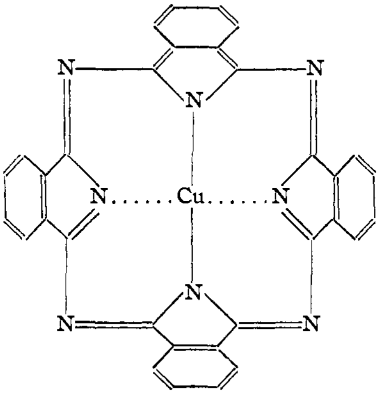
[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CALCO CHEMICAL DIVISION, AMERICAN CYANAMID COMPANY]

Some Observations on the Formation of Copper Phthalocyanine

BY H. Z. LECHER, H. T. LACEY AND H. P. OREM

Henri de Diesbach and Edmond von der Weid[1] were the first ones to observe the formation of a blue pigment when a pyridine solution of phthalonitrile and cuprous bromide was heated. However, the Swiss authors did not find the correct formula and structure of this substance. Later, R. P. Linstead and his associates[2] in their fundamental work determined that it is copper phthalocyanine (copper tetrabenzo-tetraza-porphine), having the structure



A large number of papers and patents have issued since and give evidence of the great scientific and practical importance of this new group of pigments.

During an investigation, originally started for technical purposes, we made some observations of theoretical interest which later might throw some light on the mechanism of the pigment formation from phthalonitrile. In repeating the preparation of the pigment from phthalonitrile and cuprous halides in pyridine, we had difficulty in obtaining reproducible results. There were indications that the quality of the pyridine and of the cuprous halide play their part, but even with very pure materials the results varied considerably and it was soon found that the supply of *air* had a decisive influence.

Thus, under otherwise equal conditions, pure cuprous chloride and phthalonitrile in boiling pyridine gave practically no pigment in an atmosphere of nitrogen, gave a 48.2% yield in an atmosphere of air, and gave an 82% yield in a current of air. Similar observations were made when cuprous bromide and cuprous iodide were used.

The hypothesis that oxygen or a peroxide directly initiates the polymerization of phthalonitrile in these experiments had to be discarded when we found that the solution of cuprous halide in pyridine could be pretreated with oxygen and that such a solution—which does not contain peroxides—would form the pigment also under nitrogen.

According to Linstead[3] the formation of copper phthalocyanine from phthalonitrile and cuprous chloride follows the equation

$$4C_6H_4(CN)_2 + 2CuCl = C_{32}H_{16}N_8Cu + CuCl_2$$

In other words, four molecules of phthalonitrile are reduced by the combination with one atom of copper, while half of the cuprous chloride is oxidized to form one molecule of cupric chloride. The cupric chloride supposedly does not take part in the pigment formation unless higher temperatures (above 200°) are applied. In the latter case, however, something else happens: the cupric chloride acts as a chlorinating agent to give a chlorinated derivative of copper phthalocyanine

$$4C_6H_4(CN)_2 + CuCl_2 = C_{32}H_{15}N_8ClCu + HCl$$

Dent and Linstead conclude that "the readiness with which cuprous chloride combines with phthalonitrile is due, without doubt, to the ease with which it can supply metallic copper, whereas the only way in which cupric chloride can act as a source of copper is by losing chlorine simultaneously."

From this it would appear that what is needed for the formation of copper phthalocyanine itself is cuprous halide and that cupric halide is but an undesirable by-product if a non-halogenated pigment is desired. This interpretation, however, is not applicable at least to reactions in boiling pyridine since pure cuprous halides in this solvent do not form the pigment when air is excluded. We found also that copper powder does not react with a boiling solution of phthalonitrile in py-

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(1) de Diesbach and von der Weid, *Helv. Chim. Acta*, **10**, 886 (1927).

(2) C. E. Dent, R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, 1033 (1934).

(3) C. E. Dent and R. P. Linstead, *ibid.*, 1027 (1934).

ridine in the absence of air, but does so when air is supplied.

