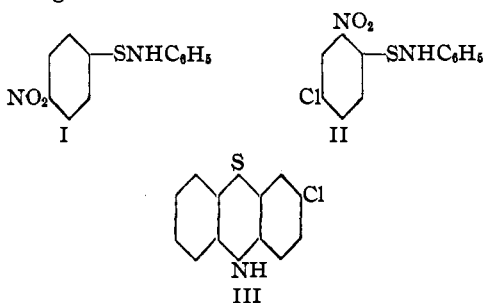


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

## The Molecular Rearrangement of Sulfenamidides in Alkaline Solution. IV

BY MAURICE L. MOORE<sup>1</sup> AND TREAT B. JOHNSON

In extending our study of the molecular rearrangement of sulfenamidides in alcoholic alkaline solution, it was interesting to find that the *p*-nitro substituted derivatives of these compounds, I, do not undergo rearrangement to give mercaptodiphenylamine compounds when heated in alcoholic sodium hydroxide solution. This is all the more interesting in view of the fact that Smiles<sup>2</sup> has not, thus far, reported the molecular rearrangement of similar derivatives in the *o*-amino sulfide series, whereas he has done so in the *o*-hydroxysulfones.<sup>3</sup> Thus, 4-nitrophenylsulfen-*o*-chloroanilide, 4-nitrophenylsulfen-*o*-toluidide and 4-nitrophenylsulfenamidide did not undergo structural changes when digested in alcoholic sodium hydroxide solution for three hours. A small amount of the corresponding disulfide was isolated from the reaction mixture, but by far the chief proportion of the recovered product was the unaltered sulfenamidide used as the starting material. Thus, it appears from our results that the substitution of a nitro group in the *p*-position does not give enough activity to the carbon atom at the sulfur linkage to produce a rearrangement as is the case when the nitro group occupies an *o*-position. The latter type of compounds undergo rearrangement upon heating to give the corresponding amino sulfides.



A rearrangement of the 2,4-nitrochlorophenyl derivatives II was observed to occur in the usual manner to give the respective mercaptodiphenylamines. Thus, 2,4-nitrochlorophenylsulfenamidide gave the sodium salt of 2-mercaptophenyl-2',4'-nitrochlorophenylamine when refluxed in alcoholic

sodium hydroxide solution for three hours. This compound was isolated and identified by conversion into its thiomethyl ether. 2-Nitrophenylsulfen-*o*-chloroanilide, 2,4-nitrochlorophenylsulfen-*o*-toluidide and 2,4-nitrochlorophenylsulfen-*o*-chloroanilide underwent a corresponding rearrangement when treated in like manner. In each case the sodium salt of the mercapto compound was isolated as a brilliant red crystalline solid, which was converted into the corresponding thiomethyl ether for characterization by the action of methyl iodide.

This isolation of the sodium salt and the thiomethyl ether by the rearrangement of the 2,4-nitrochlorophenyl derivatives is somewhat in contradiction to the results of Smiles<sup>2c</sup> with the 2,4-nitrochlorophenyl derivatives of the *o*-aminosulfides, as he was unable to isolate the free mercapto-diphenylamine or the thiomethyl ether because of the rapid formation of a thiazine compound III. The latter formation involves the splitting out of nitrous acid.

## Experimental Part

**2,4 - Nitrochlorophenylsulfen - *o* - chloroanilide.**—2,4-Nitrochlorophenylsulfur chloride (25 g.) gave 20 g. of an orange-red glistening crystalline material when treated with *o*-chloroaniline (28 g.) under the usual conditions. It was easily crystallized from boiling alcohol, m. p. 112°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>SCl<sub>2</sub>: N, 8.89; S, 10.16; Cl, 22.54. Found: N, 8.89, 8.76; S, 10.41, 10.18; Cl, 22.21, 22.40.

**Procedure for Rearrangement.**—The necessary sulfenamidide (5 g.) was placed in alcohol (25 ml.) containing 20% sodium hydroxide (5 ml.) according to the procedure previously reported<sup>4</sup> and refluxed for three hours. The reaction product was isolated and purified as the sodium salt.

**Methylation of the Mercaptan.**—The sodium salt from the above operation (5 g.) was dissolved in alcohol (15–25 ml.), refluxed for a short time (fifteen to sixty minutes) with an excess of methyl iodide (3 ml.) and worked up in the usual manner. In certain instances it was found that the thiomethyl ether would separate out of the hot alcohol after refluxing for varying lengths of time (fifteen to sixty minutes).

In Table I are recorded the results of the rearrangement of different sulfenamidides under the influence of alkali.

## Summary

Digestion of *p*-nitrophenyl derivatives of sulfenamidides in alcoholic sodium hydroxide solution

(1) A. Homer Smith Research Fellow, 1935–1936.

(2) (a) Evans and Smiles, *J. Chem. Soc.*, 181 (1935); (b) Wight and Smiles, *ibid.*, 340 (1935); (c) Evans and Smiles, *ibid.*, 1283 (1935).

