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(54) Title: METHOD OF SYNTHESIZING TETRAFLUOROPHTHALONITRILE

(57) Abstract

A process for the preparation of compounds of the general formula \( C_n F_y (CN)_x \), wherein \( x \) and \( y \) are whole integers whose sum equals 6. The process is particularly useful for the synthesis of fluorinated nitrilic containing at least two cyano groups \( (y = 2) \). Among the preferred compounds prepared is tetrafluorophthalonitrile, a key intermediate used as a building block in the pharmaceutical industry. In the process described, tetrafluorophthalonitrile is prepared by the reaction of a chlorinated compound of general formula \( C_n Cl_y (CN)_x \), wherein \( x \) and \( y \) are whole integers whose sum equals 6. Specifically, tetrachlorophthalonitrile is reacted with potassium fluoride in an aprotic solvent to prepare tetrafluorophthalonitrile. The fluoronitrile is produced in at least 80 % yield and a minimum purity of 98.5 %. Only one additional recrystallization is required to produce a material of > 99.5 % purity. In another embodiment, the crude tetrafluorophthalonitrile is recrystallized from a hydrocarbon alkane solvent to produce a product of > 99.5 % purity which can be used directly as an intermediate. This process represents an economical means to produce tetrafluorophthalonitrile on an industrial scale.
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DESCRIPTION
METHOD OF SYNTHESIZING TETRAFLUOROPHTHALONITRILE

The present invention states a method for the synthesis of tetrafluorophthalonitrile. In particular, tetrafluorophthalonitrile is produced in high yield and purity by reacting tetrachlorophthalonitrile with potassium fluoride in aprotic solvents.

BACKGROUND OF THE INVENTION

Fluorinated aromatic nitriles are important intermediates in the synthesis of pharmaceutical and herbicidal compounds. In particular, derivatives of tetrafluorophthalonitrile are increasing in demand since they form the building blocks for many of these biologically active compounds. Some synthetic routes have been reported in the literature as disclosed below. However, none of these routes appears suitable for large scale industrial manufacture. As a result of this need, we have discovered an attractive preparative route to the synthesis of tetrafluorophthalonitrile, giving product of high yield and purity. The several features and advantages of this procedure will become apparent by referring to the detailed disclosure and examples of this invention which follow.

In the prior art, the synthesis of tetrafluorophthalonitrile by reacting 1,2-dibromotetrafluorobenzene with cuprous cyanide in dimethylformamide is disclosed by Belf, et al. (J. Chem. Soc.), 1965. In that procedure, under optimum conditions, the maximum reported yield was 63%. Also, that method is plagued with the formation of a considerable quantity of by-product, a fluorinated phthalocyanine. Such contamination in the pharmaceutical intermediate is intolerable and necessitates the use of tedious purification methods before a product of sufficient purity is isolated. These methods of purification also add considerable cost to the overall economics of this process, thus rendering it of little industrial application. Furthermore, that
publication reports that impurities in the standard laboratory grade dimethylformamide caused inhibition of the reactions of the dibromides with cuprous cyanide, resulting in irreproducibility of the process. Only after considerable effort was expended in purifying the solvent by repeated distillation from phosphorous pentoxide could reproducible results be obtained. The purification of that solvent also adds considerable cost to the overall economics and is undesirable for a commercial process. Finally, 1,2-dibromotetrafluorobenzene, it was found, cannot be produced economically.

In British Patent 1,026,290 (Haszeldine), a process for producing tetrafluorophthalonitrile by heating the corresponding tetrachlorophthalonitrile with potassium fluoride in an autoclave at temperatures of 180–300°C is described. In that process, after 21 hours, the product was isolated by sublimation to only 65% yield. Independently, Ueda, et al. Bull. Chem. Soc. Jap. Vol. 40 described an identical procedure in 1967. Each of these methods suffers from the fact that large excesses of potassium fluoride are required to complete the transformation, high pressure equipment is necessary to perform the reaction and several extraction/recrystallization steps must be added to the process in order to obtain the fluorinated nitrile in sufficient purity to be used as an intermediate in the pharmaceutical industry. In addition, Ishikawa and Tanable report in Kogyo Kagaku Zasshi 73, (1970), 447, that scale up of this method results in poor reproducibility due in part to the inhomogeneous nature of this solid state reaction. It is apparent that this method has little practical use in an industrial process.