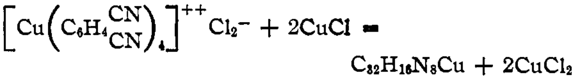
The reactions of phthalonitrile with metallic copper or with cuprous halides are rather exothermic and difficult to control when no solvent is used; they also require a comparatively high starting temperature. Therefore, we have carried out all our experiments in boiling pyridine, which not only facilitates the regulation of the reaction and ensures a proper reproducibility, but has the additional advantage, as compared with other solvents, that it dissolves also the cuprous halides. Though we have no definite proof that the conclusions reached may also be applied to the formation of copper phthalocyanine from phthalonitrile under different conditions, *e. g.*, in other diluents or without diluents at all, we do have indications that even the reaction of phthalonitrile and metallic copper without diluent is influenced by the presence of air or cupric oxide.

Cuprous chloride, bromide and iodide are all rather soluble in pyridine, the bromide more than the chloride and the iodide more than the bromide. The bright yellow solutions are stable when air is excluded. However, oxygen or air oxidize the solutions quickly. They turn dark and give a mixture of cupric compounds; voluminous blue or green precipitates of cupric halide-pyridine complexes are formed. We have determined that for 2 molecules of cuprous halide 1 atom of oxygen is absorbed. The cuprous iodide solution is slower to oxidize than the others. This oxidation very probably follows the equation:

$$2CuHlg + O + 2C_5H_5N = CuHlg_2{\cdot}2C_5H_5N + CuO$$

In the case of cuprous bromide the compound $CuBr_2{\cdot}2C_5H_5N$ has been isolated in 86.5% yield and has been analyzed. In the case of cuprous chloride it was difficult to obtain the precipitated oxidation product in pure form. In the case of cuprous iodide the precipitate very probably consisted of the compound $CuI_2{\cdot}2C_5H_5N$, but this compound is rather unstable and gives off iodine and pyridine when dried. This is not surprising since cupric iodide has never been isolated as such, but only in the form of a few complex compounds. The complexes of cupric chloride and bromide with 2 pyridine have been described by W. Lang[4] and P. Pfeiffer and V. Pimmer.[5] The mother liquors probably contain mainly colloidal cupric oxide, but their properties are such that no well defined compound could be isolated. Thus, it is evident that by passing air through a pyridine solution of cuprous halide a gradual conversion into a mixture of cupric compounds takes place, this mixture containing cupric halide, cupric oxide and possibly a cupric oxyhalide.

It therefore seems that cuprous halides—at least in pyridine solution—are not capable of reacting with phthalonitrile, but that it is the cupric compounds which react with phthalonitrile in the first phase. It is quite possible that this first phase consists in the formation of a complex $[Cu(C_6H_4(CN)_2)_4]^{++}X^{--}$ where X stands for oxygen or a bivalent anion or two monovalent anions. The formation of the pigment requires that this X be disposed of in some way or the other by a mild reducing agent. This reducing agent should not be strong enough to reduce cupric compounds to cuprous compounds because this would prevent the pigment formation. Linstead had found that in the case of cupric chloride the pigment itself might function as the reducing agent at high temperature, in that it is chlorinated. Another very suitable mild reducing agent or halogen acceptor is, obviously, cuprous chloride, the action of which we are inclined to formulate as follows:



$$\left[Cu\left(C_6H_4\begin{matrix}CN\\CN\end{matrix}\right)_4\right]^{++}Cl_2^{-} + 2CuCl = C_{32}H_{16}N_8Cu + 2CuCl_2$$

From this equation it will become apparent that when a small amount of cupric halide is brought into reaction with phthalonitrile in the presence of a large amount of cuprous halide the amount of cupric halide is doubled each time one molecule of pigment is formed and that therefore any appreciable amount of cupric chloride originally present will be sufficient to get the reaction started and keep it going. Thus, the usual contamination of cuprous chloride and bromide by cupric compounds gives the answer to the obvious question as to why the influence of air or of the presence of cupric compounds on the reaction of cuprous halides with phthalonitrile has not been observed before.

