Formation of Tetraazaporphin from Phthalic Anhydride and its Reduced Products

By Masahiro SHIGEMITSU

(Received September 25, 1958)

Phthalic anhydride easily reacts with urea and metallic salts to produce metal phthalocyanine, a kind of tetraazaporphin. Particularly, copper phthalocyanine which is obtained almost quantitatively by the above reaction is one of the most widely used blue organic pigments. But in the case of 3, 4, 5, 6-tetrahydrophthalic anhydride which is the reduced product of phthalic anhydride, the yield of tetraazaporphin is rather small[1].

In the present experiment, the effect of structure of the starting materials on the tetra-azaporphin formation was examined. Phthalic anhydride (I), 3,4,5,6-tetrahydrophthalic anhydride (II), 1,2,3,6-tetrahydro-*cis*-phthalic anhydride (III), hexahydro-*cis*-phthalic anhydride (IV) and 3,6-endomethylene-1,2,3,6-tetrahydro-*cis*-phthalic anhydride (V) were chosen as the examples for the starting materials.

Experimental

Materials.—Phthalic anhydride (I), m. p. 130~131°C. 3,4,5,6-Tetrahydrophthalic anhydride (II) was prepared by reducing phthalic anhydride with sodium-amalgam, m. p. 68~69°C (reported m. p. 68~69°C)[2] (*Anal.* Found: C, 63.09; H, 5.20. Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.26%). 1, 2, 3, 6-Tetrahydro-*cis*-phthalic anhydride (III) was prepared with the aid of Diels-Alder reaction from butadiene and maleic anhydride, m.p. 99~101°C (reported m. p. 99~101°C)[3] (*Anal.* Found: C, 63.08; H, 5.22. Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.26%). Hexahydro-*cis*-phthalic anhydride (IV) was prepared by reducing III with sodium-amalgam, m. p. 33~34°C (reported m. p. 32~33°C)[4] (*Anal.* Found: C, 62.29; H, 6.45. Calcd. for $C_8H_{10}O_3$: C, 62.34; H, 6.49%). 3, 6-Endomethylene-1, 2, 3, 6-tetrahydro-*cis*-phthalic anhydride (V) was prepared with the aid of Diels-Alder reaction from cyclopentadiene and maleic anhydride, m. p. 164~165°C (reported m. p. 164~165°C)[5,6] (*Anal.* Found: C, 65.77; H, 4.91. Calcd. for $C_9H_8O_3$; C, 65.84; H, 4.87%).

Methods.—A mixture of 15 g. of phthalic anhydride or its reduced products, cuprous chloride (1/4 mol. of starting materials as shown in Table I), 60 g. of urea, 0.5 g. of ammonium molybdate and 175 g. of nitrobenzene was heated with stirring. Tow model cases will be shown in relation to the experimental conditions. First, the mixture was stirred at room temperature for 30 min., and then heated up to 150°C during ca. 1 hr. at a definite rate, and finally at 150~155°C for 4 hr. In the second example, the mixture was stirred at room temperature for 30 min., and then heated up to 190°C during ca. 2 hr. at a definite rate, and finally at 190~195°C for 3 hr. After the reaction was completed, nitrobenzene was removed by steam distillation

---

[1] G. E. Ficken and R. P. Linstead, *J. Chem. Soc.*, **1952**, 4846.

[2] A. von Bayer, *Ann.*, **258**, 199 (1890).

[3] L. F. Fieser and E. C. Novells, *J. Am. Chem. Soc.*, **64**, 806 (1942).

[4] A. von Bayer, *Ann.*, **258**, 219 (1890).

[5] D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951).

[6] U. S. Pat. 2,424,948 (1947).

