

On the Beckmann Rearrangement. IX.

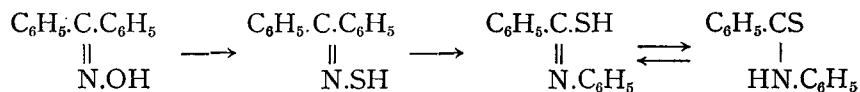
Action of Phosphorus Pentasulphide upon Benzophenoxime.

BY

Mitsuru Kuhara and Kôzô Kashima.

(Received June 27, 1919)

Dodge¹ states that he has obtained thiobenzanilide by the action of phosphorus pentasulphide upon the warm benzene solution of benzophenoxime, assuming that the reaction would be analogous to the Beckmann rearrangement. Also Ciusa² has conducted the similar experiment, expecting to prepare thiobenzophenoxime by the action of phosphorus pentasulphide upon the carbon bisulphide solution of benzophenoxime, but not succeeded to isolate the substance expected, while thiobenzanilide has been observed to be produced. He has, therefore, ascribed the reaction likewise to the Beckmann rearrangement of thiobenzophenoxime which is supposed to be formed in the intermediate stage of reaction, its primary cause being possibly due to the more acidic nature of sulphur than oxygen³; the scheme of reaction has been proposed as follows:



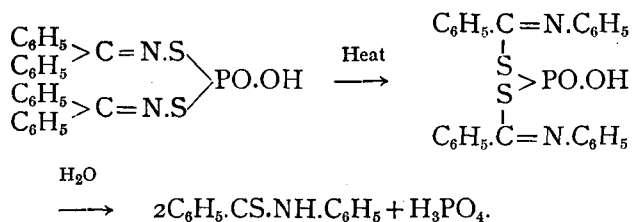
The authors have, however, noticed that the formation of thiobenzanilide from benzophenoxime by phosphorus pentasulphide may not be due to the direct rearrangement of thiobenzophenoxime, but seems to be dependent upon the rearrangement of a phosphoryl ester of

¹ Dodge, Lieb. Ann. **264**, 184 (1891).

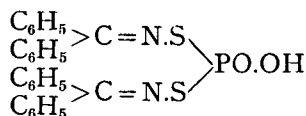
² Ciusa, Chem. Centralbl., 1907, **1**, 28.

³ Sidgiwick, Org. Chem. of Nitrogen, (1910), p.89.

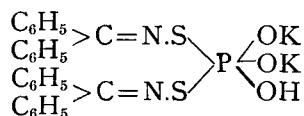
thiobenzophenoxime which is possible to be formed as an intermediate product, just as one of us (M.K.) and his collaborators have ever noticed in the rearrangement of the acylesters of ketoximes, that is, standing in harmony with Kuhara's theory of migration of the negative acyloxyl radicals,¹ the scheme of rearrangement being represented as follows :



In the authors' experiment, benzophenoxime and phosphorus pentasulphide were allowed to act upon each other in proportion of 5 mols and 1 mol respectively with the addition of 1½ mols phosphorus pentoxide, ether having been selected as solvent in order to keep the temperature of the mixture so low as to its boiling point (35°), while Dodge took benzene (boil. pt. 80°), and Ciusa carbon bisulphide (boil. pt. 46°). Driving off ether by passing the current of dry air through the ethereal solution, greenish yellow substance of fibrous structure was left as a residue, which by a slight elevation of temperature undergoes rearrangement with explosive violence. On account of such an explosive nature of the substance it was highly difficult to get in a perfectly pure state; so the substance was treated with alcoholic potash, by which process a substance consisting of white crystalline powder was obtained and purified by the repeated recrystallization from ethyl acetate. This substance also undergoes rearrangement at 149°, but not so violently as the yellow substance. Consequently, the yellow and white substances seem to possess the following constitutions, inferred from the results of analysis and their properties :



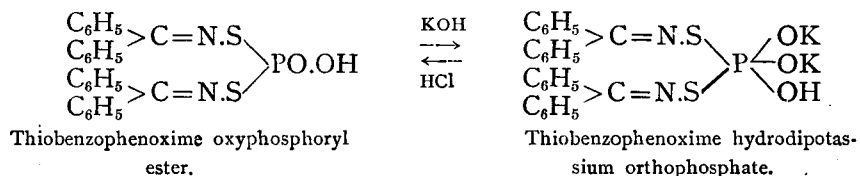
Greenish yellow fibrous substance.



