

## On the Beckmann Rearrangement. VII.

The Rearrangement of Ethylsynbenzhydroxamic Acid by the Different Acid Chlorides, and of its Benzenesulphonyl Ester.

By

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One of us (M. K.) and Okada have brought forward from their works already performed as well as from those of other investigators an inference<sup>1</sup> that the presence of the acid residue linked to nitrogen is also one of the necessary conditions in the Beckmann rearrangement of the compounds of the hydroxamic acid group, just as in the case of the ketoxime. Furthermore, the authors have examined the influence of the different acid chlorides upon the rate of rearrangement taking ethylsynbenzhydroxamic acid as a representative, and all the phenomena exhibited in the changes of its benzenesulphonyl ester. The results of experiments show that the alkylsynbenzhydroxamic acid and the ketoxime almost precisely follow the same rules for their rearrangement, consequently the facts which would support our view with regard to the Beckmann rearrangement of the oximido compounds have further been added.

### *1. The Rate of Rearrangement by the Different Acid Chlorides.*

One gram of ethylsynbenzhydroxamic acid,  $C_6H_5 \cdot C(OC_2H_5) : N \cdot OH$ , prepared according to the statement by Lossen<sup>2</sup> and an equivalent quantity of each of acetyl, monochloroacetyl and benzenesulphonyl

<sup>1</sup> These Memoirs, I, I (1914); Mem. Coll. Sci. Engin., Kyoto, 6, 1 (1913).

<sup>2</sup> Ber. D. chem. Ges., 17, 1587 (1884); Lieb. Ann., 205, 285 (1880).

chlorides was dissolved in 15 cc. of chloroform and allowed to react to each other at 120–123° in a sealed tube for 3 hours. Removing the solvent by evaporation the residue was mixed with the 3% solution of sodium hydroxide and subjected to distillation. The aniline distilled over together with water by such a process was determined as its hydrochloride, as will be shown in the following table :

Acid chlorides used.	C <sub>6</sub> H <sub>5</sub> ·NH <sub>2</sub> ·HCl in gram.	C <sub>6</sub> H <sub>5</sub> ·NH <sub>2</sub> in %.
Acetyl chloride	0.0710	4.7
Monochloroacetyl chloride	0.2422	31.0
Benzenesulphonyl chloride	0.4956	63.4

Now it is seen from the table that the rate of rearrangement of ethylsynbenzhydroxamic acid is likewise dependent upon the strength of the acid<sup>1</sup> from which a chloride has been derived. Such a relation, therefore, ought to be ascribed to the same cause as in the Beckmann rearrangement of the ketoxime.

## *2. Ethylsynbenzhydroxamic Acid Benzenesulphonyl Ester and its Rearrangement.*

For preparing ethylsynbenzhydroxamic acid benzenesulphonyl ester, a certain quantity of ethylsynbenzhydroxamic acid<sup>2</sup> was dissolved in a solution of sodium hydroxide (2%) and an equivalent quantity of benzenesulphonyl chloride was added under vigorous shaking. The reaction then began with the evolution of heat, and after an hour with occasional shaking there separated out a white crystalline mass, which was crushed, then washed with water, dried and again washed with petroleum ether until no smell of benzenesulphonyl chloride was perceived. Now the whole mass was dissolved in a small quantity of ether and by adding petroleum ether to the solution ethylsynbenzhydroxamic acid benzenesulphonyl ester separated as a crystalline precipitate.

<sup>1</sup> Zs. physik. Chem., 1, 73 (1887); J. prak. Chem., 28, 493 (1843).

<sup>2</sup> *Loc. cit.*

The ester melts at 54–55°, and is soluble in chloroform, alcohol and benzene. By treating with alcoholic soda, it decomposes into its components, sodium benzenesulphonate separating out as crystals having pearly luster, while the sodium salt of hydroxamic acid remains in the alcoholic mother liquor. The analysis of the ester gave the following values for sulphur :

I	0.2414	gram.	substance	gave	0.1615	gram.	BaSO <sub>4</sub> .
II	0.3360	"	"	"	0.2570	"	"
			Calculated for				Found
			C <sub>6</sub> H <sub>5</sub> ·C(OC <sub>2</sub> H <sub>5</sub> ):N·OSO <sub>2</sub> ·C <sub>6</sub> H <sub>5</sub>				I      II
Sulphur			10.51				10.87    10.50

Ethylsynbenzhydroxamic acid benzenesulphonyl ester, when heated to 95°, was noticed to evolve some characteristic irritating smell of phenyl isocyanate with some change of colour, and on continuing heating up to about 150° the decomposition into phenyl isocyanate and benzenesulphonic acid ethyl ester took place instantaneously with violence. Subjecting the products of decomposition of the ester to the vacuum distillation a colourless liquid was isolated; the latter had the characteristic smell of phenyl isocyanate and was found to boil at 166° (boiling point of phenyl isocyanate) at normal pressure. The liquid was also observed to change by heating with water into colourless crystals which melt at 234–235° after recrystallization from alcohol or ether. The formation of such a substance from phenyl isocyanate and water, and its melting point as well as its analysis show that it would be diphenylurea. Its analysis gave the following value for nitrogen :