TABLE I. THE CONDITIONS OF REACTION AND THE YIELD OF COLORING MATTERS

Expt.	Starting material (g.)	CuCl (g.)	Temp. (°C)	Rect. prod.		Coloring matter		
				color	wt. (g.)	color	wt. (g.)	yield (%)
1	I, 15.0	2.5	150~155	blue	11.3	blue	11.1	76.0
2	〃 〃	〃	190~195	〃	13.4	〃	13.1	90.5
3	II, 15.0	2.4	150~155	dark brown	9.8	violet blue	0.6	4.1
4	〃 〃	〃	190~195	〃	10.2	〃	0.2	1.4
5	III, 15.0	2.4	150~155	dark brown	11.7	—	—	—
6	〃 〃	〃	190~195	〃	10.6	—	—	—
7	IV, 15.0	2.4	150~155	dark brown	12.4	—	—	—
8	〃 〃	〃	190~195	〃	10.9	—	—	—
9	V, 15.0	2.3	150~155	dark brown	11.2	—	—	—
10	〃 〃	〃	190~195	〃	10.7	—	—	—

and the resulting mixture was heated with 5% hydrochloric acid and then 2% caustic soda, filtered, washed with water and dried at 60~70°C.

When I was used as the starting material, the coloring matter (copper phthalocyanine) was treated with ethanol to remove impurities. In the case of II, the coloring matter (copper tetracyclohexenotetraazaporphin) was extracted from the dark brown product with *o*-dichlorobenzene[7]. In the case of III, IV and V, the coloring matters (tetraazaporphins) could not be obtained by the extraction from the dark brown products with *α*-chloronaphthalene (good solvent of tetraazaporphins) and *o*-dichlorobenzene.

Coloring matters were formed only in the cases of I and II, both of which were of similar blue shades. Reflectance curves concerning these shades of colors were measured with a recording spectrophotometer (General Electric Co.). Samples were prepared in the following way. One part of copper phthalocyanine obtained from I was dissolved in 3 parts of 98% sulfuric acid at room temperature, and was poured into water. Fine crystals deposited were washed with water free from acid and dried at 60~70°C. One part of *β*-form copper phthalocyanine here obtained[8] and copper tetracyclohexenotetraazaporphin obtained from II were mixed respectively with 1.5 parts of polymerized linseed oil and were made into paste by grinding 400 rounds in Hoover automatic muller. To 1 part of this paste was added 70 parts of zinc white paste (obtained by grinding 2 parts of zinc oxide in 1.5 parts of polymerized linseed oil), which was applied in 0.5 mm. thickness on a coated paper with a bladeoapplicator (Gardner Laboratory). These were dried at room temperature and used as samples for measuring reflectance curves.

Results and Discussion

Table I shows the relation between the reaction conditions and the reaction products.

As is seen from Experiments 1 and 2 (Table I), the reaction proceeded easily at a reaction temperature of either 150~155°C or 190~195°C when the reaction was conducted with I as the starting material, copper phthalocyanine being obtained in good yield (*Anal.* Found: C, 66.78; H, 2.90; N, 19.38; Cu, 11.00. Calcd. for $C_{32}H_{16}N_8Cu$: C, 66.72; H, 2.78; N, 19.46; Cu, 11.04%). As is shown by Experiments 3 and 4, the use of II as starting material remarkably reduced the yield of the coloring matter (4.1 and 1.4%, respectively). The coloring matter obtained was copper tetracyclohexenotetraazaporphin (*Anal.* Found: C, 65.02; H, 5.54; N, 18.76; Cu,

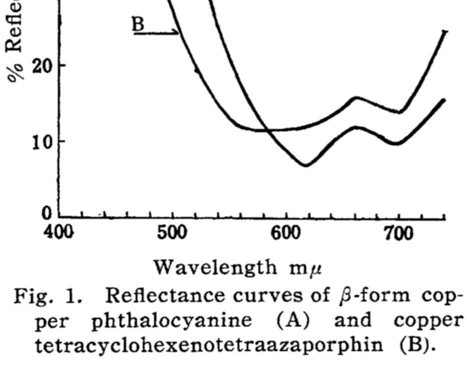

Fig. 1. Reflectance curves of *β*-form copper phthalocyanine (A) and copper tetracyclohexenotetraazaporphin (B).

---

7) British Pat., 686,395 (1953).

