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The Reaction of *N*-Phenylsulfonyl Thione *S*-Imide with Acyl Halides[1)]

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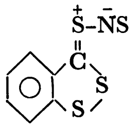
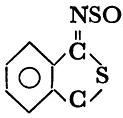
Synopsis. Thiocarbonyl *S*-imide of 1,2-dithiole-3-thione reacted with various acyl halides producing the corresponding *N*-phenylsulfonyl-1,2-benzodithiole-3-imine and elemental sulfur. The reaction was found to proceed *via* initial acylation on the nitrogen of the imide and was essentially acyl halide-catalyzed with regard to rearrangement.

The authors have shown previously that the *N*-phenylsulfonyl thione *S*-imide(I) underwent rearrangement accompanied by desulfurization producing product(II) either by heating in neat[3)] or by treating with various nucleophiles such as amines[4)] and mercaptans.[5)]

We have now extended the investigation to the reaction of I with several electrophilic reagents and it has been found that the *S*-imide(I) produces the corresponding *N*-phenylsulfonyl imine(II) in good yield upon treatment with a variety of acyl halides. This paper describes a detailed account of the reaction.



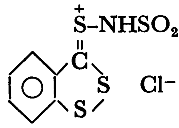
(I)



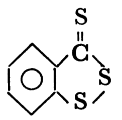
(II)

Results and Discussion

When the imide(I) was allowed to react with an equimolar amount of trichloroacetyl chloride at room temperature in CH_2Cl_2, yellowish elemental sulfur followed by a trace of hydrochloride(III) of the imide(I) precipitated from the solution within minutes, and then the imine(II) was isolated in a 75% yield along with a small amount of the reduction product, benzotrithione(IV), by preparative layer chromatography. The hydrochloride(III) seems to be produced by the reaction of imide(I) with the hydrochloric acid inevitably present or generated in normal reacting systems containing acyl halides.



(III)



(IV)

As is seen from Table 1, only less than one-half an equimolar amount of trichloroacetyl chloride is sufficient to complete the reaction. This indicates clearly that the reaction is essentially acyl halide-catalyzed with regard to the rearrangement reaction, where the halide is utilized repeatedly during the reaction. In fact, after completion of the reaction with an equimolar amount of trichloroacetyl chloride, 75% of the halide remained unchanged.

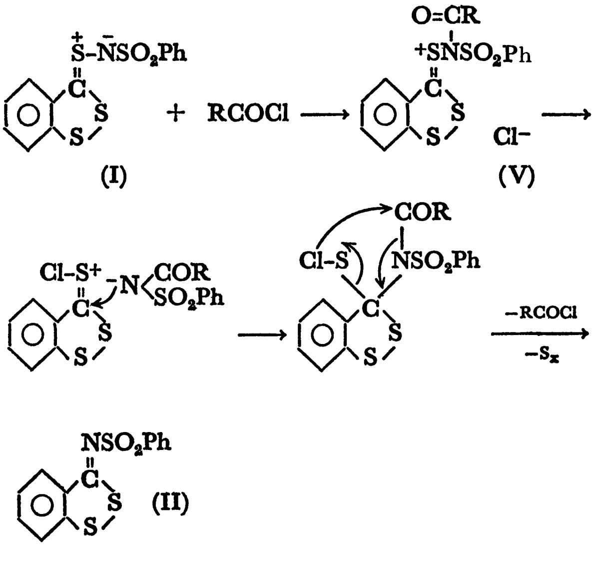
The reactions with aroyl chlorides were likewise found to produce both the rearranged product and a trace amount of benzotrithione. The reaction times required for benzoyl chlorides bearing electron-donating substituents are longer than those with electron-capturing substituents. This implies that acylation of the nitrogen atom of the imide(I), leading to an intermediate(V), is the key step in the reaction. Meanwhile, both thionyl and sulfinyl chlorides can also react in a similar manner to produce the imine(II).

Table 1. Acyl halide-catalyzed rearrangement of I in CH_2Cl_2 at room temperature

Halide	Mole ratio[a)]	Reaction time[b)]	Isolated yield, %	
			II	IV
O_2N-C_6H_4-COCl	1.0	1 hr	75	trace
Cl-C_6H_4-COCl	5.0	1 hr	70	5
C_6H_5-COCl	5.0	2 hr	80	g)
MeO-C_6H_4COCl	5.0	10 hr	40	g)
CCl_3COCl[c)]	1.0	5 min	72	5
CCl_3COCl	0.5	10 min	68	8
CCl_3COCl	0.3	10 min	89	5
CCl_3COCl[d)]	1.0	10 min	43	15
CCl_3COCl[e)]	1.0	5 min	84	10
$SOCl_2$	1.2	5 min	62	10
O_2N-C_6H_4-SOCl	1.0	10 min	26[f)]	5

a) Ratio of I to acyl halide. b) Required time for the change in color of the solution from red to yellow. c) The amount of the remaining halide was determined as 75% using the IR absorption band at 1795 cm^{-1} due to the carbonyl group in trichloroacetyl chloride. d) For *p*-nitrophenylsulfonyl thione *S*-imide. e) for *p*-methylphenylsulfonyl thione *S*-imide. f) The low yield was mainly due to the formation of III. g) No yield was determined.

Thus, based on these results and intuitive considerations, the outline of the reaction scheme may be written as follows:



Experimental

A typical run is as follows. To *S*-imide(I) (339 mg, 1 mmol) in CH_2Cl_2 well-dried over $CaCl_2$ one equivalent of trichloroacetyl chloride dissolved in the same solvent was added at room temperature. After 5 min the solution turned yellow. The solvent was evaporated under reduced pressure and then the residue was separated b preparative tlc using benzene as the eluent. The yields thus obtained are listed in Table 1.

References

1) Derivatives of 1,2-Dithiole-3-thiones. Part IX.

2) Present address: Department of Chemistry, Tsukuba University, Sakura-mura, Niihari-gun, Ibaraki-ken 300-31.

3) Part II. S. Tamagaki, K. Sakaki, and S. Oae, This Bulletin, **46**, 2608 (1973).

4) Part VII. S. Tamagaki, K. Sakaki, and S. Oae, *ibid.*, **47**, 3084, (1974).

5) Part X. Submitted for publication to this Bulletin.