(3) Kent and Smiles, *ibid.*, 422 (1934).

(4) Moore and Johnson, *THIS JOURNAL*, 57, 1517, 2234 (1935).

TABLE I

Compounds	Yield, %	M. p., °C.	Nitrogen, %			Sulfur, %		Chlorine, %				
			Calcd.	Found	Found	Calcd.	Found	Calcd.	Found			
4-Nitrophenylsulfen-			No rearrangement									
			No rearrangement									
			No rearrangement									
2,4-Nitrochlorophenylsulfen-	Na salt of mercapto-diphenylamine derivative	85				10.58	10.53		11.73	11.64		
	Thiomethyl ether of mercapto-diphenylamine derivative	95				10.11	10.19	10.03	11.22	11.23		
	Thiomethyl ether of mercapto-diphenylamine derivative	90				9.50	9.27	9.42	21.07	21.41	21.30	
	Thiomethyl ether of mercapto-diphenylamine derivative	85	135-136	9.51	9.33	9.20	10.87	10.56	10.67	12.06	12.34	12.21
2-Nitrophenylsulfen-o-chloranilide <sup>a</sup>	Na salt of mercapto-diphenylamine derivative	80	164-165	9.08	9.13	9.04	10.37	10.10	10.25	11.51	11.70	11.62
	Thiomethyl ether of diphenylamine derivative	80	158-158.5	8.51	8.30	8.44	9.73	9.88	9.82	21.58	21.77	21.65
	Thiomethyl ether of diphenylamine derivative	90					10.58	10.60	10.42	11.73	11.61	11.55
	Thiomethyl ether of diphenylamine derivative	84	144.5-145	9.51	9.61	9.59	10.87	10.90	10.96	12.06	12.05	12.12

<sup>a</sup> For the preparation of these compounds, see THIS JOURNAL, 58, 1091 (1936).

failed to bring about a rearrangement to their corresponding *o*-mercaptodiphenyl amines. The 2,4-nitrochlorophenyl derivatives, however, undergo a rearrangement to *o*-mercaptodiphenylamines when so treated, and it was possible to

isolate the sodium salt as well as the thiomethyl ether without cyclization to thiazine compounds. The study of sulfenamidides will be continued in this Laboratory.

NEW HAVEN, CONN.

RECEIVED JULY 13, 1936

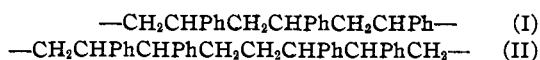
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

## Natural and Synthetic Rubber. XVI. The Structure of Polystyrene

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND HENRY M. LEICESTER

Polystyrene<sup>1</sup> is a friable solid which exhibits rubber-like properties at temperatures above 65°; it is obtained by heat polymerization of styrene.

Staudinger and his co-workers<sup>2</sup> have stated that polystyrene can be decomposed by heat into a mono-, di- and tristyrene; that the latter two compounds can be decomposed to monostyrene; and that 2,4-diphenyl-1-butene and 1,3-diphenylpropane can be detected among the heat decomposition products. They have therefore reached the conclusion that polystyrene is a long chain of styrene units bound together by ordinary valences, with a phenyl group linked to every second carbon. They have advocated formula I and rejected formula II.



Staudinger's experiments were repeated and found to be correct but the following additional facts were noted: (1) heat decomposition of polystyrene does not yield monostyrene exclusively; (2) rapid decomposition yields large amounts of monostyrene, while slow decomposition yields "di-styrene," "tri-styrene" and other

intermediate products; (3) the partially decomposed products are complicated mixtures, and their further decomposition gives a poor yield of monostyrene; (4) diphenylbutene and diphenylpropane are present in very small quantities, and only in products obtained from incomplete decomposition; (5) all efforts to analyze the dimeric fraction by oxidation, reduction, nitration, bromination, etc., gave indifferent results. These additional experimental data cast strong doubts on the significance of the decomposition products in establishing the formula of polystyrene.

An explanation of dependence of the elasticity of natural and synthetic rubbers on their structural formula has been offered by Mack.<sup>3</sup> The application of his ideas to the case of polystyrene leads directly to the conclusion that the elastic properties of this substance are consistent with formula II, and not at all with the heretofore accepted formula I, for the following reasons.

In the case of formula I, the 1,3-placement of the phenyl groups results in optimum packing of the phenyl groups, optimum contacting of the hydrogen atoms, and good satisfaction of the van der Waals forces when the chain molecule is extended; consequently there is no tendency to fold

(1) Whitby, *Rubber Chem. Tech.*, 465 (1931).

(2) Staudinger, *et. al.*, *Ber.*, 59, 3019 (1926); 62, 241-63 (1929); 62, 2406 (1929); *Ann.*, 517, 35-53 (1935).

(3) Mack, THIS JOURNAL, 56, 2757 (1934).