

On the Beckmann Rearrangement. VI.

The Rate of Rearrangement of Methylphenylketoxime by the Different Acid Chlorides, the Spontaneous Rearrangement of its Benzenesulphonyl Ester and the Synthesis of Phenylacetimido-benzenesulphonate.

By

Mitsuru Kuhara and Hikohei Watanabe.

(Received April 20, 1916.)

It has already been established by the previous works by one of us (M. K.) and his co-workers¹ that the influence of the different acid chlorides upon the rate of rearrangement of diphenylketoxime would apparently stand in harmony with the degree of acidity² of the acid from which a chloride has been derived, in other words, with the strength of the negative character of the acid residue coupled in the oxime ester which may be formed by an acid chloride, and also that the diphenylketoxime acyl ester containing a strongly negative acid residue, such as diphenylketoxime benzenesulphonyl ester, undergoes of itself the rearrangement without the aid of any reagent, simply at the elevation of temperature, its primary cause being likely due to the dissociation of the benzenesulphonic acid residue of the strongly negative character as we assume, with the subsequent formation of phenylbenzimidobenzenesulphonate. Such a rearrangement has further been confirmed by the synthesis of phenylbenzimidobenzenesulphonate which was found to be identical with that actually formed by rearrangement.³

The authors have now attempted to extend the analogous experiments toward a ketoxime of the other class such as methylphenylketoxime (acetophenoxime) anticipating that all the reactions may

¹ Mem. Coll. Sci. Engin., Kyoto, **2**, 387 (1909-1910); These Memoirs, **1**, 106 (1914).

² Zs. physik. Chem. **1**, 73 (1887); J. prak. Chem., **28**, 493 (1843).

³ These Memoirs, **1**, 106 (1914).

progress in the analogous manner as in the case of diphenylketoxime, and an expectation with regard to such a point of view has been realized.

1. *The Influence of the Different Acid Chlorides.*

For studying the influence of the different acid chlorides upon the rearrangement of methylphenylketoxime, acetyl, monochloroacetyl, benzoyl and benzenesulphonyl chlorides were taken. In every case, an acid chloride and methylphenylketoxime were allowed to react to each other in molecular proportions, each substance having been dissolved in chloroform so as to make $\frac{1}{2}$ molar solution at a definite temperature. Each of both solutions was taken in 5 cc., and two were mixed together and heated at 100° in a sealed tube for a certain period of time. Acetanilide formed was then isolated with a proximate accuracy from the contents of the tube with possible precautions, and its quantity determined. The following table shows the relative quantities of acetanilide formed by rearrangement from methylphenylketoxime by the different acid chlorides.

Time (hours).	% Acetanilide formed,			
	by acetyl chloride.	by benzoyl chloride.	by monochloroacetyl chloride.	by benzenesulphonyl chloride.
0.5	Trace	0.9	6.5	98.8
1.0	0.3	5.0	12.0	—
2.0	11.0	12.0	30.0	—
3.0	32.0	—	40.0	—
4.0	34.2	34.9	—	—
5.0	36.9	38.6	—	—
6.0	39.0	41.0	—	—

Now it is evident from the table that the rate of rearrangement of methylphenylketoxime by the different acid¹ chlorides is apparently dependent upon the strength of the acid from which a chloride has been derived, consequently more negative the acid residue coupled in methylphenylketoxime acyl ester greater the velocity of the change would be. The rearrangement of the same ketoxime, however, by

¹ *Loc. cit.*

acyl chloride from a weak acid such as acetic acid may be ascribed to the change of its acyl ester intermediately formed which must be brought about by the intervention of hydrochloric acid liberated in the reaction, since the acetyl ester does not apparently undergo rearrangement at all by heating itself at a high temperature, while it does readily as a matter of fact in the presence of hydrochloric acid. With regard to the question how hydrochloric acid may play a part in the rearrangement of the ketoxime acyl ester, we are further continuing an investigation, and expect to communicate the results in a short while.