In view of the demand for fluorinated nitriles and in particular tetrafluorophthalonitrile in the pharmaceutical and herbicidal area and the absence of an economical method suited for industrial use, we concentrated on developing solution methodology for performing the halogen exchange process on tetrachlorophthalonitrile...
nitrile. In this context, one report has appeared dealing with a solution method for this synthesis. Ishikawa, et al. Kogyo Kagaku Zasshi, 1970, Vol. 73, 447 described the synthesis of tetrafluorophthalonitrile by performing the halogen exchange reaction in dimethylsulfoxide. Although the yields approach 70% in that reported method, the coproduction of a coupled product formed via the reaction of the fluorinated nitrile with dimethylsulfoxide prevents this process from being used in the manufacture of pharmaceutical intermediates. Multistep purification procedures must be employed to yield a material suitable for this end use. The cost of incorporating these procedures in an industrial process is prohibitive from a practical standpoint. Clearly, there is a need for an economical process yielding high purity tetrafluorophthalonitrile.

It is the object of this invention to provide an economical one step solution process for the manufacture of tetrafluorophthalonitrile of high purity. A further objective of this invention is also to provide a simple one step process for purifying the crude tetrafluorophthalonitrile into a material of sufficient purity that it can be used directly in the manufacture of pharmaceutical compounds.

**SUMMARY OF THE INVENTION**

This invention provides a process for the preparation of compounds of general formula $C_6F_xCN_y$ wherein $x$ and $y$ are whole integers whose sum equals 6. In particular, the process is particularly useful for the synthesis of fluorinated nitriles containing at least two cyano groups ($y=2$). Among the preferred compounds prepared in accordance with this invention is tetrafluorophthalonitrile, a key intermediate used as a building block in the pharmaceutical industry.

In accordance with the present invention, tetrafluorophthalonitrile is prepared by the reaction of a chlorinated compound of general formula $C_6Cl_xCN_y$ wherein $x$ and $y$ are whole integers whose sum equals 6.
and in particular where \( y \) is 2. Thus in a preferred embodiment of the invention, tetrachlorophthalonitrile is reacted with potassium fluoride in an aprotic solvent to prepare tetrafluorophthalonitrile. The fluoronitrile is produced in at least 80% yield and a minimum purity of 98.5%. Only one additional recrystallization is required to produce a material of >99.5% purity. Thus in another preferred embodiment of this invention, the crude tetrafluorophthalonitrile is recrystallized from a suitable alkane hydrocarbon, e.g., hexane, heptane, etc. to produce a product of >99.5% purity which can be used directly as an intermediate in the pharmaceutical industry. This process represents the most economical means to produce tetrafluorophthalonitrile on an industrial scale. The advantages of this process will become more evident by referring to the detailed description and examples which follow.

**BRIEF DESCRIPTION OF THE DRAWING**

Fig. 1 illustrates the gas chromatographic trace of pure tetrafluorophthalonitrile prepared in accordance with the invention using dimethylformamide as solvent.

Fig. 2 illustrates the gas chromatographic trace of pure tetrafluorophthalonitrile prepared in accordance with the invention using dimethylacetamide as solvent.

Fig. 3 illustrates the gas chromatographic trace of pure tetrafluorophthalonitrile prepared in accordance with the invention using N-methylpyrrolidinone as solvent.

Fig. 4 compares the gas chromatographic traces of pure tetrafluorophthalonitrile prepared in accordance with the invention curve "a" (4a) to that prepared by prior art method curve (4b).

Fig. 5 illustrates the gas chromatographic trace of pure tetrafluorophthalonitrile isolated after the hexane volume has been reduced.

