanges between aryl sulfinamides are reported in Table I. The reaction time required for detection of new derivatives, at the temperature and concentrations employed was generally about 40 min with no other material appearing up to 16 hr.

Formation of the same product mixture from appropriate combinations of symmetrical and unsymmetrical derivatives clearly shows the reversibility of the reaction.

Comparison of the conditions presently employed with those for similar reactions of aryl disulfides and sulfenamides illustrated the more ready fission of the S(O)—N

TABLE I

Exchange reactions between aryl sulfinamides, X—C_6H_4SO—NHC_6H_4—Y

Reactants		Products		Chromatography	
X	Y	X	Y	Reaction	Controls
CH_3	CH_3			4.0[a]	4.0
		CH_3	H		3.1
		H	CH_3	3.3	3.4
H	H			2.6	2.6
		CH_3	CH_3	3.9	4.0
CH_3	H			3.2	3.1
H	CH_3				3.4
		H	H	2.6	2.6
CH_3	H			6.8[b]	6.7
		H	H	5.7	5.8
		CH_3	OCH_3	4.2	
H	OCH_3			3.5	3.5
CH_3	CH_3			7.7	7.7
		H	CH_3	6.9	6.9
		CH_3	OCH_3	4.2	
H	OCH_3			3.6	3.5

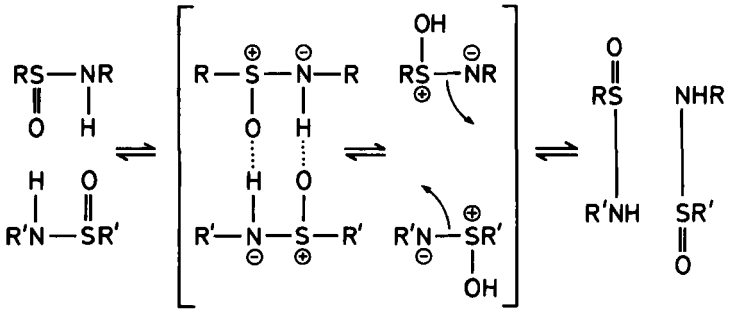
Results for this series and those for other analyses reported as distances travelled-cm.

[a]2 Rises.

[b]4 Rises.

bond. Exchange between disulfides exposed to dull light required heated solutions,[4] whereas interaction between sulfenamides similarly exposed, proceeded at room temperature.[1] In the sulfinamide series fission occurred at room temperature without need for a photo effect. The suggestion then arises that intermolecular protonation of the sulfinyl group leading to polarization of the sulfur atom provides a basis for the interchange (Scheme I).

Formation of the new S—N bonds as shown, represents an oversimplification of the process. In this mechanism it is probable that the new bond formation occurs through an approach of the amide nitrogen, acting as a nucleophile, to the alternate



SCHEME I

sulfur atom, accompanied by a compensating shift from the original bond. Deprotonation of the sulfinyl group then leads to the rearranged products.

The reversibility of the reaction is shown by the appearance of the same products irrespective of whether the exchanges concern mixtures of symmetrical or unsymmetrical derivatives.

Although hydrogen bonding in the sulfinamides was expected, assisted by the low pKa values,[5] its extent as a driving force for the exchanges was shown by cryoscopic and infrared examinations of solutions. Assuming dimer formation the calculated amounts of monomer and dimer from the cryoscopic results are shown in Table II.

In contrast molecular weight results with N-methyl-N-phenyl benzenesulfinamide were within 1.5% of theoretical.

The order of these results was confirmed by determinations of infrared absorptions of the N—H band. In a Nujol mull N-phenylbenzenesulfinamide gave only one band at 3150 cm^{-1} but changes in the spectrum in carbon tetrachloride solution reflect the typical behavior of an associated molecule. At maximum concentration possible (0.015 M) two peaks appear at 3160 cm^{-1} and at 3320 cm^{-1} representing the associated and unassociated molecules, respectively. On dilution the peak at 3160 cm^{-1} decreased and that at 3320 cm^{-1} increased (Table III).

The persistence at high dilution of absorption due to hydrogen bonding should be noted. Hydrogen bonding capacity of oxygenated derivatives of sulfur extends to the sulfonamides for which infrared measurements[6] coupled with dielectric measurements[7] have provided evidence.

With a mixture of monomer and dimer it is possible to formulate on similar principles, attack by a molecule of monomer on the dimer, in what would be

TABLE II

Dimer formation in solutions of N-phenylbenzenesulfinamide[a]

Concentration, M	Apparent molecular weight	% Monomer	% Dimer
0.02	246	86	14
0.05	321	52	48
0.07	346	37	63

[a]Solvent—benzene

TABLE III

Association of N-phenylbenzenesulfinamide in carbon tetrachloride solution

Concentration, M	Absorbances		% Monomer[a]	% Dimer
	3160 cm^{-1}	3320 cm^{-1}		
0.045	0.32	0.16	56	44
0.0075	0.10	0.24	86	14
0.0015	0.06	0.27	96	4

[a]Calculated from the ratio a_c/a where a_c is absorbance at concentration c; a is absorbance at infinite dilution.

regarded as a bimolecular reaction, with regeneration of a molecule of monomer. The first process as a four center reaction might be favored by analogy with sulfenamides allowing for faster reaction promoted by greater polarity in the system. The polar nature of the reaction, with its absence of free radical species available for recombinations, explains the absences of disulfides and (hydr)azobenzenes from the products.