2. *The Rearrangement of Methylphenylketoxime
Benzenesulphonyl Ester.*

Methylphenylketoxime benzenesulphonyl ester, $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{C}:\text{N}\cdot\text{OSO}_2\cdot\text{C}_6\text{H}_5$, was obtained by the action of benzenesulphonyl chloride upon the sodium salt of methylphenylketoxime prepared by the analogous method as suggested for that of diphenylketoxime.¹ It crystallizes in colourless needles and melts at $60-61^\circ$. Its analysis gave the following values for sulphur :

I	0.2039 grm. substance gave	0.1655 grm. BaSO_4 .	
II	0.1850 " " "	0.1603 " "	
III	0.1748 " " "	0.1440 " "	
	Calculated for		Found.
	$(\text{CH}_3)(\text{C}_6\text{H}_5)\text{C}:\text{N}\cdot\text{OSO}_2\cdot\text{C}_6\text{H}_5$.	I	II III
Sulphur	11.60	11.10	11.90 11.32

The ester gradually changes to a thick oil owing to its molecular rearrangement, kept in a desiccator at ordinary temperature for 7-8 days in winter while for 1-2 days in summer. At the elevation of temperature to $81-82^\circ$, however, it undergoes rearrangement instantaneously with hissing noise changing at once into a brownish yellow viscid oil which is almost insoluble in ether and petroleum ether while readily in chloroform and acetone. The product of rearrangement or the oil was analysed, and we obtained the following values for sulphur :

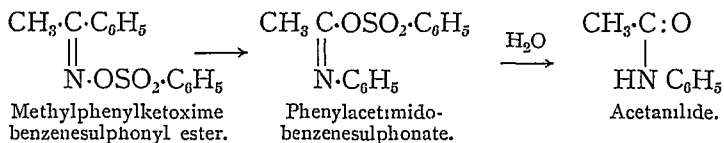
¹ These Memoirs, 1, 107 (1914).

I 0.2171 grm. substance gave 0.1752 grm. BaSO₄.
 II 0.1161 ,, ,, ,, 0.0935 ,, ,,

	Calculated for	Found.	
	CH ₃ C(OSO ₂ .C ₆ H ₅):N.C ₆ H ₅ .	I	II
Sulphur	11.60	11.06	11.07

The oil quickly decomposes by treating with water, depositing the characteristic scaly crystals of acetanilide (m. p. 112–113°), and does not give the original substance, methylphenylketoxime, any more by the action of alcoholic potash; hence it would be phenylacetimido-benzenesulphonate.

Now the change may, therefore, be represented as follows:



3. *Synthesis of Phenylacetimido-benzenesulphonate.*

It was synthesized from phenylacetimido-chloride¹ and silver benzenesulphonate². In this experiment the silver salt of benzenesulphonic acid dried at 150° was allowed to act upon phenylacetimido-chloride dissolved in acetone, producing a yellow solution. By driving out acetone by passing a current of dry air a yellow oil was left as a residue, which was carefully washed with ether and then with petroleum ether. The oil so purified was analysed and gave the following result:

0.3543 grm. substance gave 0.2607 grm. BaSO₄.

	Calculated for	Found.
	(CH ₃)(C ₆ H ₅)C(OSO ₂ .C ₆ H ₅):N.C ₆ H ₅ .	
Sulphur	11.60	10.10

The substance quickly decomposes by the action of water, producing acetanilide (m. p. 112–113°). It is identical in all respects with phenylacetimido-benzenesulphonate produced by rearrangement.

¹ Lieb. Ann., 184, 86 (1877).

² *Ibid.*, 223, 244 (1884).

4. *The Action of the Ultraviolet Rays upon Methylphenylketoxime Benzenesulphonyl Ester.*

The ester was observed to change very likely to phenylacetimido-benzenesulphonate under rearrangement when exposed, in crystals or in the chloroform or alcoholic solution, to the action of the ultraviolet rays taking a mercury lamp as a source of light, while when a glass plate was interposed between the substance and the lamp no apparent change was observed to take place. In carrying out the experiment the crystals finely powdered were held in a thin layer between a pair of two quartz plates and then exposed to the ultraviolet rays. The following table shows the results of the experiment.

Time of exposure in minutes.	Changes observed.
15	Somewhat yellowish.
30	Yellowish.
40	Yellow.
50	Brownish yellow.
65	Small oily drops visible.
100	Apparently oily form.
120	Brownish yellow oil.

5. *Conclusion.*

Interpreting from the results of the experiments thus stated, it may be concluded that all the facts so far observed with regard to the rearrangement of methylphenylketoxime are almost exactly concordant with the empirical rules found in connection with that of diphenylketoxime.
