On the Beckmann Rearrangement. V.

Rearrangement of Diphenylketoxime Benzenesulphonyl Ester and Synthesis of Phenylbenzimido-benzenesulphonate.

By

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As has already been mentioned in the previous articles¹ by one of us (M.K.) and his collaborators, diphenylketoxime benzenesulphonyl ester actually undergoes the 'spontaneous molecular rearrangement, whose primary cause may be ascribed to the dissociation of the benzenesulphonic acid residue of strongly negative character as we assume, with the consequent formation of phenylbenzimido-benzenesulphonate, thus giving a possible explanation as regards the mechanism of the Beckmann rearrangement.

Diphenylketoxime benzenesulphonyl ester used in the present work was prepared from the sodium salt of diphenylketoxime² by the action of benzenesulphonyl chloride³ at the ordinary temperature. It is a colourless crystalline substance, whose nature was confirmed by saponification with alkali by which process it splits up readily into its constituents, i.e., diphenylketoxime and benzenesulphonic acid. As a matter of fact, the ester changes by the molecular rearrangement to a yellow viscid liquid, which is no doubt phenylbenzimido-benzenesulphonate, slowly on being allowed to stand by itself in a solid state in a chloroform solution, or by exposing its powder to the ultra-violet rays, but instantaneously with explosive violence accompanied by a hissing noise on heating above its melting point 62° ; thus the change should be as follows, as has already been shown⁴:

¹ Mem. Coll. Sci. Engin., Kyoto, 2, 385 (1910); 4, 1 (1913); these Memoirs, 1, 52 (1914).

² Ber. D. chem. Ges., 17, 812 (1884).

³ Lieb. Ann., 87, 299 (1853); Z. f. Chem., 1866, 106.

⁴ Loc. cit.

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Phenylbenzimido-benzenesulphonate which is of unstable character, gradually changes to benzanilide and benzenesulphonic acid by moisture on being left in open air, but very readily by treating with water, sometimes still further decomposition taking place with the production of aniline, benzoic acid and benzenesulphonic acid, when is kept in a moist chloroform solution; thus the reactions should be as follows:

$$\begin{array}{cccc} C_{6}H_{5}.C.OSO_{2}.C_{6}H_{5} & \xrightarrow{water} & C_{6}H_{5}.CO \\ \parallel & & & & \\ N.C_{6}H_{5} & \xrightarrow{water} & & & \\ R_{6}H_{5}.C.OSO_{2}.C_{6}H_{5} & \xrightarrow{water} & C_{6}H_{5}COH + C_{6}H_{5}.SO_{2}.OH \\ \parallel & & & \\ N.C_{6}H_{5} & \xrightarrow{water} & & \\ H_{2}N.C_{6}H_{5} & \xrightarrow{water} & \\ \end{array}$$

Phenylbenzimido-benzenesulphonate was then synthesized from phenylbenzimido-chloride¹ by the action of silver benzenesulphonate². In this experiment, phenylbenzimido-chloride prepared as purely as possible with all necessary precautions, and dissolved in petroleum ether was allowed to react with silver benzenesulphonate under constant and vigorous shaking, and then the solid separated from petroleum ether by filtration was treated with chloroform. Evaporating chloroform by passing a rapid current of dry air through the solution, there was left a yellow viscid liquid, some benzanilide separated from the concentrated solution having been removed by filtration through cotton wool. The substance, thus prepared by synthesis corresponds to phenylbenzimidobenzenesulphonate, infeiring its composition from the analytical results; hence the reactions should be represented as follows:

$$\begin{array}{ccc} C_{6}H_{5}.C.Cl & & C_{6}H_{5}.C.OSO_{2}.C_{6}H_{5} \\ \parallel & +\operatorname{AgOSO}_{2}C_{6}H_{5} & \longrightarrow & \parallel & +\operatorname{AgCl} \\ N.C_{6}H_{5} & & N.C_{6}H_{5} \end{array}$$

The substance possesses the same behaviours as the benzenesulphonate formed by the rearrangement of diphenylketoxine benzenesulphonyl

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¹ Lieb. Ann., 184, 79 (1877); Ber. D. chem. Ges., 43, 892 (1910).

