Improved Synthesis of Metal-free Phthalocyanines

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The synthesis of metal-free phthalocyanines is a more formidable task than that of metal phthalocyanines. One route is to prepare a labile metallo compound and subsequently remove the metal. Another method involves heating phthalonitrile, directly, with a tertiary amine (quinoline, dimethylaniline) at 250°, in an atmosphere of ammonia (3). However, at temperatures exceeding 180°, serious side reactions occur, lowering the yield of pigment and introducing considerable impurity, which necessitates recrystallization of the pigment from sulfuric acid. Another method involves the use of alkanolamines in catalytic amounts; however, use of alkanolamines in excess of catalytic amounts lowers the yield of phthalocyanine (4).

High yields of metal-free phthalocyanine were reported from diiminoisoindoline heated in trichlorobenzene (5). In our hands, this method resulted in a low yield of phthalocyanine together with a significant amount of 2,4,6-tri-(*o*-cyanophenyl)-1,3,5-triazine. The latter was identified by m.p., ir, elemental analysis, and by reference

TABLE I

Phthalocyanines from *o*-Dinitriles

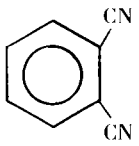
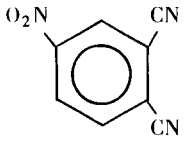
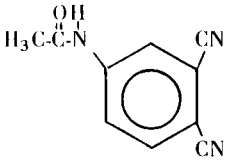
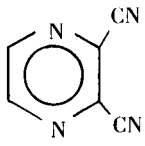
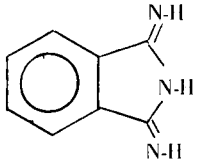
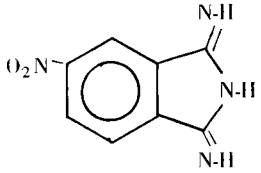
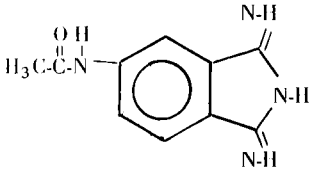
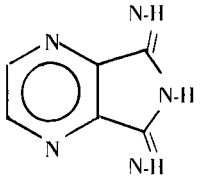
Dinitrile	Melting Point	Solvent	Product	Yield %
	140.5-141.0°	2-dimethylaminoethanol	metal-free phthalocyanine	90
	141.0-141.5°	2-dimethylaminoethanol	tetranitrophthalocyanine	70
	193.5-194.0°	2-dimethylaminoethanol	tetraacetamidophthalocyanine	50
	130.0-131.0°	2-dimethylaminoethanol	none	no reaction

TABLE II

Phthalocyanines from Diiminoisoindolines

Diiminoisoindoline	Melting Point	Solvent	Product	Yield %
	196-197°	2-dimethylaminoethanol	metal-free phthalocyanine	90
	281-282°	2-dimethylaminoethanol	tetranitrophthalocyanine	50
	250-251°	2-dimethylaminoethanol	tetraacetamidophthalocyanine	80
	320°	2-(di-*n*-butyl)aminoethanol	tetrapyrazinoporphyrazine	85

to previous literature (6).

We have found that excellent yields (75-90%) of phthalocyanines can be obtained by heating *ortho*-dinitriles with substantial amounts of the lower alkyl-alkanolamines, namely, 2-dimethylaminoethanol (b.p. 130-132°) or 1-dimethylamino-2-propanol (b.p. 127-128°), in an atmosphere of ammonia. The products obtained have less than 0.1% impurities, by weight, as determined by exhaustive extraction with boiling *N,N*-dimethylformamide for 32 hours. Another indication of purity is the total absence of the C≡N stretching frequency at 2215 cm^{-1}.

An alternate and yet simpler synthesis involves substituted and unsubstituted 1,3-diiminoisoindolines and one pyrazino analogue. These compounds can be heated directly in the aforementioned alkyl alkanolamines but without use of ammonia to yield the corresponding phthalocyanines, again containing less than 0.1% impurities.

The success of the synthesis of phthalocyanines, directly from 1,3-diiminoisoindolines, lends support to the hypothesis that 1,3-diiminoisoindoline is formed as an intermediate in phthalocyanine synthesis (5,7).

The major infrared bands are given for the four metal-free phthalocyanines prepared.

Table I gives the structure and m.p. of the *ortho*-dinitrile compounds, the solvent used and the percent yield of the respective phthalocyanine. Table II gives the data for the 1,3-diiminoisoindoline syntheses.

EXPERIMENTAL

Synthesis of Phthalocyanine.

Method A.