The ease with which cupric compounds react with phthalonitrile in boiling pyridine seems to be influenced also by their dispersion. A very active, finely dispersed form of cupric oxide is obtained by passing air through a slurry of

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(4) Lang, *Ber.*, **21**, 1578 (1888).

(5) Pfeiffer and Pimmer, *Z. anorg. allgem. Chem.*, **48**, 98 (1905).

copper bronze in boiling pyridine. Also when a pyridine solution of cuprous halide is oxidized by oxygen a colloidal solution of cupric oxide in pyridine is obtained. Either form reacts very readily with phthalonitrile to form the pigment. Cupric oxide in a coarser form or cupric hydroxide are much slower to react and cupric chloride—which forms a difficultly soluble complex with pyridine—is the slowest. In all these cases where cupric compounds react with phthalonitrile in boiling pyridine and no other mild reducing agent such as a cuprous compound is present, part of the phthalonitrile or of the pigment has to assume the function of a reducing agent and is destroyed and therefore the yield is considerably decreased. Obviously, copper powder may be used in conjunction with cupric chloride as the reducing agent, provided that not sufficient is used to convert all of the cupric halide into cuprous halide.

One word more may be added about the formation of the pigment from copper iodide. Phthalonitrile does not react with cuprous iodide in boiling pyridine if air is carefully excluded. However, in the presence of air, pigment formation takes place very readily. While in the case of cuprous chloride and cuprous bromide the reaction may be started either by air or by the corresponding cupric halide, in the case of cuprous iodide air is much more effective than the addition of iodine. While iodine probably forms to a certain extent the cupric iodide–pyridine complex, this tends to dissociate and therefore the pigment formation is sluggish. Air, on the other hand, forms with cupric iodide the colloidal cupric oxide in the same manner as it does with cuprous chloride and bromide and therefore the reaction in the presence of air is much faster than in the presence of some iodine. When cuprous iodide reacts with phthalonitrile in boiling pyridine in the presence of air most of the iodine is used up in iodinating pyridine.

It was beyond the intended scope of this work, originally started for industrial purposes, to go into a broader investigation of all the theoretical aspects of our findings.

Experimental Part

Experiments Showing the Influence of Oxygen on the Reaction of Cuprous Halide and Phthalonitrile in Boiling Pyridine.—25.6 Grams of phthalonitrile (4 molar equivalents) and 10 g. of freshly prepared, pure cuprous chloride (2 molar equivalents) reacted in 80 cc. of dry pyridine under varied conditions. In each case the mixture was refluxed for eight hours while it was stirred.

In the first experiment the air was replaced by oxygen-free nitrogen before the heating was started and the nitrogen was passed continuously through the reaction flask. The nitrogen was freed from oxygen by passing it over heated copper. There was no apparent reaction during the first hour of heating. Later after six to seven hours the liquid gradually darkened. The very small amount of pigment formed was filtered off, washed with hot dilute hydrochloric acid, with hot water and with acetone. It was purified by dissolving it in concentrated sulfuric acid and reprecipitating it in water. Note that the same procedure of separation and purification was followed in all other experiments described in this paper. The yield in this experiment was only 0.7%.

In the second parallel experiment the air was left in the flask, but no air was passed through. The yield of pure pigment was 48.2%.

In the third parallel experiment air was passed through the flask continuously and the yield obtained was 82% of the theoretical on pure pigment.

In another series of parallel experiments cuprous iodide was used. In this case the mixture was refluxed for only one hour, which was probably too short. Nevertheless, the difference in the parallel experiments was very striking.

In the first experiment a solution of 35 g. of phthalonitrile (4 molar equivalents) and 14.3 g. of cuprous iodide (1.1 molar equivalents) in 210 cc. of pure pyridine was refluxed for one hour in an atmosphere of nitrogen: no pigment formed at all. Then the nitrogen was replaced by air and refluxing continued in a stream of air for another hour. After this time 46.6% of the theoretical on pure pigment was isolated. When, all other conditions being the same, more cuprous iodide, namely, 37.1 g. (2.85 molar equivalents) was used and air was passed through the reaction flask, the yield on pure pigment was raised to 87.3%.

