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THE SYNTHESIS OF HIGHLY FLUORINATED PHTHALONITRILE RESINS AND CURE STUDIES

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SUMMARY

The reactions of the potassium salts of 1,3- and 1,4-bis(2-hydroxy-hexafluoro-2-propyl) benzene 1 and 2 with tetrafluorophthalonitrile 3 afforded three isomeric products in each case with reaction at the 4-position of 3 predominating. When each mixture was submitted to the usual thermal conditions for phthalocyanine formation [1-5], the expected characteristic color change (blue or green) did not develop.

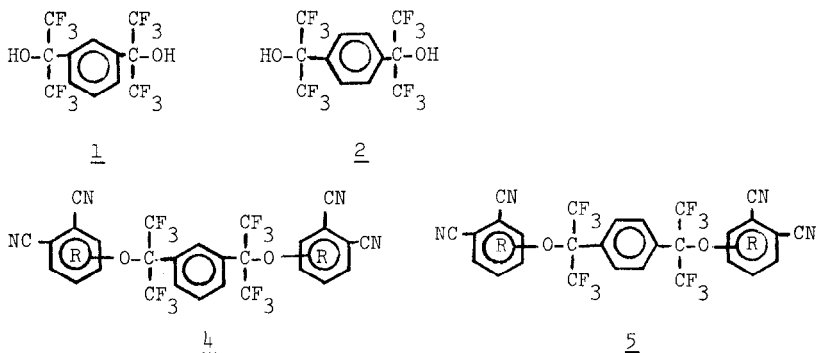
Evidence was procured from our study which indicated that fluorine substituted on the phthalonitrile moieties hindered phthalocyanine formation. Instead, as an alternative reaction, some nucleophilic displacement of fluorine from the aromatic rings by the cyano substituents appeared to have occurred.

INTRODUCTION

Just as hydrocarbon aromatic compounds provide the basis for studying electrophilic aromatic substitution, fluoroaromatic compounds are appropriate systems for studying nucleophilic aromatic substitution. Fluoroaromatic compounds are extremely susceptible to attack by even weak nucleophiles. Electron withdrawing groups activate fluoroaromatic systems to nucleophilic attack giving both para- and ortho-products although substitution at the para-position usually predominates [6-10].

We were particularly interested in compounds where fluorine was present on (1) the interconnecting linkage between two terminal phthalonitrile moieties and on (2) both the interconnecting linkage and the phthalonitrile unit itself. These compounds would then be subjected to the usual thermal conditions for phthalocyanine formation. Such a study should furnish valuable information concerning the effect of fluorine location in the molecule on

the conversion of phthalonitriles to phthalocyanines. The compounds of initial interest were structures 4 and 5, due mainly to the availability of the fluorinated diols 1 and 2 in our laboratory.

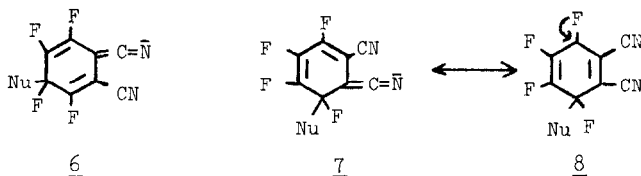


R = F or H

RESULTS AND DISCUSSION

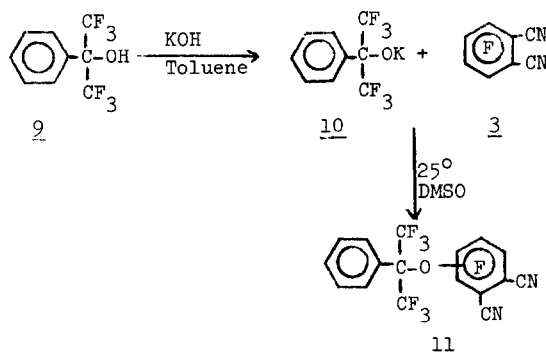
A cyano group can exert a powerful activating effect on nucleophilic substitution reactions of fluorinated aromatic compounds. For example, pentafluorobenzonitrile affords both *ortho*- and *para*-substitution products with the *para* predominating [8-10] and with the ratio depending on the solvent used [8]. Moreover, the cyano substituent has even been found to be a more powerful activator than the trifluoromethyl group [8].