A mixture of phthalonitrile (m.p. 140.5-141.0°, 25 g., 0.195 mole) and 1-dimethylamino-2-propanol (b.p. 127-128°, 100 ml.) was placed in a 4-neck, 500 ml. round-bottom flask, equipped with a mechanical stirrer, reflux condenser, thermometer and gas inlet tube. The suspension was heated to 100° and the phthalonitrile dissolved. A steady stream of ammonia gas was passed into the solution. The temperature was raised to reflux (127-128°) and maintained, along with ammonia introduction, for 7 hours. The bluish-purple precipitate was collected by filtration from the hot

TABLE III

Infrared Spectra (9)

All spectra were determined in Nujol and are reported as cm^{-1}.

β-Phthalocyanine

3290 (w), (N-H stretch), 1505 (m)
1445 (m), 1340 (m), 1325 (m), 1308 (m)
1282 (m), 1122 (m), 1095 (m), 1006 (s)
870 (m), 775 (m), 748 (s), 733 (m)
728 (m), 717 (s), 680 (w), 610 (w)

4,4′,4″,4‴-Tetranitrophthalocyanine

3400 (m), (N-H stretch), 1620 (m)
1530 (s), 1345 (s), 1140 (m), 1105 (m)
1020 (m), 840 (w), 735 (s)

4,4′,4″,4‴-Tetraacetamidophthalocyanine

3300 (broad) (N-H stretch), 1760 (s), 1610 (s)
1550 (s), 1485 (s), 1418 (m), 1345 (m)
1290 (s), 1260 (m), 1095 (m), 1015 (s)
820 (w), 735 (s), 640 (w), 510 (w)

Tetrapyrazinoporphyrazine

3200 (broad) (N-H stretch), 1725 (w)
1670 (s), 1530 (m), 1370 (m), 1300 (w)
1200 (w), 1150 (s), 850 (w), 785 (w)
725 (w), 625 (w),

solvent and washed thoroughly with water or ethyl alcohol and then acetone. The product was air-dried, yield, 22.5 g. (90%).

Anal. Calcd. for $C_{32}H_{18}N_8$: C, 74.70; H, 3.53; N, 21.77. Found: C, 74.76; H, 3.58; N, 21.74.

Method B.

A mixture of 1,3-diiminoisoindoline (20.0 g., 0.138 mole) and 2-dimethylaminoethanol (b.p. 130-135°, 100 ml.) was refluxed with stirring for 7 hours, during which ammonia was evolved. The mixture was filtered hot and the purple crystals of phthalocyanine were washed thoroughly with ethanol and then acetone. The product was vacuum dried at 80° for 3 hours, yield, 15.1 g. (85.5%).

Anal. Calcd. for $C_{32}H_{18}N_8$: C, 74.70; H, 3.53; N, 21.77. Found: C, 74.69; H, 3.49; N, 21.68.

Upon cooling the alkanolamine filtrate, a precipitate formed. The light brown crystals were removed by filtration, washed with cold ethyl alcohol and recrystallized from acetone giving greenish-white needles of 2,4,6-tri-(*o*-cyanophenyl)-1,3,5-triazine, yield, 2.0 g., m.p. 298.5-300.0°.

Anal. Calcd. for $C_{24}H_{12}N_6$: C, 75.0; H, 3.13; N, 21.87. Found: C, 74.97; H, 3.16; N, 21.74.

Synthesis of 1,3-Diiminoisoindolines.

All of the 1,3-diiminoisoindolines were made according to the method of which the following is a specific example:

Pyrazine Analog of 1,3-Diiminoisoindoline (5,7-Diimino-6*H*-pyrrolo[3,4-*b*]pyrazine).

Pyrazine-2,3-dinitrile (8) (2.5 g.), sodium methylate (0.2 g.) and methanol (50 ml.) were stirred together at room temperature for 1 hour while bubbling a rapid stream of anhydrous ammonia through the system. The temperature was raised to reflux with continuous passage of ammonia for 3 hours. During this period a light grey material precipitated. The suspension was filtered hot and the product washed several times with methanol and air dried, yield, 2.7 g. (96.5%) of a light grey material which would not melt at 320°.

Anal. Calcd. for $C_6H_5N_5$: C, 48.8; H, 3.4; N, 47.7. Found: C, 48.4; H, 3.5; N, 48.0.

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REFERENCES

(1) Present address: Economics Laboratory, Inc., St. Paul, Minnesota.

(2) Present address: c/o Samual Weinberger, 92 W. 34th St., Bayonne, New Jersey.

(3) I. M. Heilbron, U. S. Patent 2,153,620 (4/11/39).

(4) A. R. Lowe, U. S. Patent 2,155,954 (4/18/39).

(5) V. F. Borodkin and R. P. Smirnov, *Izv. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Teknol,* **4**, 287 (1961).

(6) D. S. Ross and M. Fineman, *J. Am. Chem. Soc.*, 72, 3302 (1950).

(7) F. H. Moser and A. L. Thomas, "Phthalocyanine Compounds," Reinhold Publishing Company, 1963, New York, p. 107.

(8) N. R. Patel and R. N. Castle, *J. Heterocyclic Chem.*, 3, 512 (1966).

(9) Beckman IR-10 spectrophotometer.

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