Acknowledgments. The preparation of these compounds was conducted under the sponsorship of the United States Air Force under Contract AF 33(600)-32448, monitored by Materials Laboratory, Director of Laboratory, Wright Air Development Center, Wright-Patterson AFB, Ohio. The authors also wish to express their gratitude to Dr. Harold Rosenberg for his helpful advice.

DEARBORN, MICH.

[RESEARCH DIVISION CONTRIBUTION NO. 275, JACKSON LABORATORY ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

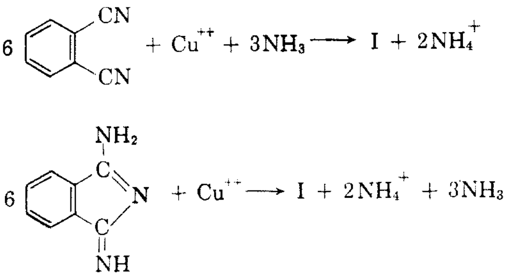
Chemistry of Copper Phthalocyanine Precursor

R. A. BROOKS, J. G. BURT, B. F. SKILES, AND M. S. WHELEN

Received October 1, 1958

The preparation and properties of a precursor of formula $C_{48}H_{25}N_{13}Cu$ which generates copper phthalocyanine upon reduction are discussed. A structure for the precursor is proposed.

Copper phthalocyanine precursor is the name given to a buff colored compound I of empirical formula $C_{48}H_{25}N_{13}Cu$ which generates copper phthalocyanine (II) upon reduction. I is formed by reaction under oxidizing conditions of phthalonitrile, ammonia and a cupric salt in dimethylformamide at about 90° or by reaction of 1-amino-3-iminoisoindolenine and a cupric salt under similar conditions. The yield by the phthalonitrile route is improved by the addition of a small amount of *N*-methylglucamine, the role of which has not been determined.



I is very soluble in dimethylformamide and in alcoholic solvents such as ethylene glycol monoethyl ether. It has limited solubility in benzene and is insoluble in aliphatic hydrocarbons. I is usually amorphous but can be crystallized from benzene. Stirring in a small amount of methyl alcohol also converts the amorphous material to a crystalline form[1] the x-ray diffraction pattern of which is reproduced in Fig. 1.

Unlike II, which is highly colored, I exhibits only very weak absorption in the visible region of the spectrum. The ultraviolet and infrared spectra are reproduced in Figs. 2 and 3, respectively.

When in crystalline form, I is quite stable and can be stored for long periods at room temperature. Its solutions decompose in a few days, especially in sunlight, to give copper phthalocyanine and other products of lower molecular weight.

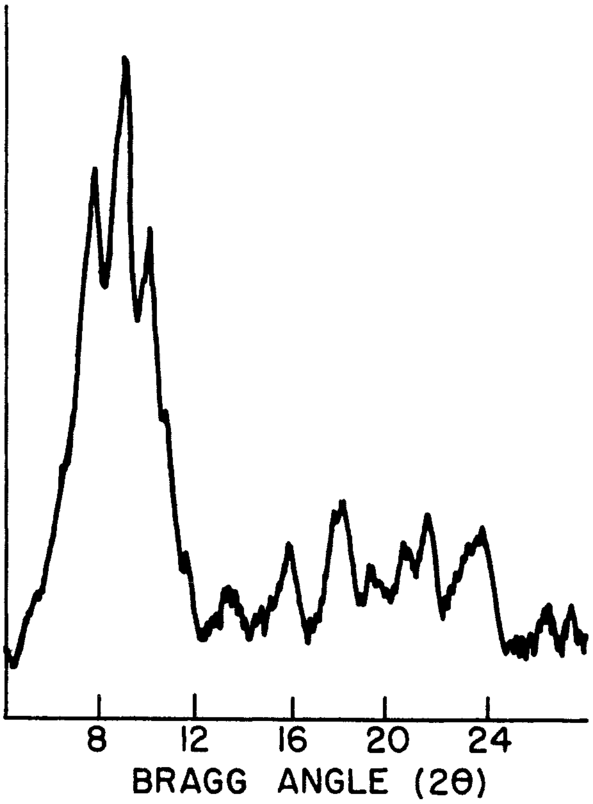


Fig. 1. X-ray diffraction pattern of copper phthalocyanine precursor

Reduction of I is easily effected with a large number of agents. The weight yield of II is 68%, the remaining weight being accounted for as ammonia and derivatives of phthalic acid. Hydrogenation over palladium indicates that reduction is a 2 electron process. Reduction with hot, alkaline glucose shows that 5 moles of ammonia are liberated. Pyrolysis of I at 180° gives about a 65% yield of II with liberation of 1 mole of ammonia and 2 moles of phthalonitrile. The slightly lowered

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(1) M. S. Whelen, U.S. Patent 2,795,586, June 11, 1957; *Chem. Abstr.*, 51, 17184 (1957).