The introduction of a second cyano group into a fluoroaromatic compound would be expected to enhance its reactivity even more toward nucleophilic reagents. The reaction of tetrafluorophthalonitrile 3 with several nucleophiles affords substitution products which depend on the reaction conditions [6, 10]. In all reported cases, the cyano groups remain intact and the products result from attack at the other positions. As expected, the 4-position of 3 was found to be more susceptible to nucleophilic attack than the 3-position. This phenomenon may be attributed to the ability of the cyano group to stabilize the carbanion intermediate 6. A similar intermediate 7 can be envisioned for



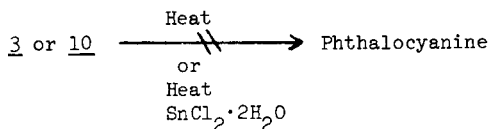
nucleophilic attack at the 3 position, but 7 would be expected to exert a smaller influence due to the carbanion-destabilizing canonical form 8, which involves I_{π} repulsion of the para-fluorine and which is absent for attack at the 4 position [11].

As a means for preparing a highly fluorinated phthalonitrile resin, the reaction of a weak nucleophile with tetrafluorophthalonitrile 3 was investigated. When the potassium salt of 2-hydroxyhexafluoro-2-propylbenzene 9 and 3 in dimethyl sulfoxide (DMSO) are reacted at 25°C, two products 11a and 11b are formed corresponding to attack at both the 4-position (80%) and the 3 position (20%) of 3. The manner of the reaction

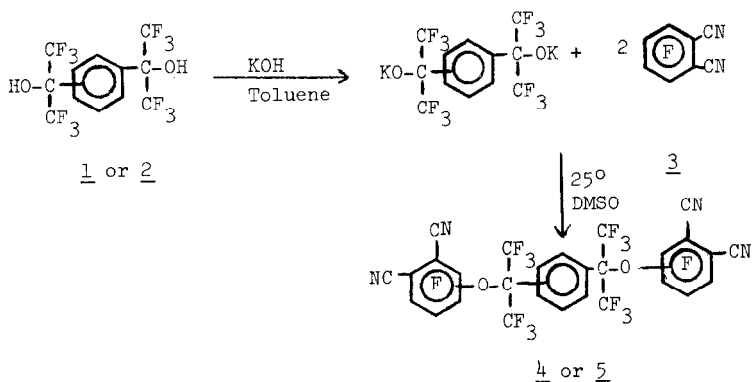


and the structures of the two products were determined by ^{19}F nmr spectroscopy. Several unsuccessful attempts were made to separate the two products.

Compounds 3 and 11 failed to polymerize when heated in the absence or presence of stannous chloride dihydrate (extremely reactive toward phthalocyanine formation). Moreover, as the temperature was slowly increased in an attempt to achieve phthalocyanine formation, both compounds volatilized with the rate of evaporation depending on the temperature and occurring more readily for 3.

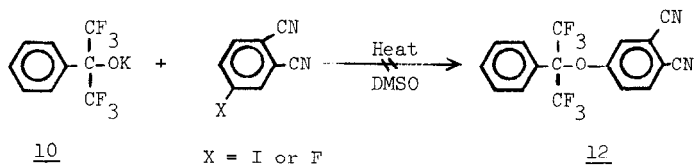


In an attempt to lessen the volatilization problem, compounds which contained two 2-hydroxyhexafluoro-2-propyl moieties substituted on the benzene ring interconnecting two fluorinated dicyanophenyl units were synthesized. The reactions of the potassium salts of 1,3- and 1,4-bis(2-hydroxyhexafluoro-2-propyl) benzene 1 and 2 with 3 each afforded three products as expected. When the mixtures were melted and heated at

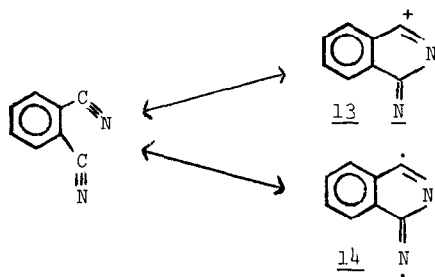


190°-240°C, with or without metallic additives, polymerization to high molecular weight polyphthalocyanines was not attained.

An unsuccessful attempt was made to prepare the corresponding less highly fluorinated model compound 12, in which fluorine is not attached to the aromatic ring containing the cyano substituents, by heating the potassium salt of 9 dissolved in dry DMSO with either 4-iodophthalonitrile or 4-fluorophthalonitrile. The salt 10 being a weak base, is apparently not a strong enough nucleophile to promote the halogen displacement at a temperature below 130°C. Above 130°C, the salt begins to decompose. The instability of 10 is not surprising, since potassium perfluoro-*tert*-butoxide, which is an analog of 10, starts to decompose at about 220°C [12].



The phthalocyanine nucleus consists of four, divalent 3-iminoisoindolenine units, which is a highly reactive mesomeric limiting form of phthalonitrile [13-14]. It is virtually of no importance whether this reactive form is formulated as a dipole 13 or a diradical 14, of which both would be short-lived reactive forms.



