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THE SYNTHESIS OF A FLUORINATED PHTHALOCYANINE

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SUMMARY

The reaction of perfluoroalkylcopper with 4-iodophthalonitrile provides a convenient route to fluorinated phthalonitriles which readily form phthalocyanines in the presence of stannous chloride dihydrate.

During the course of preparing 4-perfluoroheptylphthalonitrile 1, a secondary reaction was observed when the reaction time was extended beyond two hours. This reaction involves the interaction of the orthodinitrile with copper and/or cuprous iodide to afford the phthalocyanine nucleus. This coaction is portrayed by the appearance of a green color in the reaction media.

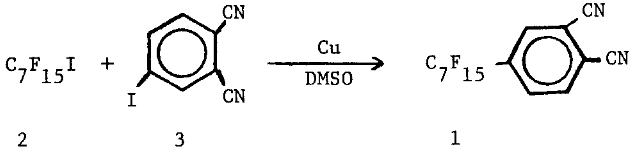
INTRODUCTION

Several types of phthalonitrile resins which do not contain fluorine have been reported [1-5] previously from our laboratory. These resins under the influence of heat, either in the presence or absence of a metallic coreactant, cure to thermosetting polymeric materials which are believed to be of the phthalocyanine type.

The present study was carried out as a prelude to an extension of the phthalocyanine synthesis to molecules containing two phthalonitrile units connected by a perfluoroalkyl moiety, which should form extensive molecular networks during the cure process. The conditions, which were determined for optimizing the yield of 1, are being applied in these syntheses. Polyphthalocyanine formation from these fluorinated resins will be reported at a later date.

RESULTS AND DISCUSSION

A phthalonitrile substituted by a perfluoroalkyl moiety has been prepared by a coupling reaction. When perfluoroheptyl iodide 2, 4-iodophthalonitrile 3 and an excess amount of activated copper in dry dimethyl sulfoxide (DMSO) are heated at 115-120°C for 2 hours under an argon atmosphere, 4-perfluoroheptylphthalonitrile 1 is formed as the sole product. It is critical that the reaction be carried out as quickly as possible due to the occurrence of a secondary reaction.



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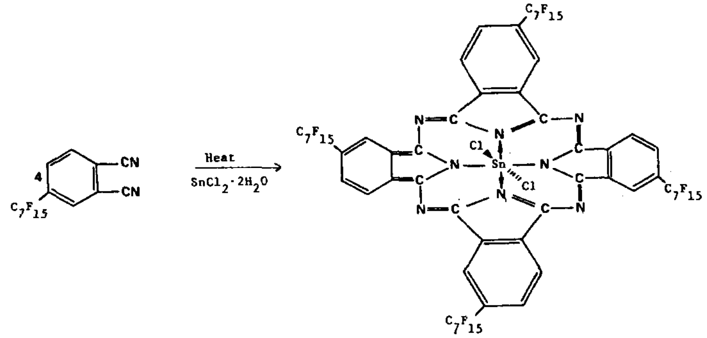
The undesirable secondary reaction predominates at prolonged reaction times. After approximately two hours, the reaction media starts to turn green. After heating for 18 hours, a green solid, whose infrared spectrum did not show cyano absorption (2242 cm^{-1}), could be isolated. Moreover, if 1 and either copper or cuprous iodide were heated to 115-120°C in DMSO, the same green solid was obtained. These observations suggest that the initially formed 4-perfluoroheptylphthalonitrile 1 is reacting with copper and/or cuprous iodide to form the corresponding phthalocyanine.

Additional evidence to support our suspicion concerning the source of the green color was obtained from the preparation of perfluoroheptylbenzene 4, which had been previously prepared by a coupling reaction [6]. When a mixture of perfluoroheptyl iodide 2, iodobenzene, and excess activated copper in dry DMSO was heated at 120-125°C for 18 hours under an argon atmosphere, 4 was formed as the sole product. The green color formation did not occur which proves that its appearance at extended reaction times in the preparation of 1 was due to the cyano substituents. Moreover, this observation also discounts the possibility of a trace amount of oxygen being in the argon and reacting with the perfluoroheptylcopper intermediate to afford the green color [6].