**DETAILED DESCRIPTION OF THE INVENTION**

In carrying out the process of the invention, the reactants tetrachlorophthalonitrile and potassium
fluoride are heated together in the presence of an aprotic solvent in a flask or kettle depending on the quantity of product required. High pressure vessels such as an autoclave are not required. The reaction is carried out in solvents chosen from the class of organic amides of general formula:

\[
\begin{array}{c}
R_1 \\
\text{O} \\
R_2 \text{N-C-R}
\end{array}
\]

wherein \( R_1 \) and \( R_2 \) can be the same or different and chosen from the class consisting of methyl, ethyl, propyl and the like and \( R_3 \) can be chosen from the class consisting of hydrogen, methyl, ethyl, propyl and the like. The most preferred solvents are chosen from the class wherein in the above formula, \( R_1 \) and \( R_2 \) are methyl and \( R_3 \) is hydrogen, i.e. dimethylformamide; or \( R_1 \), \( R_2 \) and \( R_3 \) are methyl, i.e., dimethylacetamide; and where \( R_1 \) is methyl and \( R_2 \) and \( R_3 \) are -CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\)-, the solvent comprises N-methylpyrrolidinone.

The reaction can be performed at a temperature of 25° to 200°C, the most preferred range being 130-150°C as this gives the highest yield in the shortest time period and produces a crude product of at least 98.5% purity. Reaction time can vary from one hour to 8 hours and is a function of the reaction temperature. At temperatures less than 100°C, long reaction times are required. Operating in the temperature range specified above, the preferred reaction time is one to three hours, the most preferred time being 1.5 hours.

The mole ratio of reactants is also a variable and must be controlled to ensure a product of high purity and yield. The mole ratio of potassium fluoride to tetrachlorophthalonitrile can vary from four to a large excess. The preferred operating ratios being from about 4 to 8. Using potassium fluoride to tetrachlorophthalonitrile ratios in excess of eight moles per mole of
chloronitrile has no appreciable effect. This is demonstrated in Table 1, wherein the reaction time and temperature were held constant and only the mole ratio of potassium fluoride to tetrachlorophthalonitrile was varied as indicated. Note the small change in product yield and purity.

Heating tetrachlorophthalonitrile and potassium fluoride in a 1 to 8 mole ratio at a temperature of 130°C for 1.5 hours in dimethylformamide results in the isolation of crude tetrafluorophthalonitrile in 85% yield. The crude tetrafluorophthalonitrile is precipitated from the reaction solvent by quenching in water. Filtration yields the crude fluoronitrile in 85% yield with a purity of >98.5%. After drying, the crude fluoronitrile is purified by recrystallization from hydrocarbon alkane solvent of the formula CnH2n+2 where n is between 6 and 18. Included among such alkanes are hexane, heptane, octane, dodecane and the like. The slight yellow color which is present in the crude product can be removed by treating the hot hydrocarbon solution with activated carbon, filtering the hot hydrocarbon solution to remove the carbon and cooling the hydrocarbon-tetrafluorophthalonitrile solution to ambient temperature to precipitate the pure product as white needles exhibiting a melting point of 83-85°C (see Figure 1).

An additional quantity of product can be obtained by reducing this hydrocarbon volume by 80% by volume, cooling and collecting the white crystalline precipitate which formed using standard filtration techniques. There is no detectable increase in the amount of impurity in this second crop of product. Alternatively, the hydrocarbon volume can be reduced by 80% by volume by distillation or other suitable methods immediately after the carbon is removed by filtration. In using this modification, an additional filtration step is eliminated. The product which is isolated after the remaining hydrocarbon is allowed to cool to ambient
conditions is collected by filtration. No increase in the amount of detectable impurities is observed.

The bulk of the hydrocarbon which was distilled can be recycled in the process.

