

[54] PERFLUORO-AMINO-OXAZIRIDINES

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[52] U.S. Cl. 548/959

[58] Field of Search 548/959

[56] References Cited

U.S. PATENT DOCUMENTS

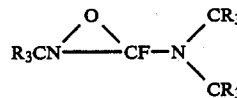
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[57] ABSTRACT

Perfluoro-oxaziridines, characterized by the presence of an aminic group in position 3 of the oxaziridine ring, of the formula:

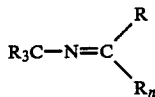


wherein each R is independently either F or a perfluoro-alkyl group, and a process for their preparation, consisting in reacting the corresponding perfluoroimine with H₂O₂, in the presence of a base in a dipolar aprotic solvent.

2 Claims, No Drawings

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wherein R has the meaning indicated previously, said process consisting in reacting a perfluoroimine of the type:

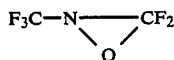


wherein R and R_n have the meanings indicated above, with H₂O₂ in the presence of a base in a dipolar aprotic solvent, at a temperature between -50° and +50° C.

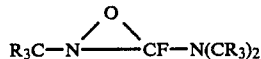
Preferably use is made of carbonates or bicarbonates of alkali metals or of alkaline earth metals as bases, and of diglyme or acetonitrile as dipolar aprotic solvents.

The contact times are not limitative in the present invention, though it is preferable to conduct the reaction in a time between 1 minute and 60 minutes, depending on the chosen reaction temperature.

With the process of the present invention it is possible to prepare any perfluoro-oxaziridine having as terminal groups F and perfluoroalkyl radicals except:

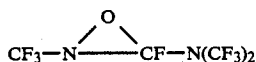


Amongst the oxaziridines prepared by means of the process of the present invention are preferred the perfluoroamino-oxaziridines of the formula:



wherein each R may be either fluorine or a perfluoroalkyl group having up to 10 carbon atoms.

Particularly preferred is 2-(trifluoromethyl)-3-fluoro-3-bis(trifluoromethyl)aminooxaziridine of the formula:



The oxaziridines of the present invention are useful as intermediates in the preparation of nitrons. Moreover, they form complexes with ions of transition metals and can be used as catalysts in the photochemical polymerization of ethylenic monomers.

Furthermore they may polymerize and copolymerize, forming liquids with a high thermal stability.

The Examples given below are intended merely for illustrative purposes and are in no way limitative of the present invention.

EXAMPLE 1

Into a 0.5 liter glass flask fitted with a magnetic stirrer, there were loaded 9 g of sodium bicarbonate, 100 ml of acetonitrile, 6.3 ml of hydrogen peroxide at 50% concentration and, through standard distillation techniques, 7.9 g of 1-bis(trifluoromethyl)aminotetrafluoro-2-aza-1-propylene.

The thus-loaded reactor was maintained at a temperature of 0° C. for 1 hour, under stirring. The raw reaction product was thereupon distilled at a pressure of 10⁻³ torr.

The vapors coming from the distillation boiler were then made to pass through refrigerated (cooled) traps

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kept at temperatures respectively of -75° C. and of -120° C.

In the trap at -75° C. there condensed acetonitrile and the water, while, in the trap kept at -120° C. there condensed 4.2 g of the desired product, 2-(trifluoromethyl)-3-fluoro-3-bis(trifluoromethyl)amino oxaziridine, in substantially the pure state. The CO₂ by-product, on the contrary, was removed by the dynamic vacuum during the distillation itself.

The conversion of the starting product was complete. The yield, defined as the ratio between the moles of desired product and the moles of reacted starting product, amounted to 50%.

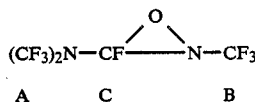
Physical properties and characterization of the product:

Boiling point	41° C.
Melting point	-130° C.

Infrared spectrum main absorption bands:

cm⁻¹ (intensity), 1422 (f), 1358 (m.f.), 1307 (m.f.), 1224 (m.f.), 1198 (m.f.), 1052 (d) (m.f. = very strong; f = strong; m = medium; d = weak).

NMR spectrum ¹⁹F: (internal reference CFC₃, solvent CDCl₃).



