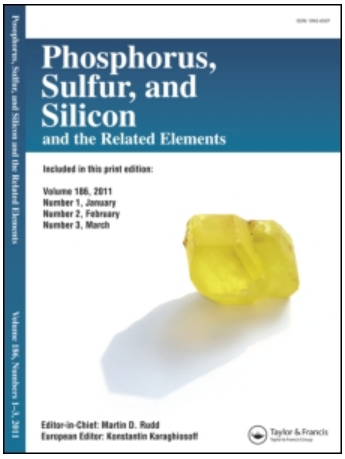

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AMINE EXCHANGE REACTIONS: I. THE SYNTHESIS OF *N*-ARYLSULFENAMIDES BY TRANSAMINATION

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Arylamine salts have been used to displace ammonia and other amines that have a higher pKa than the arylamines from the S–N bond of sulfenamides derived from mercaptobenzothiazole and thiocarbamate. The *N*-arylsulfenamides obtained by this method may be obtained only with difficulty or not at all by other methods. A mechanism for the exchange is proposed. The mechanism emphasizes the role of proton transfer in driving the reaction to completion.

1 INTRODUCTION

The sulfenamides derived from mercaptobenzothiazole are well established as accelerators for commercial rubber vulcanization processes. The most widely used derivatives are the *N*-alkyl and *N*-cycloalkyl compounds. These derivatives may be readily synthesized by several methods. These methods have been summarized.[1]

Although the various alkyl and cycloalkyl derivatives have enjoyed a wide acceptance in the rubber industry, they are not without some undesirable side effects. This is especially true when they are used in vulcanization formulations that also include antioxidants and antiozonants that tend to induce premature vulcanization, an undesirable condition known as scorch. It was reasoned that the scorchy conditions could be alleviated if *N*-arylbenzothiazole-2-sulfenamides could be used instead of the *N*-alkyl derivatives. Unfortunately, the method of oxidative condensation that is used to synthesize the latter compounds usually fails completely with the aryl derivatives. The aromatic ring undergoes oxidation in the process and virtually none of the desired product is obtained.

Some limited success was realized when the oxidative condensation reaction was carried out at low temperature.[2] The reaction that was eventually successful in giving the desired product in excellent yield was an amine exchange reaction using the arylamine salt. The reaction was virtually quantitative and proceeded with arylamines possessing a wide variety of functional groups on the aromatic ring.

The reaction was extended to thiocarbamates with similar results.

2 DISCUSSION

2.1 *Comparison of Exchange Methods*

In general, amine exchange reactions or transaminations are well known and have a long history of application in organic chemistry. They have never been as widely applied as ester exchange or transesterification, which serves as the basis for many important industrial processes. The classical method of amine exchange involves the displacement of an amine of relatively weak basicity by another of stronger basicity. The reaction proceeds because of favourable thermodynamic conditions and the equilibrium is displaced by removing the weaker amine from the reaction mixture. The success of the reaction requires that the amine being displaced be more volatile than the displacing amine. A variation of this technique, is to take advantage of mass action effects and use an excess of the displacing amine. In this case, amines of similar basicity may be exchanged.[3]

These classical methods of transamination have been applied to sulfenamide synthesis. In certain instances they have become the preferred method, especially when the alkylamine has a long chain that renders it insoluble in aqueous solution. These reactions are very limited and sometimes fail completely, even under forcing conditions.[4]

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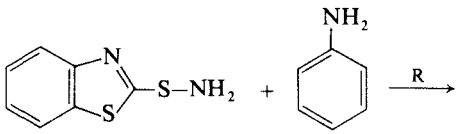
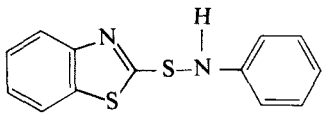
The unsubstituted 2-amino derivative of mercaptobenzothiazole (MBT) has been used in the classical exchange process and the ammonia formed by displacement is readily removed from the reaction mixture. This technique generally fails with aromatic amines as they are weaker bases than ammonia. It can be made to work, however, by providing an acceptor for the relatively small amount of ammonia that is present in the equilibrium process. The reaction is thus forced to completion by removing the ammonia as it is formed. This process is described in (**1**) below, where either a cation resin or molecular sieves may be used as acceptor for the displaced ammonia.