Phthalocyanine formation from 4-perfluoroheptylphthalonitrile 1 was not achievable by heat alone but could be initiated in the presence of stannous chloride dihydrate. When a sample of 1 was melted and heated neat at 170°C for 4 hours and then at 200°C for 18 hours, evaporation occurred leaving a thin blue film. A similar melt when heated under the same conditions in the presence of a stoichiometric amount of stannous chloride dihydrate darkened and solidified to afford a material which was insoluble in common organic solvents. Its infrared spectrum was identical to that of the green solid which formed as the secondary product during the preparation of 1. The main evidence for phthalocyanine formation was the characteristic color development [1-5] and the disappearance of cyano absorption in the infrared spectrum.

PHTHALOCYANINE REACTION



EXPERIMENTAL

Synthesis of 4-Iodophthalonitrile 3 nc

4-Aminophthalonitrile (40 g, 0.28 mol) was slowly added to 80 ml of concentrated sulfuric acid and the mixture was stirred with cooling (below 25°C) until dissolution was complete. After cooling below 15°C, ice water (175 ml) was slowly added to precipitate the amine bisulfate. A solution of sodium nitrite (20 g, 0.29 mol) in 40 ml of water was then added at such a rate as to maintain the temperature at 0-10°C. After stirring the solution for an additional 15 minutes, a few crystals of urea were added to decompose any excess sodium nitrite. The homogeneous solution was then poured into a beaker containing potassium iodide (75 g, 0.45 mol) dissolved in 150 ml of water. After the evolution of nitrogen had ceased and a negative test with alkaline p-methoxyphenol indicated that the reaction was complete, the brown precipitate was collected by suction filtration and washed with 10% sodium bisulfite, with saturated sodium bicarbonate and finally with water. Recrystallization from ethanol-water afforded 51 g (72%) of 3, m.p. 141-142°C; ir (KBr) 3098 - 3010 (=CH), 2240 (CN) and 1577 cm^{-1} (C=C).

Anal. Calcd. for $C_8H_3N_2I$: C, 37.82; H, 1.19; N, 11.03; I, 49.96.
Found: C, 37.83; H, 1.21; N, 10.85; I, 50.11.

Preparation of 4-Perfluoroheptylphthalonitrile 1 nc

A mixture of perfluoroheptyl iodide (4.0 g, 8.1 mmol), activated copper [7] (1.3 g, 20 mg. atom), 4-iodophthalonitrile (1.9 g, 7.5 mmol) and 11 ml of dry DMSO was purged for 15 minutes with argon and then heated for 2 hours at 115-120°C under an argon atmosphere. At prolonged reaction times, the mixture turned green. After cooling the content was poured into 75 ml of ice water and extracted with three 25-ml portions of ether. The combined ethereal extract was washed three times with water, charcoaled, dried over anhydrous sodium sulfate, and concentrated to afford 2.1 g (56%) of 1, m.p. 98-99°C; ir (KBr) 3110-3050 (=CH), 2242 (CN), 1608 (very weak, C=C) and 1280-1100 cm^{-1} (CF).

Anal. Calcd. for $C_{15}H_3F_{15}N_2$: C, 36.31; H, 0.61; F, 57.44; N, 5.65.
Found: C, 36.38; H, 0.69; F, 57.65; N, 5.71.

Preparation of Perfluoroheptylbenzene 4 by a Coupling Reaction

Employing the procedure of McLoughlin and Thrower [6], 4 was obtained; ir (neat) 3080-3020 (=CH), 1605 (weak, C=C) and 1280-1100 cm^{-1} (CF).

Phthalocyanine Formation From 1

4-Perfluoroheptylphthalonitrile 1 (0.1 g, 0.2 mmol) was placed in a small test tube and slowly heated to 170°C which caused the sample to darken. After 4 hours at 170°C, the sample was then heated at 200°C for 18 hours which resulted in the evaporation of the material. Only a thin film remained.

Another sample of 1 (0.1 g, 0.2 mmol) and stannous chloride dihydrate (0.011 g, 0.049 mmol) were heated to 165-170°C where homogeneity occurred. After 4 hours at 170°C, the melt was heated at 200°C for 18 hours which resulted in solidification. The blue color and the absence of any cyano absorption (2242 cm^{-1}) was taken as evidence that phthalocyanine formation had taken place.

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