δFA = (d) - 56.6 PPM JAC = 6.1 Hz

δFB = (d) - 65.7 PPM JBC = 18.3 Hz

δFC = (m) - 100 PPM

EXAMPLE 2

Following the same operational procedures described in Example 1, this time instead of sodium bicarbonate sodium carbonate was used.

Into a 0.5 liter glass flask fitted with a magnetic stirrer, there were loaded: 9 g of sodium carbonate; 100 ml acetonitrile; 6.3 ml of hydrogen peroxide and, through standard distillation techniques, 7.9 g of 1-bis(trifluoromethyl)aminotetrafluoro-2-aza-1-propylene.

The thus-loaded reactor was maintained under stirring for 1 hour, at 0° C.

The reaction product was then distilled at a pressure of 10⁻³ torr in the same way as in Example 1. In the -120° C. trap 4.6 g of substantially pure 2-(trifluoromethyl)-3-fluoro-3-bis(trifluoromethyl)amino-oxaziridine were collected.

The conversion of the starting product was complete, and the yield, defined as in Example 1, amounted to 55%.

EXAMPLE 3

Into a 0.25 liter glass flask fitted with a magnetic stirrer, there were loaded: 4.5 g of sodium bicarbonate, 50 ml diglyme, 3 ml of hydrogen peroxide at 50% concentration, and through standard distillation techniques, 3.8 g of 1-bis(trifluoromethyl)aminotetrafluoro-2-aza-1-propylene.

The so-loaded reactor was maintained under constant stirring for 15 minutes at 0° C.

The raw reaction product then distilled at a pressure of 10⁻³ torr, in the same way as in Example 1.

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In the trap at -75°C . there were collected diglyme and water, while in the trap at -120°C . there were collected 0.65 g of 2-(trifluoromethyl)-3-fluoro-3-bis(trifluoromethyl)amino-oxaziridine, in the substantially pure state.

The conversion of the starting material was complete, and the yield, defined as in Example 1, amounted to 16%.

EXAMPLE 4 (COMPARATIVE EXAMPLE)

Following the identical operational procedures as those used in Example 3, but in the absence of a basic catalyst, into a 250 ml glass flask fitted with a magnetic stirrer, there were loaded 50 ml of diglyme, 3 ml of hydrogen peroxide at 50% concentration and, through standard distillation techniques, 3.8 g of 1-bis(trifluoromethyl)amino-tetrafluoro-2-aza-1-propylene.

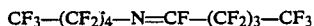
The thus-loaded reactor was kept under constant stirring for 15 minutes at 0°C .

The raw reaction product was distilled at a pressure of 10^{-3} torr, in the same way as that of Example 3. In the trap at -120°C . substantially pure 0.22 g of 2-(trifluoromethyl)-3-fluoro-3-bis(trifluoromethyl)-amino-oxaziridine was collected.

The conversion of the starting reaction product amounted to 60% while the yield equaled 5%.

EXAMPLE 5

Into a 100 milliliter glass flask fitted with a magnetic stirrer, there were loaded 2 g of sodium bicarbonate, 20 ml of acetonitrile, 1 ml of H_2O_2 at 50% b.w., and 5 g of perfluoro (6-aza-d-undecene):



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The thus-loaded reactor was maintained at a temperature of 0°C . for 1 hour under constant stirring.

The raw reaction product was thereupon distilled at a pressure of 10^{-3} torr.

The vapors coming from the distillation boiler were then passed through refrigerated traps kept at temperatures respectively of -40°C . and 120°C .

In the -120°C . trap, acetonitrile and some water were condensed, while in the trap kept at -40°C . there condensed 2 g of 2-(perfluoropentyl)-3-(perfluorobutyloxaziridine):

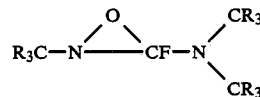


The oxaziridine contained some ppm of water. It was easily distilled over Na_2SO_4 . The CO_2 was removed during the distillation step. The conversion of the starting product was complete.

The yield, defined as in Example 1, amounted to 38%.

What is claimed is:

1. Perfluoro-oxaziridines characterized by the presence of an aminic group in position 3 of the oxaziridine ring, of the formula:



where each R is independently either F or a perfluoro-alkyl group having from 1 to 10 carbon atoms.

2. Perfluoro-oxaziridine of claim 1, characterized in that each R is F.

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