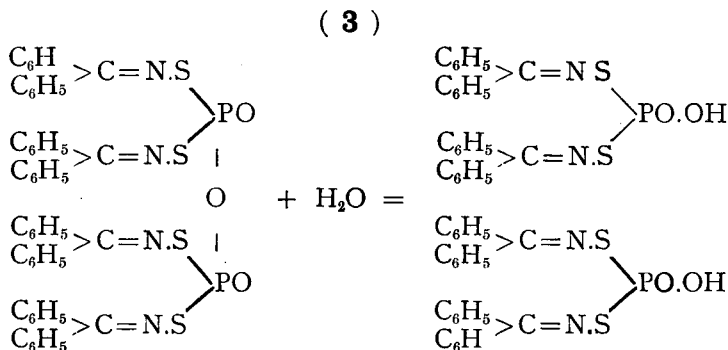
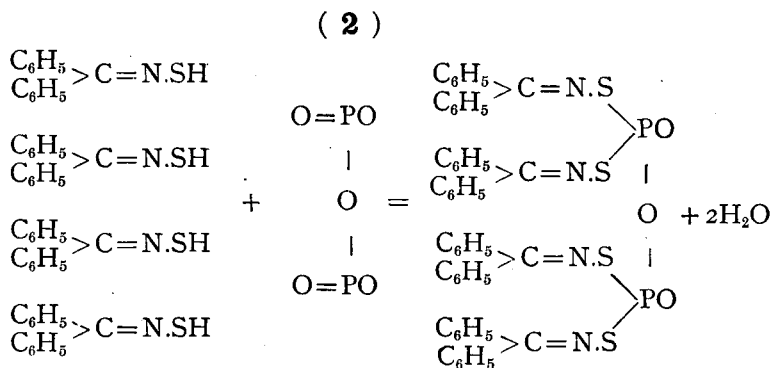
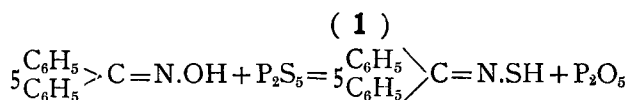
White crystalline substance.

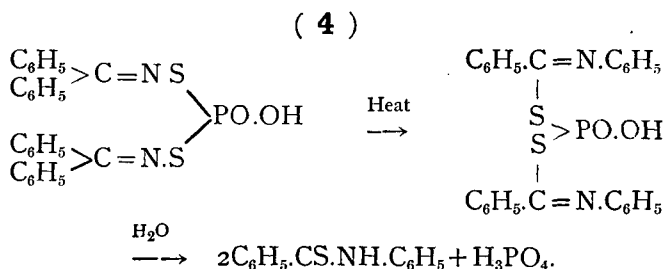
¹ Kuhara and Kainosho, Mem.Coll. Sci. Eng., Kyoto, 1, 254 (1903-1908); Kuhara and Todo, Ibid., 2, 387 (1909-1910); Kuhara, Matsumiya and Matsunami, Mem. Coll. Sci., Kyoto, 1, 105 (1914); Kuhara and Watanabe: Ibid., 1, 349 (1916); Kubara and Ishikawa: Ibid., 355 (1916); Kuhara, Agatsuma and Araki, Ibid., 3, 1 (1917).

The white substance, on treating with hydrochloric acid, was found to retransform into the greenish substance; hence the two substances are mutually transformable, viz., one into the other by alkali and vice versa by acid:

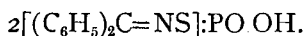


The authors have endeavoured to isolate thiobenzophenoxime, $(\text{C}_6\text{H}_5)_2\text{C}=\text{NSH}$, from those two substances by different possible ways, but not succeeded. Now, they have to interpret the reactions regarding the formation of thiobenzanilide from benzophenoxime by the action of phosphorus pentasulphide as shown in the following scheme:





EXPERIMENTAL PART.

Thiobenzophenoxime Oxyphosphoryl Ester,

19 Grms. freshly prepared benzophenoxime dissolved in 600 c.c. of absolute ether was mixed with 4.4 grms. powdered phosphorus pentasulphide with the addition of 4.3 grms. phosphorus pentoxide, and the mixture was heated over a water bath with a reflux condenser for about six hours. Now the colourless ether was charged with greenish yellow colour; then the greater part of ether was removed by distillation, and its residual part driven off by passing a current of dry air through the solution, and finally sucked by pumping for removing the last trace of ether. By such a process of treatment there was left a greenish yellow substance of fibrous structure which is assumed to be thiobenzophenoxime oxyphosphoryl ester, and an intermediate product in the Beckmann rearrangement of the hypothetical thiobenzophenoxime. Its purification was exceedingly difficult on account of its excessive readiness of rearrangement.