The amount of carbon required for this step is not critical and can vary from 1-10% by weight of crude tetrafluorophthalonitrile isolated above. The most preferred range of carbon being 2-5% by weight of isolated crude tetrafluorophthalonitrile. The assayed purity of this material as determined by capillary gas chromatography analysis is of at least 99.5% purity and may be used directly in pharmaceutical applications.

In an analogous fashion, dimethylacetamide can be used as the reaction solvent. Thus, after heating tetrachlorophthalonitrile and potassium fluoride and dimethylacetamide for 1-3 hours at 130-150°C, crude tetrafluorophthalonitrile may be isolated (after quenching in water) in 82% yield and 98.7% purity. A single recrystallization from a hydrocarbon solvent, e.g. hexane as eluted to above yields white needles of the product in 80% yield and in 99.6% purity as assayed by capillary gas chromatographic analysis; reference being made to Fig. 2.

In a modification of the procedure of the invention, tetrachlorophthalonitrile and potassium fluoride can be heated for 1-3 hours at 130-150°C using N-methylpyrroolidinone as solvent. After quenching the reaction in water and isolating the precipitated product by filtration, tetrafluorophthalonitrile is isolated in 76-78% yield with a minimum purity of 98.5%.

A single recrystallization from a hydrocarbon solvent, i.e. hexane yields white needles of the product in 99.3% minimum purity as determined by capillary gas chromatographic analysis; reference being made to Fig. 3.

This is a substantial improvement over the product obtained by the Ishikawa procedure. For comparison purposes, tetrafluorophthalonitrile was prepared in dimeth-
ylsulfoxide according to that procedure. The product which was isolated was subjected to capillary gas chromatographic analysis which revealed the existence of a deleterious impurity in levels approaching 6%.

Attempts to remove this impurity by repeated steam distillation or recrystallization failed to produce a product of suitable purity for pharmaceutical use. It is most probable that this impurity results from the reaction of the fluorinated nitrile with the dimethylsulfoxide to produce a coupled product. A comparison of the product purities as determined by this method are presented in Figs. 4a and 4b. The impurities are appropriately indicated.

As is evident, the only identifiable impurities as produced by the methods taught in this disclosure are the two isomers of chlorotrifluorophthalonitrile, 3-chloro-4,5,6-trifluorophthalonitrile and 4-chloro-3,5,6-trifluorophthalonitrile their combined concentration being <0.5%. In contrast, the procedure disclosed in the Ishikawa reference yields the tetrafluorophthalonitrile which contains not only these two isomers in higher percentages (3.6%) but an additional impurity (2.3%) appearing at a retention time of 12.5 minutes. This impurity could not be successfully removed from the bulk of the tetrafluorophthalonitrile.

Each variation for the production of tetrafluorophthalonitrile in accordance with the invention are superior in yield and purity to the prior art methods as illustrated by Figs. 1-4b of the drawing.

Tetrafluorophthalonitrile may be converted into precursors which are also important intermediates in the pharmaceutical and herbicidal industries. A particularly important derivative is tetrafluorophthalic acid. This compound can be conveniently prepared in high yield and purity by hydrolyzing the tetrafluorophthalonitrile prepared in accordance with this disclosure. Typically, treating tetrafluorophthalonitrile with 50% sulfuric acid produces tetrafluorophthalic acid, $\text{C}_6\text{F}_4(\text{CO}_2\text{H})_2$ in
90-97% yield with a product purity of >99.5%.

The features and advantages of the invention will be apparent in greater detail by referring to the following examples. It will be understood, however, that although these examples may describe in detail certain preferred operating conditions of the invention, they are given for purposes of illustration and the invention in its broad aspects is not limited thereto.

**EXAMPLE 1**

Anhydrous potassium fluoride (88g) and tetrachlorophthalonitrile (50g) were heated in 400 mL of dimethylformamide for 1.5 hours at 130°C. After the reaction period was over, the contents were cooled to room temperature and poured into 1L of water. The light yellow precipitate which formed was stirred for 0.5 hours, filtered and dried. Yield: 30.3g (85%) of the tetrafluorophthalonitrile in 98.5% purity.

