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THE METHODS FOR OBTAINING OF 1-(PERFLUOTROBUTYL)ETHYLENE AND RELATED COMPOUNDS

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Abstract: The objective of this review was to consider the methods for producing 1-(perfluotrobutyl)alkylenes of the general formula $C_4F_9(CH_2CH_2)_nCH=CH_2$, where $n=1-3$ (including 1-(perfluotrobutyl)ethylene), through the dehydroiodation of suitable perfluotrobutyliodide and ethylene adducts. The review also touches upon the methods for producing $C_4F_9(CH_2CH_2)_nI$ ($n=1-3$) adducts, making use of the telomerization of perfluotrobutyliodide with ethylene in the presence of free-radical or metal powder catalysts.

Keywords: 1-(perfluotrobutyl)alkylenes, 1-(perfluotrobutyl)ethylene, perfluotrobutyliodide.

Product description

Name: 1-(perfluotrobutyl)ethylene; (3,3,4,4,5,5,6,6,6-nonafluoro)-hexene-1 (**1-PFBE**)

CAS Registry Number: 19430-93-4

Empiric formula: $C_6H_3F_8$

Structural formula: $CF_3CF_2CF_2CF_2CH=CH_2$

Molecular mass: 246.7

Appearance: colorless liquid.

Boiling temperature: 59-60B°C;

Melting temperature: minus 9B°C

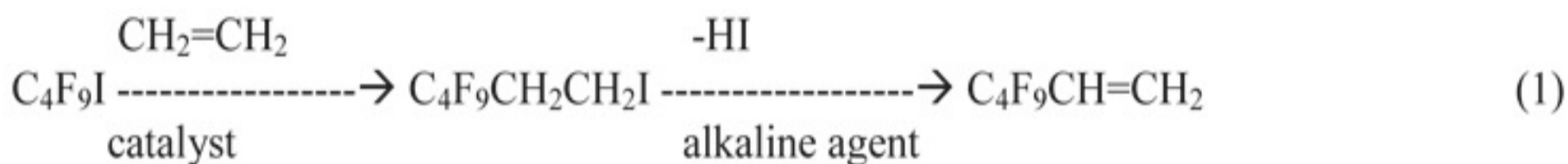
Density (d_4^{20}): 1.452 g/cm³

Field of application: The homopolymerization or co-polymerization of

$R_F(CH_2CH_2)_nCH=CH_2$ monomers (including $CF_3CF_2CF_2CF_2CH=CH_2$) with ethylene-containing co-monomers results in the formation of polymeric structures with fluoroalkyl groups in their side-chains. Therefore, it is possible to use them in the manufacture of some products with such unique properties as selective permeability, low surface tension energy, optical transparency, solvency resistance, all exceeding those of their H-analogues, etc.

Methods for the manufacture of 1-(perfluorobutyl)ethylene and related compounds

1-PFBE may be produced in a two-step process that involves dehydroiodation of 1-iodo-2-(perfluorobutyl)ethane [1, 2, 12]:



This is a general method, and if starting with another 1-iodo-2-(perfluoroalkyl)ethane or $C_4F_9(CH_2CH_2)_nCH=CH_2$ adduct one may produce related 2-(perfluoroalkyl)ethylene or $\Pi\%$ -(perfluorobutyl)alkylene-1 in similar manner.

Step 1. Manufacture of 1-iodo-2-(perfluorobutyl)ethane (1:1 adduct with $C_4F_9CH_2CH_2I$)

The comparative efficiency estimation of various (thermal, photochemical, catalytic) methods for olefin addition to perfluoroalkyliodide [3, 4, 9] in this case evidences in favor of catalytic process, because it is just the presence of free-radical [2, 3, 5-7] or metal [8-10] catalysts provides high selectivity of the target products formation.

Method 1.1. Manufacture of 1:1 adduct of $C_4F_9CH_2CH_2I$ by the addition of ethylene to perfluorobutyliodide in the presence of free-radical catalysts [5]

In the presence of free-radical catalysts ethylene is easily added to perfluorobutyliodide (or other perfluoroalkyl iodides) even under atmospheric pressure at 55-100B°C, resulting in 1:1 adduct of $C_4F_9CH_2CH_2I$ virtually in the absence of telomers (see Example 1) [5]. Much harsher conditions are required for the production of $C_4F_9(CH_2CH_2)_nI$ ($n=2-3$) telomers (see Examples 3 and 4) [2, 6].