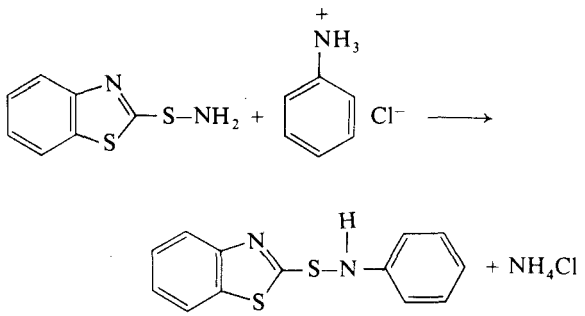


R = cation resin



$+ NH_3$ (R) (**1**)

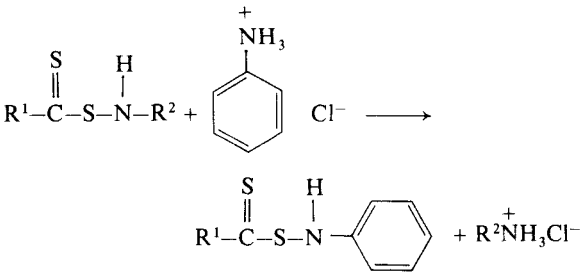
The reaction as carried out in this manner is slow and requires 24–48 hrs at reflux in benzene to go to completion. Further, the requirement that the amine being displaced be more volatile than the displacing amine is very restrictive as pointed out earlier. In searching for ways to overcome these drawbacks, it was found that the reaction proceeded rapidly to completion if the acid salt of the amine was used according to (**2**), below.[5]



(**2**)

The displaced amine can be an alkylamine as well as ammonia. The aromatic amines used for displacement covered a wide range of pK_a values. Acid is required for the reaction as a catalyst as well as a stoichiometric reactant. In all cases, the exchange is facile and proceeds to completion to give a virtually quantitative yield of the desired product. An additional advantage is that the salt of the displaced amine is water soluble and is readily separated from the sulfenamide.

Thiocarbamylsulfenamides were also found to undergo exchange, according to (**3**) below.[6,7] In all cases, the aryl group was found to impart added stability to the sulfenamide and to confer desirable properties for use in rubber vulcanization systems.[8]



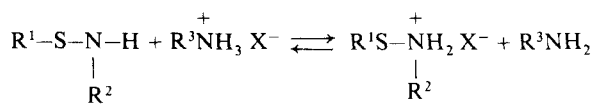
(**3**)

The elemental analyses and melting points for all of the sulfenamides obtained by the exchange process are given in Tables I and II. Satisfactory nmr and ir spectra were obtained for each of the compounds.

2.2 *Proposed Reaction Mechanism*

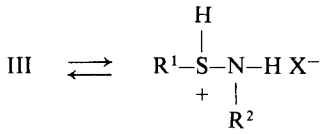
Although there have been other syntheses of sulfenamides carried out in recent years,[4,9] none of these have been acid catalyzed. The reaction described herein is characterized by (1) acid catalysis, (2) one-to-one stoichiometry with respect to acid, and (3) a lower pK_a for the displacing amine relative to that of the amine being displaced. On the basis of these facts and by analogy with ester exchange reactions[10] and carbonyl group exchange reactions,[11] the following mechanism is proposed.

(**4**) Intermolecular proton exchange



I II III IV

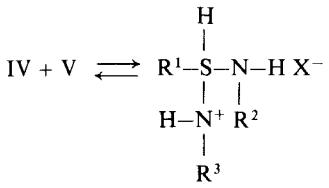
(5) Intramolecular N ⟶ S proton transfer



III ⇌ $R^1-S-N-H\ X^-$ (H on N; R^2 on N)

V

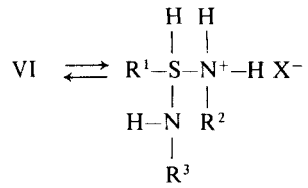
(6) Formation of tetracoordinate intermediate



IV + V ⇌ $R^1-S-N-H\ X^-$ (H on N; $H-N^+\ R^2$; R^3)

VI

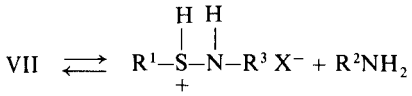
(7) Intramolecular proton transfer



VI ⇌ $R^1-S-N^+-H\ X^-$ (H on S and N; $H-N\ R^2$; R^3)