The concept of a four center reaction in a bonded dimer may have connotations for the racemization of optically active sulfinamides. Fission of the original S—N bonds and alternative recombinations by this method may be suggested applicable to the same sulfinamide. In this event the exchange could be regarded as a self catalyzed reaction. Racemization has previously been discussed as a high temperature free radical reaction.[8] Nevertheless it now seems that a thermally accelerated interchange of the type illustrated, occurring incidental to the heating, could contribute to the process. Intermolecular hydrogen bonding is not a marked structural feature of sulfenamides. However exchanges of like character occurred between sulfinamide/sulfenamide mixtures as rapidly as between sulfinamides themselves. Products were detectable after 40 min and were stable overnight (Table IV).

TABLE IV

Exchange reactions between sulfinamides and sulfenamides ($XC_6H_4SO—NHC_6H_6Y$ and $X'C_6H_4S—NHC_6H_4Y'$)

	Reactants				Products				Chromatography	
	X	Y	X′	Y′	X	Y	X′	Y′	Reaction	Controls
	H	CH_3							3.3	3.4
					H	H				2.7
(i)							CH_3	CH_3	14.5	14.6
			CH_3	H					13.8	13.7
	H	CH_3							3.4	3.2
					H	H			2.7	2.6
(ii)							CH_3	CH_3	13.6	13.5
			CH_3	H					13.1	13.1
	CH_3	H							3.3	3.4
					CH_3	CH_3			3.9	4.0
(iii)						H	H	13.6	13.7	
			H	CH_3					13.0	13.0

Reaction times (i)—49 min; (ii), (iii)—16 hr.

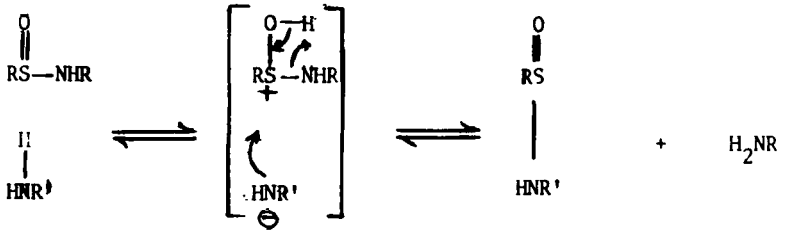
TABLE V

Displacement reactions on sulfinamides with amine

Reactants	Products	Chromatography	
		Reaction	Controls
	$CH_3C_6H_4SO—NHC_6H_4CH_3$	4.0	3.9
$CH_3C_6H_4SO—NHC_6H_5$		3.1	3.0
$CH_3C_6H_4NH_2$		11.1	11.3
	$C_6H_5NH_2$	10.2	10.3
$C_6H_5SO—NHC_6H_4CH_3$		3.4	3.3
	$C_6H_5SO—NHC_6H_5$	2.7	2.7
	$CH_3C_6H_4NH_2$	11.4	11.3
$C_6H_5NH_2$		10.3	10.3

The responses of sulfinamides to polar conditions was also shown by the rate of displacement of the nitrogen moiety at room temperature in reacting with an alternative amine. Products were detectable much more rapidly than in any other reaction. In this combination polarization of the sulfur atom is coupled with greater basicity in the displacing amine. Reactions of this type offer a method of preparing several derivatives from a master material (Table V).

A simple mechanism, in terms of the principles previously discussed, is shown.



SCHEME II

EXPERIMENTAL

Sulfenamides and sulfinamides were prepared by condensation of a sulfenyl or sulfinyl chloride with the required amine and recrystallized to satisfactory elemental analysis, melting point and single spot on chromatograms as previously described in this series.[5,9]

Thin-layer chromatography was performed on kieselguhr G plates (0.5 mm) impregnated with phenoxyethanol using a solution in acetone (3% v/v), developed with *n*-heptane saturated with phenoxyethanol. Impregnation with stronger solutions of phenoxyethanol reduced the efficiency of separations. Spots were located by three methods—(i) exposure to bromine vapor, (ii) exposure to hydrochloric acid fumes followed by spraying with starch/iodide and (iii) spraying with *p*-dimethylaminobenzaldehyde solution followed by exposure to hydrochloric acid fumes. Results are reported as distances moved by materials after two solvent rinses.

Infrared spectra were measured on Perkin-Elmer 337 and 137 spectrometers.

Exchanges. In a typical experiment N-phenylbenzenesulfinamide (50 mg) and N-*p*-methylphenyl-*p*-methylbenzenesulfinamide (50 mg) in chloroform (20 ml) were allowed to stand at room temperature. Aliquots were withdrawn at intervals for thin layer chromatography until new spots were observed. Sulfinamide/sulfenamide and sulfinamide/amine exchanges were performed in a similar manner. Results are reported in the various tables. Results from determinations of "apparent" molecular weight in benzene solution are shown in Table VI.

TABLE VI

Cryoscopic determinations of "apparent molecular weight" of sulfinamides, $C_6H_5SO—NXC_6H_5$

Compound X	Sulfinamide weight, g	F·pt depression, °C	Molecular weight	
			Apparent	Theory
Naphthalene	0.1044	0.191	129	128
H	0.1085	0.105	246	217
H	0.2659	0.195	321	217
H	0.4142	0.275	353	217
CH_3	0.1091	0.109	234	231
CH_3	0.2314	0.231	233	231

Solvent: benzene, 25 ml.

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