² Lieb. Ann. 223, 244 (1884).

ester, thus readily decomposing into benzanilide and benzenesulphonic acid, and also into benzoic acid, benzenesulphonic acid and aniline by the action of water.

Further, the absorption spectra of the two preparations of phenylbenzimido-benzenesulphonate from two different sources, that is, one formed by rearrangement and the other prepared by synthesis, were examined under the same condition. On comparing their absorption curves, as will be seen in the experimental part, it has been found that they almost agree to each other.

Now from the experimental results so far obtained a conclusion is drawn that phenylbenzimido-benzenesulphonate formed from diphenylketoxime benzenesulphonyl ester is identical with that obtained by synthesis from phenylbenzimido-chloride and silver benzenesulphonate. It is, therefore, quite evident that diphenylketoxime benzenesulphonyl ester undergoes the molecular rearrangement spontaneously, owing to the presence of the benzenesulphonic acid residue of strongly negative character without the aid of any reagent, more readily by the mere elevation of temperature; consequently the production of the acyl derivative of the substituted imido-acid from the ketoxime acyl ester must be a necessary condition of the Beckmann rearrangement.

EXPERIMENTAL PART.

1. Sodium Salt of Diphenylketoxime, (C₆^aH₅)₂C:N.ONa.

Since the method of the preparation of the sodium salt of diphenylketoxime proposed by Spiegler¹ gives a very poor yield, the authors have suggested the other method which is very simple and satisfactory. It consists in adding thin slices of metallic sodium to the solution of diphenylketoxime in absolute ether, by which treatment there was noticed a brisk evolution of hydrogen and the deposition of the sodium salt of diphenylketoxime in the form of a light white powder. The latter was then separated from the unchanged metallic sodium left în ether by decantation after shaking the whole mixture violently, and then repeatedly washed with ether until not a trace of diphenylketoxime unchanged is detected in washings. The salt thus prepared was dried in a desiccator and analysed.

¹ Ber. D. chem. Ges., 17, 812 (1884).

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0•1594 grm.	substance gave 0.08 grm. Na_2SO_4	
	Calc. for $(C_6H_5)_2$ C:N.ONa	Found
Sodium	10•47	10•56

As a by-product of the reaction there was found a small quantity of aminodiphenylmethane, $(C_6H_5)_2$ CH.NH₂, whose formation is undoubtedly due to the reduction of diphenylketoxime by hydrogen liberated.

Diphenylketoxime Benzenesulphonyl Ester, (C₆H₅)₂C:N.OSO₂,C₆H₅.

Equivalent quantities of the sodium salt of diphenylkotoxime and benzenesulphonyl chloride¹ mixed in absolute ether were allowed to react to each other for several hours under vigorous shaking. The etherial solution, then separated by filtration from sodium chloride formed in the reaction, was made to evaporate by passing a current of dry air in order to avoid the rise of temperature, by which process colourless crystals of diphenylketoxime benzenesulphonyl ester were deposited. Repeating its recrystallization from ether, it was obtained in pure state. The ester was analysed, and gave the following value for sulphur.

0.186 grm. substance gave 0.126 grm. BaSO₄. Calc. for $(C_6H_5)_2$ C:N.OSO₂.C₆H₅. Found Sulphur 9.51 9.30

The substance is soluble in alcohol, benzene and chloroform, and melts at 62° with some change.

In order to confirm the nature of the ester, it was treated with alcoholic potash by the action of which it was found to decompose into diphenylketoxime and benzenesulphonic acid. The former was identified by its melting point and the latter by the analysis of its barium salt which gave the following value for barium.

0.109 grm. of the anhydrous salt gave 0.555 grm. BaSO₄.