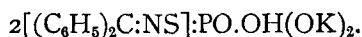
The determination of its molecular weight was, however, attempted with the crude substance by the cryoscopic method using benzene as solvent, expecting that its proximate value may be obtained so as to throw some light upon the nature of the substance :

	Grm. subst. taken	Lowering of the freez. point.		
I.	0.1151	0.085°		
II.	0.1846	0.132°		
	Mol. weight calc. for	Observed values		
	$2[(\text{C}_6\text{H}_5)_2\text{C}:\text{NS}]\text{PO.OH}$	I	II	Mean
	488.5	395.9	408.5	402.4

The substance suffers rearrangement with an explosive violence

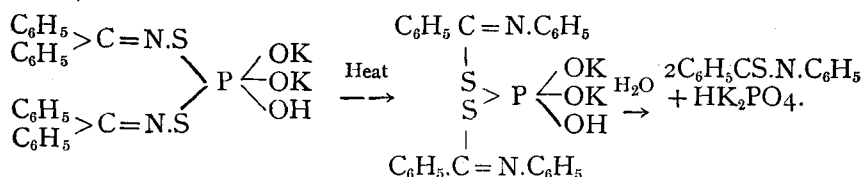
by mere heating to 70°, yielding a brownish yellow syrupy liquid with the evolution of a dense white fume. The syrup was dissolved in 10% aqueous solution of sodium hydroxide, and then by adding dilute hydrochloric acid the yellow precipitate produced. The latter was identified as thiobenzanilide by the melting point (98°) and other properties of the crystals deposited as thin plates from the alcoholic solution.

Thiobenzophenoxime Hydrodipotassium Orthophosphate,



By treating thiobenzophenoxime oxyphosphoryl ester with alcoholic potash at ordinary temperature, it has changed to a white crystalline powder. As the latter is almost insoluble in common organic solvents, its purification was exceedingly difficult; so the authors took the simple method of washing the substance with several different solvents such as alcohol, ether, petroleum ether, benzene, etc., which may dissolve the admixed impurities. So roughly purified substance was found to dissolve particularly in ethyl acetate and to crystallize in white transparent needles. The substance is sparingly soluble in cold water and behaves like soap forming froth by shaking; this may indicate that the substance would be an alkaline salt of a complex organic acid or soap, standing in harmony with the constitution of the substance above shown.

It also undergoes rearrangement with violence by heating up to 149°, producing thiobenzanilide and phosphoric acid by treating the product with water; the scheme of reaction may be assumed to be:



The substance was analysed and the following results were obtained.

For the determination of carbon and hydrogen, the substance was ignited with lead chromate.

	Grm. subst. taken	Grm. CO ₂ found	Grm. H ₂ O found
I.	0.1363	0.2704	0.0343
II.	0.2019	0.3919	0.0588
III.	0.1548	0.3047	0.0497

For the determination of nitrogen, the substance was also ignited with lead chromate.

	Grm. subst. taken	C.c. Nitrogen found	Temp. and press. observed
IV.	0.1325	5.72	20° and 758.1 m.m.
V.	0.2442	10.50	20° and 757.8 m.m.
VI.	0.2742	12.10	19.5° and 754.3 m.m.

For the determination of sulphur the substance was oxidized with fuming nitric acid (sp. gr. 1.5) in a sealed tube, and sulphur estimated as BaSO₄ as usual.

	Grm. subst. taken	BaSO ₄ found
VII.	0.2000	0.1718
VIII.	0.4246	0.3807
IX.	0.5834	0.5210

For the determination of phosphorus, the substance was similarly treated as in the case of sulphur, and phosphorus estimated as magnesium pyrophosphate.

	Grm. subst. taken	Mg ₂ P ₂ O ₇ , found
X.	0.2525	0.0530
XI.	0.2135	0.0399

For the determination of potassium the substance was oxidized with fuming nitric acid in a sealed tube, and potassium estimated as its chloroplatinate.

	Grm. subst. taken	Grm. K ₂ PtCl ₆ , found
XII.	0.3887	0.2986
XIII.	0.4097	0.3454

The percentage composition of the substance is given in the following table.

Constituents.	Calc. for $C_{26}H_{21}O_3$ $S_2N_2PK_2$	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	Mean
Carbon	53.58	54.11	52.94	53.69	—	—	—	—	—	—	—	—	—	—	53.58
Hydrogen	3.63	3.53	3.31	3.57	—	—	—	—	—	—	—	—	—	—	3.47
Nitrogen	4.81	—	—	—	4.98	4.95	5.00	—	—	—	—	—	—	—	4.98
Sulphur	11.01	—	—	—	—	—	—	11.82	12.28	12.24	—	—	—	—	12.17
Phosphorus	5.33	—	—	—	—	—	—	—	—	—	5.86	5.21	—	—	5.54
Potassium	13.42	—	—	—	—	—	—	—	—	—	—	—	12.33	13.26	12.79
Oxygen	8.24	—	—	—	—	—	—	—	—	—	—	—	—	—	7.47 (diff.)

On the Beckmann Rearrangement. IX.