The crude product was dissolved in 2L of hexane and treated with 10g of activated carbon. After heating for 0.5 hours at 69°C, the solution was filtered hot to remove the carbon. The colorless hexane solution was cooled to ambient temperature to yield white crystals of tetrafluorophthalonitrile (29.9g, 83%) with a melting point of 83-85°C. The minimum purity of this material as determined by capillary GC analysis was 99.7%. The GC trace is depicted in Fig. 1.

**EXAMPLE 2**

*(Comparative)*

A mixture of 9.3 g of potassium fluoride, 5.3g of tetrachlorophthalonitrile in 20 mL of dimethylsulfoxide was slowly heated to 130°C in 1 hour. The reaction was continued for an additional 30 minutes at this temperature. The contents were poured into one liter of water and precipitate isolated by filtration. The melting point of this product ranged from 78-84°C, the broad range indicative of a very impure product. This material was steam distilled. The crystals which formed in the distillate were separated by filtration and
dried. The melting point of this product was 81-85°C. The capillary GC analysis (Fig. 4b) indicates that the product was contaminated with an impurity.

Another recrystallization was necessary to produce a product of reasonable purity (98%), but this is still inferior to the tetrafluorophthalonitrile produced by the methods of the invention.

**EXAMPLE 3**

Anhydrous potassium fluoride (88g), tetrachlorophthalonitrile (50g) and 350 mL of dimethylacetamide were heated for 1.5 hours at 130°C. After the reaction period was over, the contents of the flask were poured into 1L of water, stirred for an additional 0.5 hours, filtered and dried. The purity of this crude product, as determined by capillary GC analysis, was 98%. The isolated product amounted to 29.9g (83%).

The crude product was dissolved in 2L of hot hexane and 10g of activated carbon was added to remove the yellow impurity. The solution was filtered hot to remove the carbon and the colorless hexane solution cooled to ambient temperature to crystallize the product as white needles (29.1g, 81%) mp=83-85°C. The purity of this material as determined by capillary gas chromatographic analysis, see Fig. 2, was 99.6%.

**EXAMPLE 4**

Anhydrous potassium fluoride (9g) and tetrachlorophthalonitrile (5g) were heated for 1 hour at 130°C in 30 mL of N-methylpyrrolidinone. After the reaction period was over, the contents of the flask were poured into 200mL of water, stirred for an additional 0.5 hours, filtered and dried. The purity of this crude product as determined by capillary gas chromatographic analysis was 98.6%; isolated yield: 2.73g (76%).

The crude product was dissolved in 200 mL of hot hexane and lg of the activated carbon added to remove the yellow impurity. The solution was filtered hot to remove the carbon. The colorless hexane solution was cooled to ambient temperature to yield white crystals of
tetrafluorophthalonitrile (2g, 56%) with a melting point of 84-85°C. Reducing the hexane volume by 80% by distillation resulted in the isolation of an additional 0.62g of product. An overall yield of 2.62g (73%) of a product of 99.4% purity was obtained (see Fig. 3).

EXAMPLE 5

Anhydrous potassium fluoride (8.7g) and tetrachlorophthalonitrile (5g) were heated in 50 mL of dimethylformamide for 1.5 hours at 135°C. After the reaction temperature was over, the contents were cooled to ambient temperature and poured into 50 mL of water. The light yellow precipitate which formed was collected by filtration and dried. Yield: 3.1g (87%) with a GC purity of 98.8%.

The crude product was dissolved in 200 mL of hot hexane and treated with one gram of activated carbon. After heating for 0.5 hours at 69°C, the solution was filtered hot to remove the carbon. The volume of hexane was reduced to 80 mL (80% reduction) by distillation. The distillation flask was cooled to ambient temperature to precipitate the pure tetrafluorophthalonitrile as white needles. Yield: 2.86g (80%). The capillary gas chromatographic analysis, see Fig. 5, indicated that the product was 99.5% pure.