If the phthalocyanine nucleus materializes from either of these reactive forms, the substitution of the highly electronegative fluorine atom on the aromatic ring would greatly reduce the possibility of their existence, since electron deficient sites alpha to a highly fluorinated ring would be unfavorable. Similar mesomeric forms are probably nonexistent for 4 and 5, which could explain the absence of phthalocyanine formation from these compounds.

The observation of a new band at $\sim 1715 \text{ cm}^{-1}$ in the infrared spectra during the attempted cure of resin mixtures 4 and 5 suggests that some nucleophilic attack by the cyano substituents on the fluorinated aromatic rings occurs under the extreme thermal conditions necessary for phthalocyanine formation. A similar absorption which is attributed to the carbon-nitrogen stretching vibration has been observed for other fluorinated imines with the position of the band depending on the pattern of substitution [15-18].

We are now actively engaged in the preparation of several fluorinated phthalonitrile resins in which fluorine is substituted only on the aliphatic side chain connecting the phthalonitrile moieties. A model system, 4-perfluoroheptylphthalonitrile, has been prepared and did cure to afford the phthalocyanine nucleus [19].

EXPERIMENTAL

Reaction of the Potassium Salt of 2-Hydroxyhexafluoro-2-Propylbenzene 9 with Tetrafluorophthalonitrile 3

Compound 9 (4.0 g, 16 mmol) and potassium hydroxide (0.90, 16 mmol) were heated at reflux for 4 hours in toluene and the water as formed was collected in a Dean Stark trap. After removing the toluene at reduced pressure, the potassium salt was dissolved in 15 ml of dry DMSO.

To tetrafluorophthalonitrile 3 (3.3 g, 16 mmol) in 10 ml of DMSO and under a nitrogen atmosphere was slowly added the above potassium salt solution at such a rate to maintain the reaction temperature below 30°C. After the addition was complete, the temperature gradually dropped to 25°C; the mixture was stirred at this temperature for 16 hours and finally at 60-70°C for 3 hours. The mixture was then cooled, poured into 200 ml of ice water and extracted with three 50-ml portions of ether. The combined ethereal extract was washed several times with water, charcoaled, and dried over anhydrous sodium sulfate. After concentrating at reduced pressure, a viscous, slightly yellow material 11 (5.5 g, 82%) remained which was composed of two products as determined by both ¹⁹F nmr and thin layer chromatography; ir (neat) 3090 (=CH), 2260 (CN), 1618 (C=C), 1505-1485 (fluoroaromatic), 1330-1125 (CF), 1060-950 cm⁻¹ (CO).

The major component (80%) was identified as 2-phenyl-2-(3,4-dicyanotrifluorophenoxy) hexafluoropropane; ¹⁹F nmr (acetone-d₆, external Freon 11 ref) 70.0 (2 CF₃, multiplet), 113.7 (=CF, multiplet), 128.0 (=CF, quartet), 129.3 ppm (=CF, multiplet).

The minor component was identified as 2-phenyl-2-(2,3-dicyanotrifluorophenoxy) hexafluoropropane; ¹⁹F nmr (acetone-d₆, external Freon 11 ref) 70.0 (2 CF₃, multiplet), 114.4 (=CF, multiplet), 125.6 (=CF, quartet), 130.9 ppm (=CF, quartet).

Anal. Calcd for C₁₇H₅F₉N₂: C, 50.02; H, 1.23; F, 41.89; N, 6.86.
Found: C, 50.09; H, 0.81; F, 41.85; N, 6.67.

The Reaction of the Dipotassium Salt of 1,3-Bis(2-Hydroxyhexafluoro-2-Propyl) Benzene 1 with Tetrafluorophthalonitrile 3

Compound 1 (10.0 g, 24 mmol) and potassium hydroxide (2.8 g, 49 mmol) were refluxed for 4 hours with the water formed as a by-product

being removed from the system with a Dean Stark trap. After removing the toluene at reduced pressure, the white dipotassium salt was dissolved in 30 ml of dry DMSO.

To tetrafluorophthalonitrile 3 (9.8 g, 49 mmol) in 15 ml of DMSO and under a nitrogen atmosphere was slowly added the solution of dipotassium salt prepared above at such a rate that the temperature remained between 30-35°C during the addition. The temperature slowly receded to 25°C; and the mixture was stirred at this temperature for 16 hours and at 55-60°C for 4 hours which resulted in a copious amount of white precipitate (KF). After cooling, the reaction content was poured into 300 ml of ice water and extracted with three 75-ml portions of ether. The combined ethereal extract was washed several times with water, charcoaled and dried over anhydrous sodium sulfate. After removing the solvent at reduced pressure, the slightly colored viscous resin was heated at 105°C (5 mm) for 5 hours to remove remaining volatile materials. The resin (15.5 g, 84%) upon standing afforded a slightly colored glassy solid, which was found by thin layer chromatography (TLC) to be composed of three products. Several unsuccessful attempts were made to separate the three isomers from the product mixture; ir (KBr) 3080 (=CH), 2258 (CN), 1618 (C=C), 1505-1485 (fluoroaromatic), 1338-1125 (CF), 1035-950 cm^{-1} (CO).

