gen sulfide was passed through a mixture of 0.250 g. (0.0024 mole) of 5-pyrimidinecarbonitrile in 3 ml. of alcohol previously saturated with ammonia. After a short time all the solids went into solution and the product started crystallizing. The hydrogen sulfide addition was continued for another 15 min. Cooling and filtration of the mixture gave 0.230 g. of yellow, well defined crystals melting at 169–170°. An analytical sample prepared from 30 parts of alcohol melted at 170–170.5°.

*Anal.* Calcd. for $C_5H_5N_3S$: C, 43.15; H, 3.62. Found: C, 43.25; H, 3.68.

**2,4-Dichloro-5-pyrimidinecarbonitrile.**—A mixture of 123 g. (0.90 mole) of 2,4-dihydroxy-5-pyrimidinecarbonitrile,[4] 290 ml. of diethylaniline, and 720 ml. of phosphoryl chloride was stirred without the application of heat for *ca.* 0.5 hr. After the initial exothermic reaction had subsided, the dark solution was heated under reflux for an additional 1–2 hr. Removal of the excess phosphoryl chloride *in vacuo* and keeping the internal temperature below 65° left a viscous residue. This material was poured on ice and was caused to crystallize by prolonged stirring. The crude product was removed by filtration, and melted between 50° and 58°. Further purification was achieved by dissolving the material in 800 ml. of ether, washing with dilute sodium bicarbonate solution, and drying the ether phase. Subsequent removal of the solvent left a red crystalline mass which was distilled to give 101 g. of a yellow product, b.p. 110–112°/2 mm. solidifying in the receiver. An analytical sample was prepared from isooctane to give lemon-yellow needles, m.p. 62–63°.

*Anal.* Calcd. for $C_5HCl_2N_3$: N, 24.15. Found: N, 24.19.

**Acknowledgment.**—Microanalytical determinations were performed by Mr. C. E. Childs and associates. Special thanks are due to Mr. W. M. Pearlman for carrying out the hydrogenations as well as for valuable suggestions in connection therewith.

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[4] G. Shaw, *J. Chem. Soc.*, 1827 (1955).

## Formation of Copper Phthalocyanine

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It has remained an open question in the formation of copper phthalocyanine from phthalic anhydride and urea whether the α-carbon atoms in the maleic anhydride ring of phthalic anhydride are replaced by the carbon atom in urea, or whether the α-carbon atoms in the maleic anhydride ring in phthalic anhydride remain intact to constitute the eight porphin carbons in the tetraazaporphin ring.

This question relates to the formation of phthalonitrile which has been considered to be a reaction intermediate but the presence of which remains to be detected.[1,2] If the α-carbons supplied by the

Table I

| | Run No. 1 | | | Run No. 2 | | | Run No. 3 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Weight in G. | | Activity counts/ min./mg. | Weight in G. | | Activity counts/ min./mg. | Weight in G. | | Activity counts/ min./mg. |
| Material | Initial | Final | | Initial | Final | | Initial | Final | |
| C-14 urea | $8.0 \times 10^{-5}$ | ... | ... | $8.0 \times 10^{-5}$ | ... | ... | $8.0 \times 10^{-5}$ | ... | ... |
| Urea mix | 2.000 | ... | 12 ± 2 | 2.000 | ... | 12 ± 2 | 2.000 | ... | 12 ± 2 |
| Phthalic anhydride | 1.250 | ... | 0 | 1.250 | ... | 0 | 1.250 | ... | 0 |
| Reaction mixture | 3.540 | ... | 6.5 ± 1 | 3.540 | ... | 6.5 ± 1 | 3.540 | ... | 6.5 ± 1 |
| Reaction crude | ... | 1.8459 | 3.2 ± 1 | ... | 1.9090 | 3.4 ± 1 | | 1.8132 | 3.2 ± 1 |
| Copper phthalocyanine | ... | 0.792 | 0 | ... | Lost during purification | 0 | | 0.382 | 0 |
| Drierite | 14.9959 | 15.2425 | 0 | 11.7162 | 11.9406 | 0 | 10.9004 | 11.1839 | 0 |
| Ascarite in tower | 42.4878 | 43.7240 | 0.44 ± .05 | 40.9385 | 42.0769 | 0.46 ± .05 | 42.8473 | 44.0681 | 0.41 ± .05 |
| Ascarite in tube | 12.4081 | 12.5040 | 0 | 13.6144 | 13.6912 | 0 | 14.1807 | 14.2718 | 0 |
| Ammonia in $H_2SO_4$ tower | 0 | 0.1104 | ... | 0 | 0.1621 | ... | 0 | 0.2098 | ... |

phthalic anhydride remain intact, it is postulated no phthalonitrile is formed and the immediate precursors of copper phthalocyanine are either or both monoiminophthalimide or 1-amino-3-imino-isoindolenine.

It is shown, using urea tagged with carbon-14, that under the set of reaction conditions described below, urea does not contribute carbon atoms in the formation of copper phthalocyanine from phthalic anhydride and urea.