EXAMPLE 6

The following experiments were performed to determine the effect of the potassium fluoride/tetrachlorophthalonitrile mole ratio on the overall yield and purity of the tetrafluorophthalonitrile produced. In all of the experiments, the volume of dimethylacetamide was kept constant (30mL), as was the reaction time (1.5h), temperature (130°C) and quantity of tetrachlorophthalonitrile (2.5g). The results are summarized in Table 1.
In all of the above experiments, the purity of the tetrachlorophthalonitrile was 95%. Product yields are corrected accordingly.

**EXAMPLE 7**

50g of crude tetrachlorophthalonitrile as prepared by Example 1 was dissolved in 800mL of hot heptane. The yellow solution was treated with 5.0g of activated carbon and the mixture maintained at 95°C for 0.5hr. The solution was filtered hot to remove the carbon. The colorless heptane solution was cooled to ambient temperature to yield 48g of pure tetrafluorophthalonitrile of 100% purity as determined by capillary GC analysis.

**EXAMPLE 8**

Anhydrous potassium fluoride (35g) and tetrachlorophthalonitrile (20g) were heated in 150mL of dimethylformamide for 1 hour at 135°C. After the reaction period was over, the flask was cooled to 10°C and water added directly to the organic phase to induce precipitation of crude tetrafluorophthalonitrile. A total of 200mL of water was required. After stirring for an additional 0.5h, the light yellow needles were filtered and dried. A yield of 12.34g (86%) was obtained with a corresponding purity of ≥ 98% as determined by capillary GC analysis.

It will be understood that variations may be made in the several conditions and ranges disclosed and that the disclosed limitations, provided in order to more particularly describe the invention, should not be regarded as limitations except as set forth in the claims which follow.
What is claimed:

1. A process for preparing fluoro aromatic nitrile compounds of the formula:

$$C_6F_x(CN)_y$$

which comprises introducing potassium fluoride and a chloro-aromatic nitrile of the formula:

$$C_6Cl_x(CN)_y$$

into a dipolar aprotic solvent, wherein $x$ and $y$ in each of the above formulas are integers whose sum is 6, and heating the reaction mixture to yield the desired reaction product.

2. The process according to claim 1 wherein $x$ is 4 and $y$ is 2.

3. A process according to claim 1 where the aprotic solvent is chosen from the amide class of the general formula:

$$\begin{array}{c}
R_1 \\
\overline{\text{O}} \\
R_2 \\
\text{N-C-R}_3
\end{array}$$

wherein $R_1$ and $R_2$ and $R_3$ can be the same or different.

4. A process according to claim 3, wherein $R_1$ and $R_2$ are methyl and $R_3$ is hydrogen; such that the aprotic solvent is dimethylformamide.

5. A process according to claim 3 wherein $R_1$, $R_2$ and $R_3$ are methyl; such that the aprotic solvent is dimethylacetamide.

6. A process according to claim 3 wherein $R_1$ is methyl and $R_2$ and $R_3$ are $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$; such that the aprotic solvent is N-methylpyrrolidone.

7. A process according to claim 1 wherein the optimum temperature is maintained in the range of 130-150°C.
8. A process according to claim 1 wherein the optimum time is in the range of 1-3 hours.

9. A process according to claim 1 wherein the crude tetrafluorophthalonitrile is precipitated from the aprotic solvent by quenching in water.

10. A process according to claim 9 wherein the crude tetrafluorophthalonitrile is purified by dissolving the crude product in a hot alkane hydrocarbon solvent of the formula

\[ C_nH_{2n+2} \]

wherein \( n \) has a value of 6 to 18, treating the hot hydrocarbon solvent with carbon, filtering to remove the carbon, and cooling the hydrocarbon solvent to induce the precipitation of high purity tetrafluorophthalonitrile.