The Reaction of the Dipotassium Salt of 1,4-Bis(2-Hydroxyhexafluoro-2-Propyl) Benzene 2 with Tetrafluorophthalonitrile 3

Compound 2 (3.0 g, 7.3 mmol) and potassium hydroxide (0.82 g, 15.6 mmol) were refluxed in 45 ml of toluene for 5 hours and the water which formed during the preparation of the dipotassium salt was collected in a Dean Stark trap. The toluene was removed at reduced pressure and the white salt was dissolved in 30 ml of DMSO.

To tetrafluorophthalonitrile 3 (2.9 g, 14 mmol) dissolved in 10 ml of DMSO and under a nitrogen atmosphere was slowly added the salt solution prepared above. The mixture was stirred at 25°C for 16 hours and at 70-75°C for 3 hours. After cooling, the reaction content was poured into 200 ml of ice water. The syrupy material which settled out was dissolved in 100 ml of ether. The ethereal extract was washed several times with water, charcoaled, dried over anhydrous sodium sulfate and concentrated at reduced pressure to afford 5.0 g (88%) of a glassy material which was found by TLC to be composed of three components.

Several unsuccessful attempts were made to isolate these products; ir (KBr) 3080 (=CH), 2258 (CN), 1616 (C=C), 1502-1485 (fluoroaromatic), 1338-1125 (CF), 1035-950 cm^{-1} (CO).

The Attempted Preparation of 2-phenyl-2-(3,4-Dicyanophenoxy)-Hexafluoropropane 12

2-Hydroxyhexafluoro-2-propylbenzene 9 (4.5 g, 18 mmol) and potassium hydroxide (1.1 g, 85%, 18 mmol) were heated at reflux for 3 hours in toluene and the water which was formed during the reaction was collected in a Dean Stark trap. The toluene was removed at reduced pressure to afford the salt 10, which was dissolved in 10 ml of DMSO. 4-Iodophthalonitrile (4.5 g, 18 mmol), dissolved in 20 ml of DMSO, was added to the reaction vessel in one portion. The mixture was heated at 80-85°C for 12 hours and at 120-125°C for 18 hours. Analysis by infrared spectroscopy after both heating periods, showed only starting materials to be present. The mixture was then heated at 130-135°C for 15 hours which resulted in the precipitation of a solid which was inorganic. After cooling, the reaction content was poured into 100 ml of cold dilute hydrochloric acid solution which resulted in the precipitation of a brown solid (6.0 g). Recrystallization from benzene-heptane resulted in the settling out of a dark viscous material whose infrared spectrum showed an intense absorption at 1715 cm^{-1} (C = O). Apparently, 10 decomposes in DMSO at temperatures greater than 130°C to form phenyltrifluoromethylketone and potassium fluoride. The mother liquor was poured into another beaker which resulted in the precipitation of a white solid upon cooling, m.p. 138-141°C, that was identified as 4-iodophthalonitrile. None of 9 was recovered.

The Attempted Phthalocyanine Formation from Highly Fluorinated Resins 4 and 5

One gram samples of resins 4 and 5 were placed in separate test tubes and heated for 16 hours at 190°-195°C which caused the resins to darken slightly. The temperature was increased to 210°-215°C and both samples were heated at this temperature for 24 hours. Unreacted resins sublimed from the samples during the entire heating process. At 215°C both materials had turned to a deep brown but gelation had not occurred. Apparently, phthalocyanine formation was not being achieved since the characteristic color change (green or blue) was not being formed [1-5].

Additional samples (1.0 g, 2.4 mmol) of resins 4 and 5 and 0.076 g (1.2 mmol) of activated copper were placed in planchets and heated with occasional stirring at 190°-195°C for 16 hours, at 215°C for 24 hours and finally at 240°C for 60 hours. After melting, the samples almost immediately started turning green but gelation was very slow. As above, volatiles again ensued from the samples. At 240°C, solidification was achieved but the materials (brown) were extremely brittle and full of voids. An infrared spectrum of the residues still showed intense cyano absorption and a new peak at 1715 cm⁻¹.

Both resins when heated with a stoichiometric amount of stannous chloride dihydrate (fairly reactive toward phthalocyanine formation) yielded the same results as with copper.

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