Typically, 2,2-azo-bis-isobutyronitrile (AIBN), di-tert-butylperoxide, benzoyl peroxide, etc. are used for free-radical initiators.

Perfluoroalkyl iodide adducts with other non-halogenated olefins (propylene, isobutylene, acetylene, etc.) may be produced in similar manner.

Method 1.2. Manufacture of 1:1 adduct of $C_4F_9CH_2CH_2I$ by the addition of ethylene to perfluorobutyliodide in metal-catalyzed reaction

It has been shown [8-10], that in the presence of some metals (Zn, Cu, Cr, Ni, Mo, Pt/C, Ru/C, Pd/C, etc.) at 120-150B°C, under the pressure of ethylene from autogenic to ~2MPa,

and at ethylene : R^FI mole ratio from ~4:1 to ~1:3, perfluoroalkyl iodides with ethylene form 1:1 adducts R^FCH₂CH₂I with selectivity exceeding 95%. That is how C₄F₉CH₂CH₂I adduct was produced, e.g., in the presence of Ru/C catalyst at 120B°C, the pressure of ethylene being ~2MPa, and the ethylene : C₄F₉I mole ratio being ~4:1 (conversion and selectivity were ~97%) (see Example 2.1) [9], or when the reaction was catalyzed with fine (~300mesh) metal powders (Cu, Sn, Zn, Ni or mixture thereof) at 135B°C, autogenic pressure of ethylene and ethylene : C₄F₉I mole ratio 1: 2Γ·3 (yield ~95%, purity ≥98%) (see Example 2.2) [10].

Field of application: R^F (CH₂CH₂)_nI adducts are typical intermediates with wide field of application. They are used for telogens in telomerization with ethylene, tetrafluoroethylene or their derivatives. They are used in the production of many surfactants applied, e.g., for components of oil- or water-repellants used in textile processing, or for stable emulsifiers, e.g., in electrolysis process. The reactions of iodine substitution are used in the synthesis of various fluorinated substances (alcohols, amines, nitriles, ethers, etc.); their dehydroiodation results in perfluoroalkylethylenes, etc.

Step 2. Manufacture of 1-(perfluotrobutyl)ethylene and Π%- (perfluotrobutyl)alkylene-1 by way of dehydroiodation of C₄F₉ (CH₂CH₂)_nI adducts [1, 2, 11, 12].

Some alkaline agents (e.g., sodium (potassium) hydroxides or carbonates, alcoholates of alkaline metals) are usually applied for dehydroiodation agents. The process is conducted in alcohol (methanol, ethanol) or, preferable, in water-alcohol environment. It is also possible to use some organic solvent (hexane) (see Examples 5-7). When dehydroiodation is conducted in water, they use some phase-transfer catalysts, such as tetraalkylammonium or tetraalkylphosphonium salts.

Examples

Example 1. Manufacture of 1:1 adduct of C₄F₉CH₂CH₂I by addition of ethylene to perfluotrobutyliodide in the presence of free-radical catalysts [5]

The process is conducted in a pear-shaped flask (volume 25 ml), equipped with a thermometer, gas-supply tube and reflux condenser cooled with dry ice. The flask is charged with 10.38 parts of perfluotrobutyliodide and 0.2 parts of isobutylperoxide and at 50-54B°C ethylene is slowly bubbled through the mixture at rate a little higher than that of its absorption. The reaction process is GLC-controlled. After ~11 hours the process is finished. GLC analysis revealed the presence of a sole product. The yield of C₄F₉CH₂CH₂I 1:1 adduct was 10.7 parts (~96%); b.p. 86B°C at 150 mm Hg.

Example 2. Manufacture of 1:1 adduct of C₄F₉CH₂CH₂I by the addition of ethylene to perfluotrobutyliodide in metal-catalyzed reaction

Variant 2.1 Manufacture of 1:1 adduct of C₄F₉CH₂CH₂I (catalyst Ru/C) [9]

A steel joggling autoclave (volume 250ml) connected to the ethylene supply line was charged with 138g (0.4 mole) of perfluotrobutyliodide, 5mole% Ru/C and 5mole% of water

(as calculated to C_4F_9I). The autoclave is closed and after flushing with nitrogen, at first, and ethylene, filled with ethylene to pressure 2MPa. Maintaining this pressure constant, the autoclave under jogging is heated to 120B°C, and kept for 6 hours. (Therefore, in the autoclave the molar excess of ethylene over C_4F_9I was maintained constant (~4:1)). As the reaction is over, the autoclave is cooled and opened. The catalyst is filtered away and NMR analysis is used to determine the product content in filtrate. The conversion of C_4F_9I was ~100%. The product ($C_4F_9CH_2CH_2I$) virtually does not contain C_4F_9I or C_4F_9H impurities.