Experiments Dealing with the Action of Oxygen on Cuprous Halide Solutions in Pyridine.—Dry oxygen was passed through 200 cc. of dry pyridine. Then while the pyridine was stirred a solution of 4.0 g. of pure cuprous bromide in 150 cc. of dry pyridine was dropped in slowly over a period of two hours. The solution darkened as oxidation took place. The mixture was then heated at 90–100° for three hours while oxygen was bubbled through. After cooling, the separated dark green crystals were filtered off, washed with pyridine and dried over sulfuric acid under reduced pressure; yield 4.6 g. or 86.5%.

Anal. Calcd. for $CuBr_2 \cdot 2C_5H_5N$: C, 31.5; H, 2.6; N, 7.4; Cu, 16.6; Br, 42.0. Found: C, 31.5; H, 2.6; N, 7.9; Cu, 16.9; Br, 41.3.

The material left in the mother liquor had very unpleasant properties and could not be isolated in a state suitable for analysis. Very probably the mother liquor contained either a colloidal pyridine complex of cupric oxide or colloidal cupric oxide; in addition there might have been some cupric oxybromide present.

The oxygen absorption was determined in the following manner: a three-necked, round-bottom flask was fitted with a mercury-seal stirrer. One of the necks was connected with the top of an azotometer. Another neck was used for the introduction of the materials and was stoppered during the experiment. Only glass connections and ground glass joints and stoppers were used. The air was replaced by oxygen. Then the dry pyridine and the pure cuprous bromide were introduced, the latter in a floating glass boat. The equipment was closed, the azotometer adjusted and the stirrer started. The boat capsized and the cuprous bromide dissolved. The cuprous bromide solution obtained was about 1%. The gas absorption stopped after about eighty hours and then corresponded to 101.7%. A blank run without cuprous bromide gave a negligible oxygen consumption. The experiment was carried out at an approximately constant temperature of 25°.

An analogous experiment with cuprous chloride showed essentially the same behavior. However, the products of the reaction were less homogeneous and more difficult to isolate. The oxygen absorption was measured as described above for cuprous bromide. It stopped after about seventy-one hours and then equalled 98.7%. It was also proved that cupric chloride in pyridine does not absorb oxygen.

Oxygen was bubbled through a solution of 8 g. of cuprous iodide in 150 g. of dry pyridine. The mixture was then heated at 90° for two hours and cooled afterward. All the time a current of oxygen was bubbled through and the liquid was stirred. As in the case of the chloride and the bromide a dark precipitate separated. It was filtered off and washed with pyridine and dried on a porous plate at room temperature. Even there it gave off iodine and pyridine and therefore it seems that the complex $CuI_2 \cdot 2C_5H_5N$ is rather unstable.

The oxygen absorption of a pyridine solution of cuprous iodide is much slower than that of a cuprous chloride or cuprous bromide solution. No quantitative measurements were made since only 10% of the theoretical was absorbed at room temperature within twenty hours.

Experiments Concerning the Pigment Formation from Cupric Compounds and Phthalonitrile in Boiling Pyridine.—The following experiments were carried out under similar conditions: each reaction mixture was refluxed for eight hours and worked up as usual. Obviously air was not excluded in any of these experiments.

In this experiment a mixture containing 7.5 g. of anhydrous cupric chloride (1.1 molar equivalent), 25.6 g. (4 molar equivalents) of phthalonitrile and 40 cc. of dry pyridine was used. Very little reaction took place during the first hour and a half, then the mixture gradually darkened and some pigment formed. The yield was only 8.3% of the theory. The pigment obtained contained only a trace of chlorine. This experiment shows that cupric chloride alone is very sluggish to react if there is no mild reducing agent or halogen acceptor present.

Cupric hydroxide was prepared from 24.9 g. (2 molar equivalents) of cupric sulfate pentahydrate and was finally washed with dry pyridine. The reaction mixture contained 25.6 g. (4 molar equivalents) of phthalonitrile and 80 cc. of pyridine. The pigment yield was somewhat higher than with the chloride in spite of the greater dilution, namely, 20.7%.