11. A process according to claim 10 wherein the alkane hydrocarbon solvent is hexane.

12. A process according to claim 10 where the pure tetrafluorophthalonitrile is isolated by filtration.

13. A process according to claim 10 wherein the hydrocarbon solvent is reduced up to 80% by volume by distillation, the remaining 20% cooled to ambient temperature to induce an additional amount or pure tetrafluorophthalonitrile to crystallize.

14. A process according to claim 13 wherein the additional amount of pure tetrafluorophthalonitrile is isolated by filtration.

15. A process according to claim 10 wherein the hydrocarbon solvent volume is reduced up to 80% by volume immediately after the removal of carbon and the solvent remaining in the reaction kettle cooled to ambient temperature to induce the crystallization of tetrafluorophthalonitrile.

16. A process according to claim 15 wherein the pure tetrafluorophthalonitrile is isolated by filtration.
17. A process according to claim 13 wherein the distilled hydrocarbon solvent is recycled in the process.

18. A process according to claim 1 wherein the mole ratio of potassium fluoride to organic is in a mole ratio of 4:1 to 8:1 respectively.

19. A process according to claim 1 including hydrolyzing the pure tetrafluorophthalonitrile to the corresponding acid, tetrafluorophthalic acid of similar high purity.
**FIG. 1**

\[
\begin{align*}
\text{% COMPOSITION} & \\
C_8F_4N_2 & 99.7% \\
3-\text{ClC}_8F_3N_2 & 0.13% \\
4-\text{ClC}_8F_3N_2 & 0.17%
\end{align*}
\]

**FIG. 2**

\[
\begin{align*}
\text{% COMPOSITION} & \\
C_8F_4N_2 & 99.48% \\
3-\text{ClC}_8F_3N_2 & 0.18% \\
4-\text{ClC}_8F_3N_2 & 0.34%
\end{align*}
\]

**FIG. 3**

\[
\begin{align*}
\text{% COMPOSITION} & \\
C_8F_4N_2 & 99.36% \\
3-\text{ClC}_8F_3N_2 & 0.19% \\
4-\text{ClC}_8F_3N_2 & 0.45%
\end{align*}
\]
FIG. 4a

\[
\begin{array}{c|c}
\text{% COMPOSITION} & \\
\hline
\text{C}_8\text{F}_4\text{N}_2 & 99.7 \% \\
3-\text{ClC}_9\text{F}_3\text{N}_2 & 0.13 \% \\
4-\text{ClC}_9\text{F}_3\text{N}_2 & 0.17 \%
\end{array}
\]

FIG. 4b
(Prior Art)

\[
\begin{array}{c|c}
\text{% COMPOSITION} & \\
\hline
\text{C}_8\text{F}_4\text{N}_2 & 94.16 \% \\
3-\text{ClC}_9\text{F}_3\text{N}_2 & 1.16 \% \\
4-\text{ClC}_9\text{F}_3\text{N}_2 & 2.42 \% \\
"COUPLED PRODUCT" & 2.26 \%
\end{array}
\]

FIG. 5

\[
\begin{array}{c|c}
\text{% COMPOSITION} & \\
\hline
\text{C}_8\text{F}_4\text{N}_2 & 99.44 \% \\
3-\text{ClC}_9\text{F}_3\text{N}_2 & 0.18 \% \\
4-\text{ClC}_9\text{F}_3\text{N}_2 & 0.38 \%
\end{array}
\]
INTERNATIONAL SEARCH REPORT
International Application No PCT/US 86/02662

I. CLASSIFICATION OF SUBJECT MATTER
According to International Patent Classification (IPC) or to both National Classification and IPC

| IPC | C 07 C 121/50; C 07 C 120/00; C 07 C 63/68 |

II. FIELDS SEARCHED
Minimum Documentation Searched

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Documentation Searched other than Minimum Documentation to the extent that such documents are Included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

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IV. CERTIFICATION
Date of the Actual Completion of the International Search 18th March 1987
Date of Mailing of this International Search Report 24 APR 1987

International Searching Authority EUROPEAN PATENT OFFICE

Signature of Authorized Officer M. VAN MOL
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