Variant 2.2 Manufacture of 1:1 adduct of $C_4F_9CH_2CH_2I$ (catalysts Cu, Sn, Cu-Zn, Zn- AlF_3) [10]

A stainless steel reactor (volume 5l) was charged with 15g of copper powder (300mesh). The reactor was evacuated and flushed with pure nitrogen to reduce the content of oxygen less than 10ppm, and that of other impurities less than 100ppm. Then the reactor was evacuated to ~0.1MPa and 3kg of perfluotrobutyliodide was pumped into it. The blend was stirred, heated to 80B°C and kept under continuous stirring for 60 minutes, in order to prepare suspension. Then 31.5g of ethylene was slowly added into the reactor, under continuous stirring, and its temperature was increased to 135B°C. When the pressure stopped changing, at the same temperature, further portions of ethylene were added, till pressure drop stopped for long time period. The total amount of added ethylene was 95.5g; the mole ratio ethylene : C_4F_9I was ~ 1:3. By the end of the process the reactor was cooled, the product was separated and GLC-analyzed. The purity of thus produced 1:1 adduct of $C_4F_9CH_2CH_2I$ was 98.4%, the content of C_4F_9I impurity was ~1.5%; the product yield was 96.4% (as calculated to the reacted C_4F_9I).

Note. At the same conditions similar result was obtained when tin powder (300mesh), copper/zinc powder blend (mole ratio Cu:Zn=65:35), or Zn- AlF_3 (5% Zn) were used for catalyst.

Example 3. Manufacture of 1:2 adduct of $C_4F_9(CH_2CH_2)_2I$ by adding of ethylene to 1:1 adduct of $C_4F_9CH_2CH_2I$ [2]

A steel reactor (volume 1l) was charged with 374g (1mole) of $C_4F_9CH_2CH_2I$ and 5g of azobisisobutyrylnitrile (free-radical initiator). The reactor was cooled to -80B°C, evacuated, heated again to room temperature, and charged with ethylene to pressure ~100psig (~0.7MPa). Then the reactor was heated to 80B°C, and at this temperature the pressure of ethylene in it was maintained ~700psig (~5MPa) for 6 hours. When the reaction was over and the reactor cooled, the product was discharged from it. GLC-analysis revealed the presence of two products: 85% of $C_4F_9(CH_2CH_2)_2I$ and 15% of $C_4F_9(CH_2CH_2)_3I$, and small amount of non-identified impurity.

Note: Igumnov et al. [6] modified the synthesis of 1:2 adduct of $R^F(CH_2CH_2)_2I$ as follows. A rotating autoclave (volume 0.5l) equipped with a needle valve was charged with 1:1 adduct of $C_4F_9CH_2CH_2I$ (0.89 mole) and azobisbutyrylnitrile (3g). The blend, under initial pressure of ethylene 4.5MPa, was heated for 4 hours at 110B°C. After separation and rectification cleaning it resulted in 1:2 adduct of $C_4F_9(CH_2CH_2)_2I$ (b.p. 96-97B°C at 85 Hg mm) with purity ~97%. The yield was ~75% (conversion of 1:1 adduct of $C_4F_9CH_2CH_2I$ was 50%).

Example 4. Manufacture of 1:3 adduct of $C_4F_9(CH_2CH_2)_3I$ by adding of ethylene to 1:1 adduct of $C_4F_9CH_2CH_2I$ [2]

The 1:3 adduct was produced via the interaction between 374g of 1:1 adduct with ethylene by the method described in Example 3, except that the pressure of ethylene was increased to ~1200psig (~8.5MPa), and the reaction time to 9-12 hours. The target product fraction (160g, b.t.90-110B°C at ~3 Hg mm) was separated by vacuum fractional distillation. The yield was ~37%.