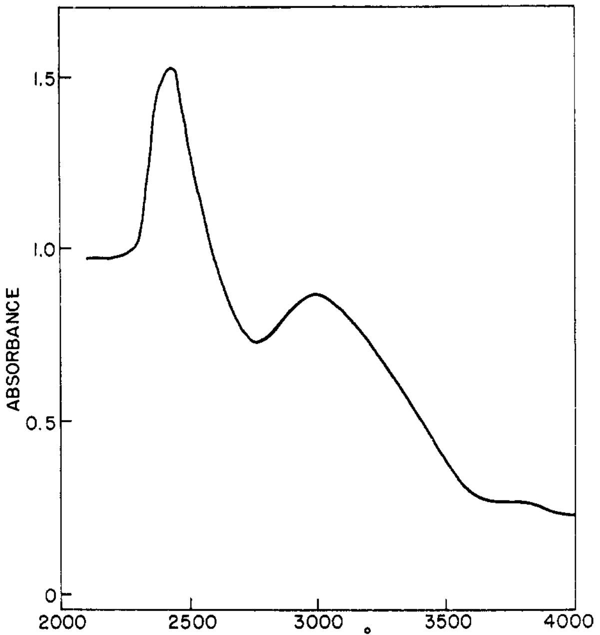

Fig. 2. Ultraviolet spectrum of copper phthalocyanine precursor. Chloroform solvent, 0.0134 mg./ml.