Calc. for $(C_6H_5.SO_2O)_2Ba$ Found

Barium

30.42 30.13

1 Lieb. Ann., 87, 299 (1853).

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3. Phenylbenzimido-benzenesulphonate, C₆H₅.C.(OSO₂.C₆H₅):N.C₆H₅

By heating the crystals of diphenylketoxime-benzenesulphonyl ester above its melting point, they change instantaneously to a yellow viscid liquid with an explosive violence accompanied by a hissing sound. Such a change is, however, gradually effected on allowing the crystals to stand under a desiccator for a long while, or by dissolving them in chloroform, the solution getting slowly yellow, It was also observed that the ester in the form of fine powder, when introduced between a pair of thin quartz plates and exposed to the ultra-violet rays from a mercury lamp, changes yellow on its surface in an hour. The analysis of the substance gave the following values for sulphur.

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I. 0.1140 grm. substance gave 0.0762 grm. BaSO<sub>4</sub>,
II.
       0.1552
                                                  0.1214
                     "
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                                                                         ,,
III. 0·1062
                                                  0.0741
                                 "
                     ,,
                                            ,,
                                                                         ,,
                              Calc. for
                                                                             Found
                C<sub>6</sub>H<sub>5</sub>.C.(OSO<sub>2</sub>.C<sub>6</sub>H<sub>5</sub>):N.C<sub>6</sub>H<sub>5</sub>
                                                               Ι
                                                                        Π
                                                                                  III
                                                                                          Mean
    Sulphur
                                9.51
                                                            9.17
                                                                      10.07
                                                                                 9.30
                                                                                           9.52
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The yellow viscid liquid is without doubt phenylbenzimido-benzenesulphonate formed by the molecular rearrangement of diphenylketoxime benzenesulphonyl ester, as it readily decomposes into benzanilide and benzenesulphonic acid by treating with water. Benzanilide was confirmed by its melting point and other properties, and benzenesulphonic acid by the analysis of its barium salt.

0.2 grm. of the anhydrous barium salt gave 0.108 grm. BaSO₄.

	Calc. for $(C_6H_5.SO_2O)_2Ba$	Found
Barium	30•42	31•79

The substance, when exposed to air, slowly decomposes into benzanilide and benzenesulphonic acid owing to its unstable nature in presence of moisture; it is, however, pretty stable in vacuum. It is soluble in alcohol, chloroform and acetone. By keeping its solution in moist chloroform for a while, some colourless silky needle-shaped crystals were found to separate out. They melt above 200° with decomposition, and soluble in water, alcohol and acetone. They decompose into aniline and benzenesulphonic acid by treating with a solution of alkali; aniline isolated by extracting with ether was confirmed by its colourreaction with a bleaching powder solution, and benzenesulphonic acid contained in the alkaline aqueous part by the analysis of its barium salt.

0.115 grm. of the anhydrous barium salt gave 0.0598 grm. BaSO₄.

	Calc. for $(C_6H_5.SO_2O)_2Ba$	Found
Barium	30•42	3 0• бо

The mother liquor consisting of the chloroform solution was evaporated, and from the residue benzoic acid was isolated and confirmed by its melting point and other characteristic properties. The substance which consists of silky needles is, therefore, the aniline salt of benzenesulphonic acid; and on comparing it with the salt prepared according to Gericke¹ from aniline and benzenesulphonic acid, both were found to be identical. Hence phenylbenzimido-benzenesulphonate in the chloroform solution decomposes, in fact, into aniline benzenesulphonic acid and benzoic acid through the action of moisture contained in it.

Synthesis of Phenylbenzimido-benzenesulphonate. 4.

Phenylbenzimido-benzenesulphonate was synthesized from phenylbenzimido-chloride and silver benzenesulphonate, and the process will be described below. Phenylbenzimido-chloride (benzanilidimide chloride) was prepared according to the method proposed by Wallach² and purified by the process suggested by Mumm³ with all possible precautions, and the anhyduous silver benzenesulphonate was obtained by Hübner's method.⁴ Phenylbenzimido-chloride, thus prepared, was dissolved in dry petroleum ether, and anhydrous silver benzenesulphonate added in some excess over an equivalent quantity. With the constant and vigorous shaking of the mixture, silver benzenesulphonate gradually changed yellow on its surface, and finally a yellow substance deposited in the wall of a vessel. After removing petroleum ether by decantation, the yellow substance was extracted by treating the residue with chloroform which produced a deeply yellow-coloured solution. Evaporating chloroform by passing a current af dry air through the chloroform solution

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¹ Lieb. Ann., 100, 217 (1857).