A mixture containing 4.4 g. (1.1 molar equivalents) of commercial cupric oxide powder, 0.75 g. (0.11 molar equivalent) of anhydrous cupric chloride, 25.6 g. (4 molar equivalents) of phthalonitrile and 40 cc. of dry pyridine was used: pigment yield 61.5%. The same experiment with cupric oxide only and no cupric chloride present gave only 12.5% yield and the same experiment with the inverse ratio, namely, with 0.44 g. cupric oxide and 7.5 g. cupric chloride gave 28.3%. It seems that the simultaneous presence of cupric oxide and cupric chloride is favorable.

The cupric oxychloride having the formula $CuCl_2 \cdot 3CuO \cdot 4H_2O$ was prepared according to H. P. Rocksby and R. C. Chirnside[6] and was dehydrated azeotropically in boiling nitrobenzene. The product obtained was filtered, washed with benzene and dried at 110°. A mixture containing 7.6 g. (1.1 molar equivalents) of this compound and 31 g. (12 molar equivalents) phthalonitrile and 40 cc. of dry pyridine was used; yield 71%. However, the higher concentration in this experiment should be noted.

A solution of 105 g. (2.1 molar equivalents) of cuprous chloride and 25.6 g. (4 molar equivalents) of phthalonitrile in 80 cc. pyridine was saturated with oxygen to completely oxidize the cuprous halide. Then the oxygen in the flask was displaced by nitrogen and the mixture was refluxed for eight hours in an atmosphere of nitrogen. The yield was 80% pigment which, however, in this case had not been purified by sulfuric acid.

In this experiment the cupric oxide was produced during the reaction from copper bronze. A mixture containing 102.4 g. (4 molar equivalents) phthalonitrile, 13.1 g. (1.03 atom equivalent) copper bronze and 150 g. of dry pyridine was refluxed for eight hours in a current of air. The yield on pure pigment was 74.5%. A similar experiment in which no air was passed through did not give any pigment.

The following experiment deals with the formation of the pigment from the hypothetical cupric iodide–pyridine complex. A solution of 41 g. (3 molar equivalents) cuprous iodide in 210 cc. pyridine containing 7.6 g. (0.5 molar equivalent) iodine was heated in an atmosphere of nitrogen. Then 35 g. (4 molar equivalents) of phthalonitrile was introduced and the refluxing in a current of nitrogen was continued for one hour. The yield on pure pigment was only 14.3% while the same experiment without iodine, but in a current of air, as described above, had given 87.3% yield.

Summary

Pure cuprous halides or copper powder do not react with phthalonitrile in boiling pyridine if air is excluded.

Oxygen oxidizes cuprous halides dissolved in pyridine. Cupric halide–pyridine complexes precipitate and a colloidal solution of cupric oxide is formed. Besides, cupric oxyhalides might be present.

Oxygen oxidizes copper powder suspended in boiling pyridine.

The conversion of phthalonitrile into copper phthalocyanine in boiling pyridine requires cupric compounds, preferably in the presence of a mild reducing agent such as cuprous halide or

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[6] Rocksby and Chirnside, *J. Soc. Chem. Ind.*, **53**, 33–5T (1934).

copper. Cuprous halides in the presence of oxygen are reactive. So are finely dispersed cupric oxide, cupric oxyhalides or mixtures of cupric halides and cupric oxide. In the absence of any reducing agent part of the pigment formed assumes this function.

BOUND BROOK, NEW JERSEY

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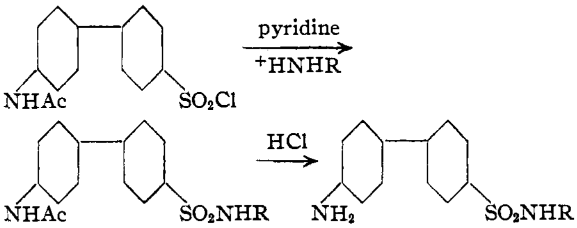
p-(*p*-Aminophenyl)-benzenesulfonamide and Derivatives. II

BY C. T. VAN METER AND ALEXANDER LOWY

Utilizing methods analogous to those employed in the benzene series, the preparation of the parent molecule in the biphenyl series has been described in a previous article.[1] The purpose of this work was to prepare some derivatives in which one of the hydrogens on the sulfonamide nitrogen has been replaced.