8) G. von Susich, *Anal. Chem.*, **22**, 425 (1950).

10.67. Calcd. for $C_{32}H_{32}N_8Cu$; C, 64.91; H, 5.41; N, 18.93; Cu, 10.76%).

While copper phthalocyanine slightly dissolves only in α-chloronaphthalene, copper tetracyclohexenotetraazaporphin easily dissolves in *o*-dichlorobenzene and has a color somewhat more reddish than copper phthalocyanine. Their reflectance curves are shown in Fig. 1 and their C. I. E. Notations are given in Table II. In this table, Y denotes luminosity, P_e purity and λ_D dominant wavelength.

TABLE II. C. I. E. NOTATIONS

Sample	Y%	P_e%	λ_D mμ
A	19.10	55.8	475.8
B	17.00	47.0	470.2

A; Copper phthalocyanine (β-form).
B; Copper tetracyclohexenotetraazaporphin.

The dominant wavelength of copper tetracyclohexenotetraazaporphin is shorter by 5.6 mμ than that of β-form copper phthalocyanine with blue color tinged with red.

In the Experiments 5 and 6 where III, which carries the bond in a different position from that in II, was used as starting material; only alkali-soluble dark brown products were obtained, but coloring matters could not be isolated either by α-chloronaphthalene or *o*-dichlorobenzene.

When IV (Experiments 7 and 8) which has no double bond, and V (Experiments 9 and 10) were used as starting materials, only alkali-soluble dark brown products were obtained without formation of tetraazaporphin. Thus, it was confirmed that, when I is reduced and aromaticity is weakened, or when aromaticity is very small as in the case of V, tetraazaporphin can not be produced. However, when the double bond between carbonyl groups is not reduced, tetraazaporphin is produced, though the yield is small.

In Experiments 1 and 2, higher reaction temperature increased the yield of the coloring matter, but, on the contrary, the increase in the temperature decreased the yield in the Experiments 3 and 4. This may be due to the decomposition of II which on heating over approximately 200°C, gives up carbon dioxide and converts into resinous material of m. p. 50~55°C. Fig. 2 shows infrared spectrum of II and Fig. 3 that of its product obtained by heating. These spectra (in potassium bromide pellet) were obtained with Perkin Elmer 12B instrument.

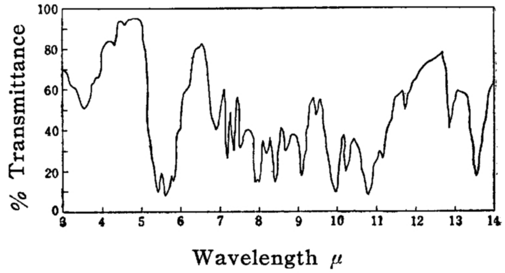

Fig. 2. Infrared spectrum of 3, 4, 5, 6-tetrahydrophthalic anhydride (KBr).

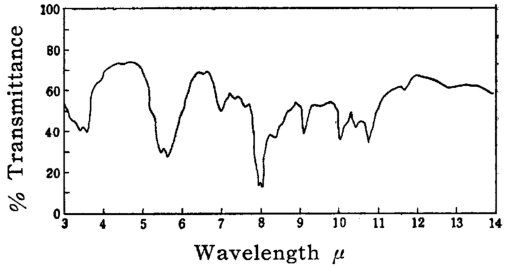

Fig. 3. Infrared spectrum of the product obtained by heating 3, 4, 5, 6-tetrahydrophthalic anhydride (KBr).

In the reaction of II, higher reaction temperature seemed to decrease the yield of the coloring matter and accelerate the conversion into resinous material.

The author gratefully acknowledges the instruction of Dr. Ryozo Goto, Professor of Kyoto University; also Dr. Takahisa Nakamura and Dr. Wataru Ishikawa, Toyo Ink Mfg. Co. The author's thanks are also due to Mr. Ryuichi Kimura, Kyoto University, in measuring the infrared spectra.

Central Research Laboratory
Toyo Ink Mfg. Co.
Sumida-ku, Tokyo