## Experimental

The reaction was carried out in a 250-ml. flask with nitrogen carrier gas flow through the reactor and downstream gas train at 1–2 ml./sec. The flask was heated in an oil bath held at 200°. The gas train system consisted of an air condenser, to trap sublimed organic by-products, Drierite tube to trap water, Ascarite tower (50:50 mixture of Ascarite and Drierite to prevent clogging of tower from traces of moisture) to trap carbon dioxide, Ascarite tube to test efficiency of Ascarite tower, back-up flask, and concd. sulfuric acid bubbler to collect ammonia gas, followed by exhaustion to atmosphere of the nitrogen purge.

The urea mix for the reaction was prepared as follows: 0.4 mg. of carbon-14 urea (Source: Tracer Laboratories, Inc.; specific activity: 3.69 mc./mM.) and 10 g. of urea were dissolved in 20 ml. of distilled water; the solution was evaporated. The residue was ground in a mortar preparatory to introduction into the crude reaction mix. For each of the three test reactions that were made, 15.93 g. of mix was prepared from which three samples, each weighing 3.54 g., were drawn: 1.25 g. of phthalic anhydride, 2.00 g. of urea mix, 212 mg. of cuprous chloride, 26 mg. of copper, and 52 mg. of molybdic trioxide.[3] The constituents were weighed in a Nettler Balance with stated sensitivity of about ± 0.02 mg. The reaction mixture was ground and blended with mortar and pestle. The reaction mass was heated to temperature 1 hr. and held at 200° for 4 hr. The reaction product in the 250-ml. flask was weighed and purified in sulfuric acid solution. The acid suspension was filtered and the filter cake was washed acid free to Congo Red paper, dried, and weighed to determine the yield. In the second test run there was no filter cake, presumably due to solution or sulfonation of the copper phthalocyanine in sulfuric acid solution. Infrared absorption characteristics of the purified residues of the first and third test runs, made with a Perkin-Elmer Model 21 spectrophotometer, over 2.5 μ to 15.5 μ, gave no evidence of compounds other than copper phthalocyanine. One hundred-milligram samples of reaction mix, crude reaction product, purified reaction product, and contents of Drierite and Ascarite tubes were tested for radioactivity with a Nuclear Corp. Model 2612-P portable radiation survey meter. The only samples that gave radioactive counts were from the reaction mixture, crude reaction product, and Ascarite tower. Copper phthalocyanine gave no count. Drierite and Ascarite tubes gave no count. Although not necessary to the purpose at hand, the amount of ammonia absorbed in the concd. sulfuric acid tower was determined by the formaldehyde method.

Yield data, radioactive counts, and weight of reaction mixture, reaction crude, copper phthalocyanine, Drierite and Ascarite tubes, Ascarite tower, and ammonia are given in Table I.

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(1) N. H. Haddock, *J. Soc. Dyers Colourists*, **61**, 68 (1945).

(2) G. Rosch, W. Wolf, and H. Vollman, U. S. Patent 2,739,155 March 20, 1956.

(3) A. Riley, U. S. Patent 2,214,477, September 10, 1940.

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# Compounds Containing the Trifluoromethyl Group[1]

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Details of the preparation and polymerization of monomers containing the trifluoromethyl group have appeared elsewhere.[3] We would like to report here related work, for the most part concerned with the attempted preparation of compounds bearing a trifluoromethyl group on a tertiary carbon atom. Compounds of this type are not reported in the literature except for the special example of 1,1-bis(trifluoromethyl)cyclobutane. This compound was prepared by Hasek[4] from the reaction of cyclobutane dicarboxylic acid with sulfur tetrafluoride. We were unable to convert α,α-dimethyl substituted carboxylic acids, specifically 2,2-dimethylpent-4-eneoic and 2,2-dimethyl-3-acetoxybutyric acid to the corresponding trifluoromethyl derivatives using sulfur tetrafluoride. Severe reaction conditions caused carbonization and milder conditions gave no reaction. The lack of reactivity in the latter two instances is attributable to steric hindrance of the carboxyl group. The steric requirements are somewhat lessened in the case of cyclobutanedicarboxylic acid because of the presence of fewer interfering hydrogen atoms and the removal of the hydrogen atoms from the site of reaction due to the ring structure.

Sulfur tetrafluoride easily converted isobutyric acid to 2-trifluoromethylpropane. This compound was obtained also from hydrogenation of 2-trifluoromethylpropene. The former reaction is preferable for the preparation of large quantities of this material. It was felt that 2-trifluoromethylpropane might be alkylated in a manner similar to that for isobutyronitrile. Alkylation was attempted with phenyllithium and allyl bromide in ether and sodium amide and allyl bromide in ammonia. The reactions were not successful. Ethyl 2-cyano-3-trifluoromethylbutenoate was prepared by condensation of trifluoroacetone with ethyl cyanoacetate in pyridine solvent with piperidine as catalyst. It is interesting to note that the intermediate ethyl 2-cyano-3-hydroxy-3-trifluoromethylbutyrate was not isolated; it dehydrated at room temperature to give the desired product. This can be contrasted to the dehydration of 2-trifluoromethyl-2-propanol which required prolonged heating at

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(2) Present address: Esso Research and Engineering Co., Linden, N. J.

(3) C. G. Overberger and E. B. Davidson, *J. Polymer Sci.* in press.

(4) W. Hasek, W. Smith, and V. Englehardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).