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SYNTHESIS OF DIFLUORODIAZINE

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This invention relates to a novel process for the synthesis of difluorodiazine (N_2F_2).

Difluorodiazine has been found to be a valuable polymerization initiator for such monomers as tetrafluoroethylene and methyl methacrylate and various hydrocarbon monomers. Syntheses of difluorodiazine which have been recognized by the art include the thermal decomposition of fluorine azide (FN_3), the electrolysis of either molten ammonium bifluoride or a 5–10% solution of ammonium fluoride in dry liquid hydrofluoric acid, the reaction of nitrogen trifluoride with mercury in an electric arc and the reaction of fluorine with ammonia. A limitation of the first procedure is the highly explosive nature of fluorine azide, while the other procedures yield only small amounts of difluorodiazine, frequently because of the formation of such by-products as tetrafluorohydrazine, nitrogen trifluoride or the explosive difluoroamine (HNF_2).

An object of the present invention is to provide a novel method of synthesis of difluorodiazine. Another object is to provide a synthesis which is less hazardous than those employed in the art. A still further object is to prepare difluorodiazine by a one step reaction. Other objects will become apparent hereinafter.

The objects of the invention are achieved through reaction of molecular fluorine with a mixture of a metal azide and an inert diluent. The reaction may be carried out by contacting gaseous fluorine, alone or diluted with an inert carrier gas, with the mixture of metal azide and solid or liquid inert diluent.

A wide variety of metal azides may be used in the process of this invention. Because they normally do not present serious explosion hazards the alkali metal and alkaline earth metal azides are preferred. The alkali and alkaline earth metals are the metals of Groups IA and IIA, respectively, of the Periodic Chart of Elements such as may be found on pp. 448–9 of the Handbook of Chemistry and Physics, 41st edition, 1959. Patricularly preferred are the alkali metal azides, and espeically sodium azide, because of their more ready availability.

The diluent may be any solid or liquid that is inert towards fluorine, nitrogen fluorides and metal azides. Mixtures of diluents, likewise, may be employed. Suitable, for example, are perfluorinated liquids or solid metal fluorides. The preferred diluents are the solid metal fluorides, and especially the fluorides of metals of Groups IA, IIA and IIIA of the Periodic Chart of Elements. The use of alkali metal fluorides provides a further advantage in that these materials complex with and remove any hydrogen fluoride which may be formed, for example, because of the presence of a trace of moisture. Because of their ready availability, however, the alkaline earth metal fluorides, and particularly calcium fluoride, are preferred. Although less desirable, substantially inert metals, also, may be utilized as diluents. Nickel chips may be cited to exemplify this class of materials. Suitable liquids which may be employed as diluents include the perfluorinated hydrocarbons which are liquid under reaction conditions. Examples of these perfluorinated hydrocarbons include perfluorobutane, perfluorocyclobutane and the higher liquid members of this series. The diluent and metal azide should be intimately mixed when being contacted by the molecular fluorine. If the diluent is a liquid, the azide may be dispersed therein by means of

suitable agitation. The flow of fluorine, alone or admixed with an inert carrier gas, may provide sufficient agitation for this purpose. When the diluent is a solid, it is preferably subdivided so as to provide the maximum possible moderating influence. In order to facilitate mixing and to achieve optimum control of the reaction the particle size of both the solid diluent and the metal azide is maintained below 250 microns.

The relative amounts of azide and diluent are not critical although a balance must be met between a minimum quantity of diluent necessary for adequate moderation of the reaction and a maximum quantity of diluent based upon limitations in equipment size and the amount of product which may be formed from a given charge of metal azide. Ordinarily, the ratio of diluent to metal azide should be at least 1:1. The preferred ratio when using solid diluents is between 10:1 and 30:1.

The fluorine gas may contact the metal azide-diluent mixture directly or it may be diluted with a carrier gas prior to contacting the azide-diluent. The latter procedure serves to provide further control over the exothermic reaction. Suitable carrier gases are those perfluorinated hydrocarbons which are gaseous at the reaction conditions employed, for example, carbon tetrafluoride, hexafluoroethane and the like, as well as nitrogen and the inert gases helium, neon and argon.

