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## The Reaction of Aryl-thio-glycolic acid chlorides with sodium azide

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The reaction between acid chlorides and sodiumazide is known since a long time in the literature.<sup>1</sup> The formed azide decomposes readily with evolution of nitrogen and rearranges into the corresponding isocyanate. This reaction proceeds very easily particularly in the case of the aliphatic acid-azides. The isocyanate compounds react readily, e. g. with water and yield primary amino-compounds on evolving carbon dioxide.

According to the as yet not published results of E. Vinkler the phenyl-thio-glycolic acid azide (II. a.) recovered at the reaction between phenyl-thio-glycolic acid chloride (I. a.) and sodium azide is spontaneously converted into phenyl thiomethyl isocyanate (III. a.). This compound could be separated in the form of a solution which can readily be distilled. In consequence of its great reactivity it reacts with various agents, e. g. with water and is converted into N, N'-bis-(phenyl-thiomethyl)-carbamide (V. a.). If it is allowed to stand in an open vessel for several days the isocyanate yields the same carbamide derivative.

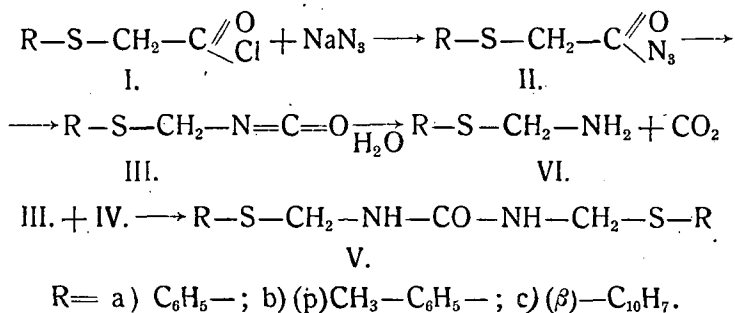
The purpose of this paper is to study to what an extent the various aryl radicals exert an influence on the reactivity of the isocyanate synthesized from aryl-thiomethyl-glycolic chlorides. In the following experiments the conversion of  $\beta$ -naphthyl- and p-tolyl-thio glycolic acid which had formed as intermediates was investigated. To enable the synthesis of these substances p-methyl-thiophenol<sup>2</sup> and thio- $\beta$ -naphthol were prepared from the suitable sulfochloride in phosphorus acid through reduction with potassium iodide in the presence of red phosphorus.

This method enabled the preparation of thio- $\beta$ -naphthol in a far better yield and under far simpler experimental conditions than

the procedure described in the literature.<sup>3</sup> The thiophenol derivatives were submitted in the usual manner to a basic reaction with monochloro-acetic acid<sup>4</sup> and the p-tolyl-respectively  $\beta$ -naphthyl-thio-glycolic acid was converted with thionyl chloride, or phosphorus trichloride into the suitable acid chloride. Both thio-glycolic acid derivatives were made to react in abs. toluene with sodium azide, previously activated by hydrazine hydrate, under the conditions described in the experimental part.

In analogous manner to that of the isolation of phenyl derivatives the isolation of isocyanates was also attempted. These experiments failed as the crystals separating out from the abs. toluene solution, on cooling, did not exhibit the expected properties of isocyanates. They did not react with water, alcohol etc. According to their behaviour and to their analytical data the compounds obtained in this way proved to be carbamide derivatives. The intermediate p-tolyl-, resp.  $\beta$ -naphthyl-thiomethyl isocyanate (III. b., III. c. resp.) is converted probably by the moisture of the air into p-tolyl-, resp.  $\beta$ -naphthyl-thiomethylamine (IV. a. and b.) which in turn reacts immediately with the simultaneously present isocyanate yielding N, N'-bis(p-tolyl-, resp.  $\beta$ -naphthyl-thiomethyl carbamide (V. b. and c.).

A similar phenomenon was reported by Goldstein and Viaud<sup>5</sup> in the case of 5,8-dichloro-2-naphthazide. The formed isocyanate reacts readily with the moisture of the air yielding bis-5,8-dichloro-2-naphthyl carbamide. The authors mentioned above did not either succeed in separating the corresponding isocyanate, their experimental results were analogous to ours.



On comparing the experimental results mentioned above the question arises as to the cause of the enhanced reactivity of the p-tolyl- and  $\beta$ -naphthyl-thiomethyl isocyanate as compared with that of the analogous phenyl-thiomethyl isocyanates. The greater reactivity of the former can probably be attributed to the less symmetrical distribution of the electrons on the radical of the p-tolyl-, resp.  $\beta$ -naphthyl than in the case of benzene and to the fact of this asymmetric being transferable to the radical attached to the thiomethyl-isocyanate group, thus promoting its polarisation and thereby increasing its reactivity.