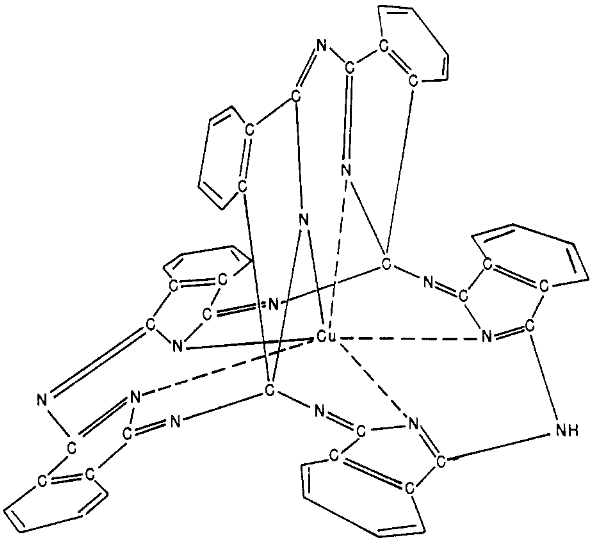

Fig. 4. Copper phthalocyanine precursor

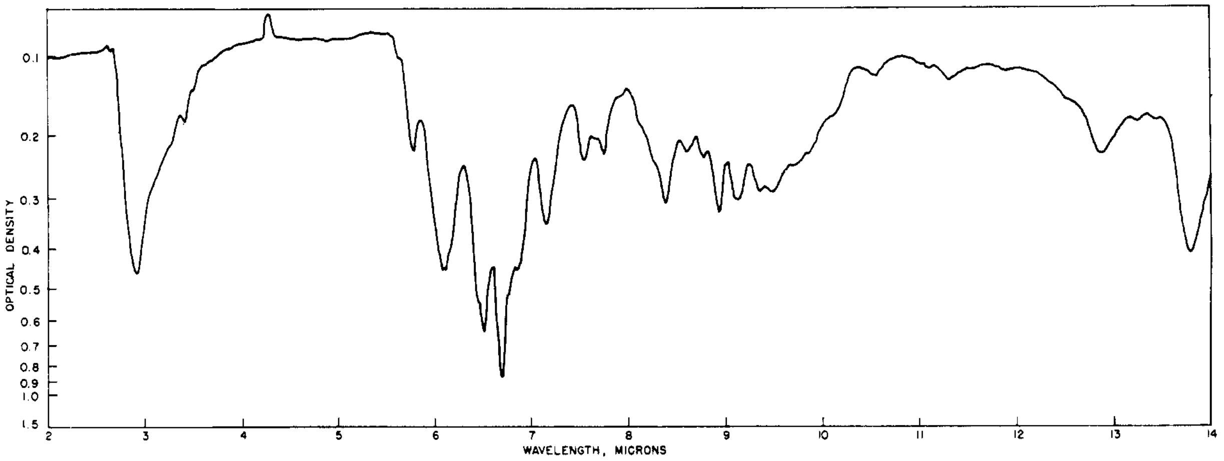

Fig. 3. Infrared spectrum of copper phthalocyanine precursor, KBr disk, NaCl prism

yield of II suggests that autoreduction has taken place.

On the basis of its reactions and a study of molecular models, it is concluded that I is a condensation polymer of 1-amino-3-iminoisoindolenine containing bound copper. A triplanar structure, as shown in Fig. 4, has been suggested[2] to explain the solubility and weak color. This structure cannot be considered as proven and alternatives can be written, for example, an open chain structure. It is felt, however, that the triplanar cage structure is supported by all known facts and serves best to explain the properties of I. A similar structure has been proposed for a pyridine complex of a copper-containing polymer of 1-amino-3-iminoisoindolenine.[3]

EXPERIMENTAL

Copper phthalocyanine precursor (I) was prepared from phthalonitrile by the method of Barnhart, Skiles, and Stevenson.[4] The product was obtained as a buff colored powder which slowly turned green upon heating over 100° but had no definite melting point. A sample was crystallized from benzene.

Anal. Calcd. for $C_{48}H_{25}N_{13}Cu$: C, 68.0; H, 2.97; N, 21.5; Cu, 7.50. Found: C, 67.5, 67.7; H, 2.84, 3.21; N, 21.5, 21.4; Cu, 7.43, 7.77.

Reduction of 0.760 g. (0.0009 mole) of I over palladium in methanol required 24.1 ml. (0.0009 mole) of hydrogen at 25°. The reduction products included 0.520 g. (0.0009 mole) of copper phthalocyanine (II) and 0.015 g. (0.0009 mole) of ammonia.

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(2) G. Barnhart, B. F. Skiles, and A. C. Stevenson, French Patent **1,068,092**, June 22,1954.

(3) F. Baumann, B. Bienert, G. Rosch, H. Vollmann, and W. Wolf, *Angew. Chem.*, **68**, 133 (1956).

(4) G. Barnhart, B. F. Skiles, and A. C. Stevenson, British Patent **745,359**, Feb. 22, 1956; *Chem. Abstr.*, **50**, 12491 (1956).

Reduction of 8.47 g. (0.01 mole) of I with excess alkaline glucose at 80° gave 5.77 g. (0.01 mole) of copper phthalocyanine (II) with the liberation of 0.85 g. (0.05 mole) of ammonia. A fluorescein test on the residue indicated the presence of phthalic acid or a derivative.

Pyrolysis of 8.47 g. (0.01 mole) of I at 180° gave 5.50 g. (0.0009 mole) of copper phthalocyanine (II) and 0.17 g. (0.01 mole) of ammonia. Phthalonitrile, m.p. 141°, sublimed and was collected; yield 2.56 g. (0.02 mole).

1-Amino-3-iminoisoindolenine. Phthalonitrile (128 g., 1.0 mole) and liquid ammonia (119 g., 7.0 moles) were placed in a 400-ml. stainless steel pressure vessel sealed with an aluminum gasket. The vessel was heated to 150° and shaken at that temperature for 5 hr. at about 500 p.s.i.g. It was then cooled, vented, and the product was discharged; yield 145 g. (100%). Titration with hydrochloric acid to an endpoint at *p*H 5.25, assuming monobasicity, indicated a purity of 99%.

Anal. Calcd. for $C_8H_7N_3$: C, 66.2; H, 4.83; N, 28.9. Found: C, 65.7, 65.9; H, 4.88, 4.76; N, 28.3; 28.2.

A sample of 1-amino-3-iminoisoindolenine was converted to I by the method of Brooks.[5] The product was identical to that prepared from phthalonitrile.

WILMINGTON 99, DEL.

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[5] R. A. Brooks, U.S. Patent **2,772,285,** Nov. 22, 1956; *Chem. Abstr.*, **50,** 17464 (1956).