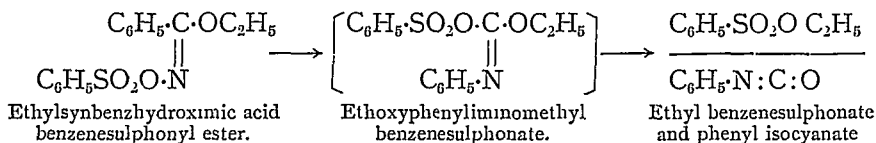
	0.1495	gram.	substance	gave	17.2	cc.	N at 15° and 757 mm.
			Calculated for				Found
			CO(C <sub>6</sub> H <sub>5</sub> ·NH) <sub>2</sub>				
Nitrogen			13.21				13.51

The residue left after the distillation of phenyl isocyanate was then boiled with water, by which process the decomposition of ethyl benzenesulphonate into its components took place. The aqueous part was neutralized with barium carbonate and the filtrate by evaporation deposited the crystals of barium benzenesulphonate which was confirmed by analysis :

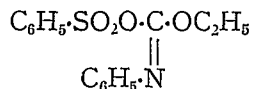
I 0.1908 grm. substance gave 0.0919 grm. BaSO<sub>4</sub>.  
 II 0.2567 ,, ,, ,, 0.1275 ,, ,,

	Calculated for	Found	
	(C <sub>6</sub> H <sub>5</sub> ·SO <sub>2</sub> O) <sub>2</sub> Ba·H <sub>2</sub> O	I	II
Barium	29.25	28.34	29.22

Interpreting from the results of experiments so far mentioned the nature of the change of ethylsynbenzhydroxamic acid benzenesulphonyl ester, it may be assumed that the ester would suffer the spontaneous Beckmann rearrangement simply at the elevation of temperature to 150°, but an intermediate product which ought to be ethoxyphenyliminomethyl benzenesulphonate, C<sub>2</sub>H<sub>5</sub>O·C(OSO<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>):N·C<sub>6</sub>H<sub>5</sub>, can not be isolated in the present case, as it may immediately decompose, possibly on account of its unstable nature in such a high temperature, into phenylisocyanate and ethyl benzenesulphonate<sup>1</sup> whose productions were confirmed by the formation of diphenylurea, benzenesulphonic acid and ethyl alcohol by the action of water upon the products of reaction. Thus the mechanism of decomposition may be represented in accordance with the following scheme :



By using pyridine, however, as a medium in the rearrangement of ethylsynbenzhydroxamic acid by the action of benzenesulphonyl chloride, the authors have succeeded to isolate the intermediate product, ethoxyphenyliminomethyl benzenesulphonate,



In this experiment a certain quantity of ethylsynbenzhydroxamic acid was dissolved in anhydrous pyridine to which an equivalent quantity of benzenesulphonyl chloride was added, and the mixture heated at 65–70° for 5 hours over a water bath, the colour of the solution changing from yellow to reddish brown. The reaction product was then poured into dilute sulphuric acid, by which process the needle-shaped crystals and reddish yellow thick oil separated out.

<sup>1</sup> Refer the descriptions in "the Beckmann Rearrangement. III."—These Memoirs, I, 1.

The crystals and oil were severed by filtering through cotton wool, and the former purified by repeated recrystallization from alcohol was found to possess the melting point of  $235^{\circ}$  which corresponds to that of diphenylurea. The oil was treated with ether, and the ethereal solution, by evaporation, deposited the crystals of diphenylurea still mixed. Repeating the same process several times by dissolving the oil in ether and by evaporating the ethereal solution until no crystals appeared, almost pure oil was obtained. Its analysis gave the following values for sulphur :

I	0.2076 grm. substance gave 0.1461 grm. BaSO <sub>4</sub> .		
II	0.1970 " " " 0.1551 " "		
	Calculated for		Found
	$C_6H_5 \cdot SO_2O \cdot C(:N \cdot C_6H_5)OC_2H_5$		I      II
Sulphur	10.51		9.69    10.01

When the oil was heated to  $150^{\circ}$ , it suffered decomposition evolving the characteristic irritating vapour of phenyl isocyanate, while by treating with alkali and chloroform the disgusting smell of carbylamine. On allowing the oil to stand in contact with a dilute solution of alkali for a long while it partly changed into a solid mass from which diphenylurea was isolated.

By exposing ethylsynbenzhydroxamic acid benzenesulphonyl ester to the ultraviolet rays, it seems to change first to ethoxyphenylaminomethyl benzenesulphonate which further decomposes into phenyl isocyanate and ethyl benzenesulphonate. Such an experiment was carried out in the same manner as in the case of ketoxime benzenesulphonyl esters, as mentioned in the previous articles<sup>1</sup>, and the results are as follows :

Time of exposure in minutes.	Changes observed.
10	Slightly coloured brownish yellow on surface.
20	Brownish yellow.
60	Somewhat oily form.
120	Oily state evolving the smell of phenyl isocyanate.

<sup>1</sup> These Memoirs, I, 109 (1914);

3. *Conclusion.*

A conclusion is drawn from the results of experiments that the rearrangement of ethylsynbenzhydroxamic acid by the different acid chlorides and of ethylsynbenzhydroxamic acid benzenesulphonyl ester obeys the same rules as that of the ketoximes and of their benzenesulphonyl esters, excepting the decomposition of an intermediate product which progresses in somewhat different way on account of its unstability.

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