Example 5. Manufacture of 1-perfluorobutylethylene by the dehydroiodation of 1:1 adduct of $C_4F_9CH_2CH_2I$

Variant 1. A three-necked flask (volume 1l) equipped with a reflux condenser, mechanic stirrer and thermometer, was charged with 550g (1.47mole) of 1:1 adduct of $C_4F_9CH_2CH_2I$, 215g 28% of sodium methylate methanol solution (60.2g; 1.15 mole) and 8g (0.44mole) water. The mole ratio was 1:1 adduct : CH_3ONa : $H_2O \simeq 1: 0.76 : 0.3$. The reaction blend under stirring was being boiled for 15-24 hours. As the reaction was over (under GLC control) the blend underwent fractional distillation in an effective column (h=1.2m), taking off the target product fraction (b.p. 59-60B°C) and alcohol. The product ($C_4F_9CH=CH_2$) yield was ~250g (~70%); its GLC-purity was ~98%. Then sodium iodide precipitate was filtered out from the still residue, and non-reacted 1:1 adduct of $C_4F_9CH_2CH_2I$ (~150g) was separated by vacuum distillation.

Notes:

1. The reaction of dehydroiodation is water-catalyzed. In the absence of water the yield was ~3%.
2. Instead of methanol solution of sodium methylate it is possible to use ethanol solution of 280g 28% sodium ethylate (78g of C_2H_5ONa (1.15mole));
3. The technique is composed by analogy with the general method for dehydroiodation of 1:1 adducts of $R^FCH_2CH_2I$, tested by the examples of adducts with $R^F = C_6F_{13}$, C_8F_{17} , $C_{10}F_{21}$ [1];

Variant 2. 60ml of 10% $PbPh_2$ solution was added to 37.5g (0.1mole) of 1:1 adduct of $C_4F_9CH_2CH_2I$ dissolved in 35ml of ethanol under continuous stirring during 1 hour. The reaction mixture was being boiled for 2 hours (under GLC control), then diluted with water to 250ml and extracted with ether. The ether extract was washed with $CaCl_2$ solution, then with water, dried with $MgSO_4$ and distilled in an efficient rectification column, taking off the fraction with b.p. 59-60B°C. The yield was ~50%.

Note: The technique is composed by analogy with the method for dehydroiodation of 3,3,4,4,5,5,6,6-octafluoro-1,8-diiodooctane [12].

To produce 1-(perfluorobutyl)ethylene by way of dehydroiodation it is also possible to use potassium tert-butylate (see Examples 6 and 7) or another alkaline agent.

Example 6. Manufacture of 4-(perfluorobutyl)-butane-1 ($C_4F_9CH_2CH_2CH=CH_2$) by dehydroiodation of 1:2 adduct of $C_4F_9(CH_2CH_2)_2I$ [2]

A three-necked flask (volume 2l) equipped with a reflux condenser, mechanic stirrer and thermometer, was charged with 402g of $C_4F_9(CH_2CH_2)_2I$, 800ml of hexane, and 200g of potassium tert-butylate. After heating and stirring for 2 hours the mixture was filtered, and solid residue was washed with small amount of hexane. By fractional distillation a fraction

with b.p.100-110B°C corresponding to olefin $C_4F_9CH_2CH_2CH=CH_2$ was separated from filtrate. The yield was 160g (~60%). The product structure was confirmed by NMR spectra.

Example 7. Manufacture of 6-(perfluotrobutyl)-hexene-1 ($C_4F_9(CH_2CH_2)_2CH=CH_2$) by dehydroiodation of 1:3 adduct of $C_4F_9(CH_2CH_2)_3I$ [2]

1:3 adduct of $C_4F_9(CH_2CH_2)_3I$ (85g of distillate produced in Example 4) and 57g of potassium tert-butyrate under stirring was boiled with a reflux condenser for 6 hours in the presence of 287ml of hexane. After vacuum distillation of volatile products, the distillate was exposed to the second distillation, and the target product fraction was separated (~30g; b.p.49-50B°C at 15 mm Hg). The product yield was ~35%. The structure of 6-(perfluotrobutyl)-hexene-1 was confirmed by spectroscopy and elemental analysis.

Conclusion

1. The methods for the production of 1-(perfluotrobutyl)alkylenes of general formula $C_4F_9(CH_2CH_2)_nCH=CH_2$ ($n= 1\text{--}3$) by way of dehydroiodation of suitable perfluotrobutyliodide/ethylene adducts using alcohol solutions of potassium hydroxide (yield ~50%), sodium alcoholate (yield ~70%); potassium tert-butyrate in inert solvent (yield ~60%) for alkaline agents were considered.
2. The methods for the production of $C_4F_9(CH_2CH_2)_nI$ ($n= 1\text{--}3$) adducts through the telomerization of perfluotrobutyliodide with ethylene catalyzed by some free-radical catalysts or by fine metal powders (Zn, Cu, Sn, Cr, Ni, Mo, Pt/C, Ru/C, etc.) were reviewed as well.

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