VII

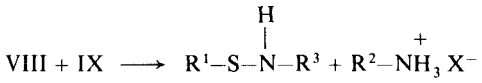
(8) Elimination of stronger amine



VII ⇌ $R^1-S-N-R^3\ X^- + R^2NH_2$ (H on S and N)

VIII IX

(9) Intermolecular proton transfer



VIII + IX ⟶ $R^1-S-N-R^3 + R^2-NH_3\ X^-$ (H on N)

X XI

The mechanism as presented here is suggested as a working hypothesis. Much more work is needed and contemplated in order to substantiate the various steps presented here.

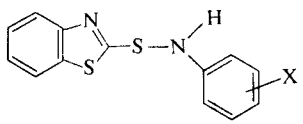
EXPERIMENTAL

Reagent Chemicals. The amines and amine hydrochlorides used were all commercial products and were used without further treatment. Benzothiazole-2-sulfenamide was synthesized by a standard literature procedure[12] as were the dialkylthiocarbamates.[13] *N-t*-Butylbenzothiazole-2-sulfenamide was a commercial sample that was purified before use by recrystallization.

N-Arylbenzothiazole-2-sulfenamides. The following procedure is illustrative. Benzothiazole-2-sulfenamide (2.71 g, 0.015 mole) was dissolved in methanol (*ca.* 25 ml). Aniline hydrochloride

TABLE I

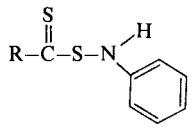
Elemental analyses annd melting points of *N*-aryl benzothiazole-2-sulfenamides



X	M.P.	Calculated for			Found		
		C	H	N	C	H	N
H	128–128	60.43	3.90	10.84	50.21	4.04	10.76
o-CH_3	115–116	61.73	4.44	10.28	62.05	4.45	10.04
p-CH_3	138–139	61.73	4.44	10.28	61.98	4.51	10.50
o-OCH_3	150–152	58.29	4.20	9.72	58.64	4.14	9.44
m-OCH_3	112–114	58.29	4.20	9.72	58.35	4.20	9.56
p-OCH_3	122–123	58.29	4.20	9.72	58.50	4.23	9.47
o-NO_2	148–153	51.30	3.31	13.81	50.77	2.90	13.50
p-NO_2	169–171	51.30	3.31	13.81	51.77	3.09	13.88
p-Br	148–149	46.30	2.69	8.31	47.11	2.91	8.50

TABLE II

Elemental analyses and melting points of *N*-aryl thiocarbamyl sulfenamides



R	M.P.	Calculated			Found		
		C	H	S	C	H	S
$(CH_3)_2N$	82–84	50.31	5.83	31.10	50.91	5.70	30.20
$(C_2H_5)_2N$	93–95	54.96	6.70	26.68	54.83	6.81	26.80
$O<^{CH_2CH_2}_{CH_2CH_2}>N$	133–135	51.79	5.64	25.80	51.94	5.55	25.20

(1.9 g, 0.015 mole) was also dissolved in methanol and added to the above solution. The methanol was removed by rotary evaporation to leave a white solid residue. The solid was taken up in ether (*ca.* 100 ml) and washed with 3-100 ml portions of water to remove ammonium chloride. The ether solution was dried over $MgSO_4$ and solvent removed to give a 90–100% recovery of the sulfenamide.

Similar results were obtained when *N-t*-butylbenzothiazole-2-sulfenamide was used as a reactant, along with the other arylamine hydrochlorides. Analytical samples were prepared by recrystallization from an appropriate solvent or by treating the material on a chromatographic column. The melting points and elemental analyses for these compounds are given in Table I.

N,N-Dialkylthiocarbamyl-N¹-arylsulfenamides. A methanolic solution containing equimolar quantities of an *N,N*-dialkylthiocarbamyl-*N*¹-cyclohexylsulfenamide and amiline hydrochloride was stirred at room temperature, whereupon the *N*-aryl derivative crystallized from solution. The yield of crystalline material obtained as a first crop amounted to ca. 70% of theory. Additional *N*-arylsulfenamide was obtained by workup of the mother liquors. The melting points and elemental analyses for all of these compounds are given in Table II.

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