[CONTRIBUTION FROM THE McPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

New Reactions on Decomposition of a Hindered α-Diazoketone[1]

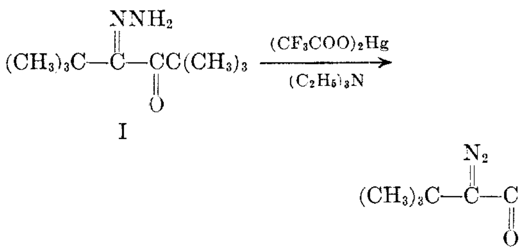
MELVIN S. NEWMAN AND A. ARKELL[2]

Received October 6, 1958

A new procedure for the conversion of monohydrazones of α-diketones to α-diazoketones by oxidation of the hydrazone with mercuric trifluoroacetate in acetonitrile in the presence of triethylamine is described. The rearrangements of 4-diazo-2,2,5,5-tetramethyl-3-hexanone under several conditions are described. The main product of these rearrangements is 2,2,4,5-tetramethyl-4-hexen-3-one, a product in which a methyl migration has occurred.

In connection with work on the synthesis of highly hindered aliphatic compounds we wished to prepare a quantity of di-*t*-butylacetic acid as it represents a disubstituted acetic acid with a *six number*[3] of eighteen. One method which appeared promising was the pyrolysis of 4-diazo,2,2,5,5-tetramethyl-3-hexanone, II, to di-*t*-butylketene (III)[4] a compound which would be expected to yield di-*t*-butylacetic acid on hydration.

The preparation of II was accomplished by a new method which involved oxidation of the monohydrazone of dipivaloyl (I) with mercuric trifluoroacetate and triethylamine in acetonitrile at room temperature. During this treatment about 20% of the theoretical amount of nitrogen to be expected from the diazoketone was evolved.



$$(CH_3)_3C-\overset{\overset{NNH_2}{\|}}{C}-\underset{\underset{O}{\|}}{C}C(CH_3)_3 \xrightarrow[(C_2H_5)_3N]{(CF_3COO)_2Hg} (CH_3)_3C-\overset{\overset{N_2}{\|}}{C}-\underset{\underset{O}{\|}}{C}C(CH_3)_3$$

I

II

The entire reaction mixture thus obtained was then treated by three methods in attempts to obtain III. However, only minute amounts (0–3%) of ketene (III) were obtained by heating, either alone or in solvents, by treatment with boron trifluoride etherate, or by irradiation with ultraviolet light at 40°. The small amount of III obtained in any experiment precluded its isolation in sufficient quantity for analysis. However, by means of gas chromatography a homogeneous fraction was isolated which was undoubtedly the ketene (III) as judged by strong infrared absorption bands at 4.83μ and 5.80μ. This ketene III appears to be much more stable than other aliphatic ketenes, as no great tendency to dimerization was apparent. Because of the low yields of III obtained in spite of many attempts at improvement, this method for the synthesis of di-*t*-butylacetic acid was abandoned.[5]

Although the original purpose was not attained, the rearrangements of the diazoketone, II, produced results of interest. These are outlined in Chart 1.

The major product of pyrolysis (or irradiation, or acid-catalyzed rearrangement) was 2,2,4,5-tetramethyl-4-hexen-3-one (IV). In addition small amounts of 2,2,4,5-tetramethyl-5-hexen-3-one (V) and of a saturated (hence cyclic) ketone, $C_{10}H_{18}O$-(VI) were formed. In both IV and V a carbon skele-

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[1] The material herein presented was taken from the Ph.D. thesis, Ohio State University, 1958, of A. Arkell.

[2] This research was supported in part by the United States Air Force under Contract No. AF33(616)-3412, monitored by the Aeronautical Research Laboratory, Wright Air Development Center.

[3] M. S. Newman, *J. Am. Chem. Soc.*, **72,** 4783 (1950); K. L. Loening, A. B. Garrett, and M. S. Newman, *J. Am. Chem. Soc.*, **74,** 3929 (1952).

[4] For an example of the rearrangement of a *t*-butyl group in the decomposition of a diazoketone, see K. B. Wiberg and T. W. Hutton, *J. Am. Chem. Soc.*, **76,** 5367 (1954).

[5] The synthesis of di-*t*-butylacetic acid in good yield by another method will soon be reported.