² Ibid., 184, 79 (1877).

³ Ber. D. chem. Ges., 43, 892 (1910).

⁴ Lieb. Ann., 223, 244 (1884).

well excluded from moisture, there was left a yellow viscid liquid, mixed with some colourless crystals. The liquid was then separated from the crystals by filtering through cotton wool with the aid of a suction pump. The crystals were identified as benzanilide by its melting point and all other properties. In order to remove the trace of chloroform admixed in the viscid liquid, the latter was left in a desiccator for several hours under constant exhaustion, until no evolution of the bubbles of chloroform was noticed. The substance was analysed and gave the following values for sulphur.

I. 0.5749 grm. substance gave 0.3835 grm. BaSO₄ II. 0.6092 ,, , , , 0.4522 ,, ,

	Calc. for		Found	Į
	$C_6H_5.C.(OSO_2.C_6H_5):N.C_6H_5$	I	II	Mean
Sulphur	9 · 51	9.19	10•2 2	9 · 71

The substance is soluble in alcohol, chloroform and acetone, but difficultly in ether and petroleum ether. By adding water to its solution in acetone, there was found to separate out a flocky precipitate which, when recrystallized from alcohol, melted at 161°, thus proving to be benzanilide. From the filtrate benzenesulphonic acid was isolated as its barium salt by adding some baryta water and removing the excess of barium by means of carbon dioxide. The barium salt recrystallized from water was analysed.

0.425 grm. of the salt gave 02.13 grm. BaSO₄

Barium

Calc. fo	$r \operatorname{Ba}(C_6H_5SO_2O)_2\frac{1}{2}H_2O$	Found
	29•83	29•49

The substance dissolved in moist chloroform was also noticed to deposit some colourless silky crystals of the aniline salt of benzenesulphonic acid whose formation must be due to the decomposition of phenylbenzimido-benzenesulphonate into aniline, benzoic acid and benzenesulphonic acid through the action of moisture contained in chloroform, since by treating the crystals with aqueous alkali they yield aniline and benzenesulphonic acid. The former was confirmed by its colour reaction with a bleaching powder solution and the latter by the production of its barium salt.

0.2381 grm. of the crystals gave 0.2306 grm. BaSO₄ by analysis.

Calc. for C_6H_5 .SO2O.NH3.C6H5FoundSulphur12.7813.30Aniline benzenesulphonate, thus formed, is identical with that prepared

according to Gericke's method.¹ As has been shown so far, phenylbenzimido-benzenesulphonate prepared by synthesis shows no difference in all of its properties in comparison with that formed by the molecular rearrangement of diphenylketoxime benzenesulphonyl ester, hence they should be identical.

5. Absorption Spectra of the two Preparations of Phenylbenzimido-benzenesulphonate.

For the further confirmation of identity of the two preparations of phenylbenzimido-benzenesulphonate, spectrographic experiments were

Oscillation frequencies



1 Loc cit.

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conducted according to the well known method by Hartley.¹ For this purpose, their solutions were prepared in absolute alcohol and a Hilger quartz spectrograph was employed with an iron arc as the source of light. An observation was repeated in each case for the different thicknesses of the liquids of several different dilutions with the use of Baly's adjustable cell,² and the absorption curves were plotted with the oscillation frequencies and the relative thicknesses of liquids in terms of the dilution of N/100000. On comparing the curves showing the absorption spectra of the two preparations from the different sources, as represented in the figure, they almost agree to each other, so that they may be concluded to be identical. Thus the full line curve represents the absorption spectra of phenylbenzimido-benzenesulphonate formed by the rearrangement of diphenylketoxine benzenesulphonyl ester and the dash line curve that of the same substance prepared by synthesis from phenylbenzimido-chloride and silver benzenesulphonate.

¹ J. chem. Soc., 47, 685 (1885).

² Ibid., 85, 1039 (1904).

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