In the course of further investigations the work described above will be continued and extended towards the accurate determination of the differences between the reaction rates of the un-

substituted and the substituted phenyl-thiomethyl isocyanates on yielding carbamides. Furthermore, the studies will also be pursued in the direction of how far the position of the substituents influencing in various manners the reactivity, and thus the distribution of the electrons on the aromatic ring, modifies the above described reaction, resp. reaction rate of the thiomethyl isocyanate group.

#### *Experimental.*

##### *Thio $\beta$ -naphthol.*

10g naphthaline  $\beta$ -sulfochloride purified in ether is ground with 8.5 g potassium iodide and 3.2 g red phosphorus and then mixed with 42 ml of syrupy phosphorus acid in a glass bulb and kept boiling through an asbestos wire gauze with reflux. Shortly after the boiling sets in a vigorous reaction is started the wall of the reflux condenser is coated with iodine which is rinsed off with 10 ml of alcohol. After boiling it for 10 hours it is cooled and subsequently extracted with 100 ml of ether, the ethereal extract is shaken with 100 ml N sodium hydroxyde and then the mercaptan liberated with hydro-chloric acid. Finally the thio  $\beta$ -naphthol is again extracted. The ether is distilled off in vacuo yielding pale yellow crystals. M. p. 81°, yield 6.6 g (94.3%).

##### *$\beta$ -naphthyl-thioglycolic chloride.*

7.8 g of recrystallized naphthyl-thio-glycolic acid is heated with 1.8 g phosphorus trichloride for an hour at 60—70°, and then after standing for an hour extracted with 25 ml ether. The solvent is removed from the ethereal solution in vacuo. A colourless transparent syrup is obtained which desomposes on being distilled in vacuo. For the following reactions purified by extraction in ether is used.

##### *The reaction of $\beta$ -naphthyl-thioglycolic chloride with sodium azide.*

12 g  $\beta$ -naphthyl-thioglycolic chloride is dissolved in 40 ml abs toluene and 4.1 g of sodium azide added which had been activated with hydrazinehydrate.<sup>6</sup> The reaction mixture instantaneously warms up to 80° and gas is evolved. It is heated on the water-bath for an hour and then filtered hot. The precipitate is rewashed with 30 ml hot toluene. On standing for a few hours the separation of the crystals which starts immediately the solution cools down is completed. The filtered crystals are recrystallized from toluene, or aqueous alcohol. Fine white needles, M. p. 142—144°.

Analysis: Calcd. for  $C_{23}H_{20}ON_2S_2$ : C, 74.14; H, 5.41;  
Fond C, 73.88; H, 5.26.

##### *p-Tolyl-thioglycolic chloride.*

7.3 g of p-tolyl-thioglycolic acid purified by recrystallization is added to 2 g phosphorus trichloride and kept for about an hour at 60—70° till the evolution of hydrochloric acid ceases. It is allowed to stand for an hour and then extracted with 25 ml of ether. After distilling off the ether in vacuo a colourless oil is obtained which is used without further purification.

##### *The reaction of p-tolyl-thioglycolic chloride with sodium azide.*

7.1 g acid chloride is dissolved in 25 ml abs. toluene, 3.3 g sodium azide is added which was previously activated by hydrazine hydrate. A significant rise

in temperature can be observed. It is heated on the water-bath at 80° for an hour. The toluic solution is filtered hot, the precipitate remaining on the filter is washed with 20 ml of hot toluene. On cooling of the toluic solution white, needle-shaped crystals separate out. After filtering off the crystals (3.3 g), the toluene solution is evaporated down to 20 ml in vacuo. The crystals which separated after cooling are again filtered off (1.6 g). *M.* p. 124—126°. Both crystal hulks are recrystallized together from toluene. *M.* p. 134°.

Analysis: Calcd. for  $C_{17}H_{20}ON_2S_2$ : C, 61.39; H, 6.03

Found C, 61.61; H, 6.21.

#### *Summary.*

The reaction between  $\beta$ -naphthyl- and p-tolyl-thioglycolic chloride and sodium azide was investigated. The isocyanate, which formed during the reaction could not, in contrast to the analogous phenyl derivative, be separated, but was converted by the moisture of the air into aryl-thiomethylamine; yielding with the simultaneously present isocyanate the corresponding carbamide derivative.

#### *In memoria.*

We conform to a pious duty in recalling the memory of our most efficient collaborator *Ferenc May*, who took part in the experimental work until his death caused by tragic consequences of the II. world war.

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