In the benzene series, such substituted sulfanilamide derivatives are commonly prepared by coupling the *p*-acetamidobenzenesulfonyl chloride with amino compounds containing the desired substituents, and then deacetylating. Various methods have been utilized to effect removal of the hydrogen chloride from the coupling components.[2] The analogous sulfonyl chloride in the biphenyl series having been prepared in good yield,[1] the formation of such substituted derivatives was investigated. The general reaction may be represented as



The amino compounds used in preparing this series of derivatives were: (1) aniline, (2) benzylamine, (3) cyclohexylamine, (4) *p*-xenylamine, (5) sulfanilamide, and (6) *p*-(*p*-aminophenyl)-benzenesulfonamide.

Experimental

Except for minor differences in concentrations of reactants and conditions for recrystallization and deacetylation, the procedure was essentially the same for all derivatives. The following experimental details for preparing the phenyl derivative are offered as typical.

Five grams of pure *p*-(*p*-acetamidophenyl)-benzenesulfonyl chloride[1] was dissolved by warming in a mixture of 180 cc. of dry acetone and 5 cc. of dry pyridine. After adding 1.6 g. of aniline dissolved in 20 cc. of acetone, the mixture was heated to 50° and set aside at room temperature for twenty-four hours. The reaction mixture was then diluted with three times its volume of cold water. The gelatinous material separating out soon coagulated to a granular precipitate which was filtered off and washed with cold water until the odor of pyridine was no longer perceptible. After drying on a water-bath, there remained 5.1 g. (86% yield) of a light pink product. The crude reaction product was dissolved in hot alcohol, hot water added until a slight turbidity developed, then a little decolorizing carbon added and the mixture refluxed for one-half hour. After filtering and cooling, *p*-(*p*-acetamidophenyl)-benzenesulfon-N-phenylamide separated in short white needles. The mother liquor yielded a small additional quantity on further dilution with water and cooling in an ice-bath. For analysis and melting point determination, a small sample was recrystallized from alcohol until no further change in melting point was observed.

To deacetylate, 1 g. of the above product was mixed with 30 cc. of alcohol and 10 cc. of concd. hydrochloric acid, and the mixture refluxed for one-half hour beyond the time necessary for complete solution. The reaction mixture was filtered and rendered ammoniacal at once by adding concd. ammonium hydroxide. The dense white crystalline precipitate was collected, washed well with water, and recrystallized from an alcohol-water mixture and decolorized as described above. There resulted 0.7 g. of *p*-(*p*-aminophenyl)-benzenesulfon-N-phenylamide representing a deacetylation efficiency of 80%. This sample was recrystallized from alcohol for analysis and melting point determination. A further recrystallization produced no change in melting point.

The following new compounds have thus been prepared:

I *p*-(*p*-acetamidophenyl)-benzenesulfon-N-phenylamide
II *p*-(*p*-aminophenyl)-benzenesulfon-N-phenylamide
III *p*-(*p*-acetamidophenyl)-benzenesulfon-N-benzylamide
IV *p*-(*p*-aminophenyl)-benzenesulfon-N-benzylamide
V *p*-(*p*-acetamidophenyl)-benzenesulfon-N-cyclohexylamide
VI *p*-(*p*-aminophenyl)-benzenesulfon-N-cyclohexylamide
VII *p*-(*p*-acetamidophenyl)-benzenesulfon-N-*p*-xenylamide

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[1] C. T. Van Meter, J. A. Bianculli and A. Lowy, THIS JOURNAL, **62**, 3146 (1940).

[2] E. H. Northey, *Chem. Rev.*, **27**, 188 (1940).