The reaction may be carried out over a broad range of temperatures, although it is best conducted above about —25° C., with the preferred maximum temperature being limited to about 100° C. Since the reaction is exothermic, the process most conveniently is started at 20–30° C., depending upon the amount of diluent and carrier gas employed and the rate of production of difluorodiazine, external cooling may be required to preclude operation above 100° C. If the temperature is allowed to exceed 200° C., the process loses most of its practical significance because of excessive thermal degradation of the desired product.

Pressure within the reactor is not critical and the difluorodiazine synthesis may be carried out at subatmospheric as well as superatmospheric pressures. Because of economic feasibility, however, the reaction normally is run at or near atmospheric pressure.

The process may be carried out by a batch, continuous or semi-continuous method. In the latter, the fluorine stream may be passed intermittently or continuously over or through a fixed quantity of azide-diluent until the azide is spent. The reactor should be fabricated from material inert to fluorine and the nitrogen fluorides. Suitable metals which may be employed herein include nickel, aluminum and alloys such as mild steel or the iron, nickel, molybdenum, chromium alloy sold under the trademark, "Hastelloy" C.

The following example serves to demonstrate but not limit the invention as hereinabove described.

Example I

The forward section of a nickel tube of length about 18" and inside diameter about 1", equipped with a thermocouple along its center axis, is packed with an intimate mixture of 4 grams of powdered, anhydrous sodium azide and 80 grams of powdered, anhydrous calcium fluoride. The after section of the tube is packed with 25 grams of powdered, anhydrous potassium fluoride. At approximately 25° C. and atmospheric pressure, fluorine gas flowing at about 10 cc./minute is mixed with nitrogen flowing at about 95 cc./minute, and the gas mixture is passed through the tube, beginning at the end containing the sodium azide and calcium fluoride, for 90 minutes. During this time a hot zone, approximately 65–80° C., slowly migrates along the tube from the forward end. The exit gases are collected in a Monel metal trap at

—196° C. The fluorine-nitrogen flow is stopped, and the entire apparatus is flushed with helium for approximately five minutes to remove unreacted fluorine from the system and reaction products from the nickel tube. The contents of the trap are distilled into an evacuated 300 cc. Monel metal cylinder maintained at —196° C. By employing a gas-chromatographic technique the product is separated into its cis and trans isomers having boiling points of —107° C. to —104° C. and —112° C. to —110° C., respectively. In the instant example the ratio of trans to cis isomers in the product is about 1.5:1, as determined by gas-chromatographic analysis. If desired, the product may be separated into its isomers by distillation.

I claim:

1. In a process for preparing difluorodiazine the steps which comprise contacting fluorine and a mixture of a metal azide which is stable at temperatures up to 100° C., which metal is selected from the group consisting of Groups IA and IIA of the Periodic Chart of Elements, and a diluent at a temperature from —25° C. to 100° C. and collecting the difluorodiazine.

2. A process according to claim 1 wherein the metal azide is an azide of a Group IA metal.

3. A process according to claim 1 wherein the fluorine is admixed with a carrier gas selected from the group

consisting of perfluorinated hydrocarbons, nitrogen, helium, neon and argon.

4. A process according to claim 3 wherein the carrier gas is nitrogen.

5. A process according to claim 1 wherein the thermally stable metal azide is sodium azide.

6. A process according to claim 1 wherein the diluent is selected from the group consisting of perfluorinated hydrocarbon liquids and fluorides of metals of Groups IA, IIA and IIIA of the Periodic Chart of Elements.

7. A process according to claim 1 wherein the diluent is calcium fluoride.

8. A process according to claim 1 wherein the ratio of diluent to thermally stable metal azide is 10:1 to 30:1.

9. A process for preparing difluorodiazine which comprises the steps of contacting at atmospheric pressure and 20–100° C. in a nickel tube a mixture of fluorine and nitrogen and a mixture of sodium azide and calcium fluoride, and thereafter collecting said difluorodiazine in a cold trap at less than —115° C.

References Cited by the Examiner

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