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A NEW METHOD FOR RECOVERING WASTE ALKALINE PERFLUORO-n-BUTANESULFONATE

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SUMMARY

A new method for recovering perfluoro-n-butanesulfonic acid from its waste alkaline salts and re-converting it into the corresponding 2,2,2-trifluoroethyl ester alkylating agent is described. Alkaline perfluoro-n-butanesulfonate can be converted into the corresponding acid by treating it with gaseous HCl in methanol; perfluoro-n-butanesulfonic acid is then directly esterified by treatment with 2,2,2-trifluoroethanol in thionyl chloride. Easy procedures and high yields could make this method important for industrial application, with possible economic and environmental benefits.

INTRODUCTION

The introduction of a 2,2,2-trifluoroethyl group into a basic compound (such as benzophenones, benzisoxazoles, anilines, diazepines) leads to a wide variety of pharmaceutically active products or intermediates [1,2,3]. These processes use 2,2,2-trifluoroethylation agents of the formula $F(CF_2)_nSO_2OCH_2CF_3$ wherein *n* is from 3 to 8 [1,2]. However 2,2,2-trifluoroethyl-

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perfluoro-n-butanesulfonate (n=4) was a particularly preferred reagent in this respect [3]; its alkylating ability results from the particular strength of perfluorobutanesulfonic acid, $C_4F_9SO_3H$.

A particular problem in this alkylation process is the formation of a waste alkaline (usually sodium) perfluorosulfonate. Disposal of this by-product involves environmental and economic aspects. Due to the presence of a straight perfluorinated chain, its spontaneous degradation is slow and can produce dangerous pollutants; further, $C_4F_9SO_2OCH_2CF_3$ is prepared from $C_4F_9SO_2F$, whose cost is rather high: therefore for economic reasons it should be important to recover this product by re-converting it into the alkylating agent.

For these reasons a process **which makes possible the** recovery and the re-use of waste alkaline perfluorosulfonates resulting from these alkylation reactions can take on a particular interest. The method **described here** converts the alkaline perfluoro-n-butanesulfonate into the corresponding acid $C_4F_9SO_3H$, from which 2,2,2-trifluoroethyl ester can be prepared either directly or *via* acyl halide (chloride or fluoride).

RESULTS AND DISCUSSION

Waste resulting from trifluoroethylation reactions using 2,2,2-trifluoroethyl perfluoro-n-butanesulfonate as alkylating agent is normally a complex mixture of products, of which sodium perfluoro-n-butanesulfonate is about 50% by weight. It is thus necessary to make a preliminary hot-treatment with organic solvents in order to separate the pure alkaline salt.

Conversion of pure alkaline perfluoro-n-butanesulfonate into the corresponding 2,2,2-trifluoroethyl ester was accomplished by the following steps:

- preparation of perfluoro-n-butanesulfonic acid from its alkaline salt;
- direct esterification of the acid.

Alternatively the ester can be prepared by previous transformation ofthe acid into the corresponding acyl halide (chloride or fluoride) then reacting it with 2,2,2-trifluoro--ethanol [1].

Preparation of perfluoro-n-butanesulfonic acid

The only present method for preparing perfluorosulfonic acids from their alkaline salts consists of vacuum distillation of these salts from excess 100% sulfuric acid [4]. However, this method is not very suitable for industrial applications as yields are generally not particularly high (60-70%), and there are problems with regard to disposal of waste from the distillation.

It is however possible to prepare perfluoro-n-butanesulfonic acid from its alkaline salt by the following equilibrium process:

$$C_4F_9SO_3Na + HCl \rightleftarrows C_4F_9SO_3H + NaCl$$

In order to favour the acid formation it is sufficient to displace the equilibrium by NaCl removal from the reaction mixture as it is formed. That was effected by bubbling an HCl stream through a solution of alkaline perfluoro-n-butanesulfonate in an organic solvent where NaCl is insoluble. Different compounds (acetone, methanol, chlorosulfonic acid, etc.) were tested as solvents for this purpose, but methanol appeared the best. Acetone also gave good results, but this solvent seemed to undergo some degradation during the treatment leading to black final reaction mixtures.

At the end of the treatment, after solvent removal by distillation, a tail of perfluoro-n-butanesulfonic acid about 80% pure was obtained in about 90% yield; a higher purity of the acid could be reached by vacuum distillation of the tail.

Preparation of 2,2,2-trifluoroethyl-perfluoro-n-butanesulfonate

The direct transformation of perfluoro-n-butanesulfonic acid into the corresponding 2,2,2-trifluoroethyl ester can be carried out by reacting the acid and 2,2,2-trifluoroethyl alcohol with thionyl chloride. For best results it is essential to prepare a solution of alcohol in thionyl chloride and feed it into the acid. Particular care must be paid to the feed rate of **this alcoholic solution, because the temperature must be kept as high as possible (at least at 115-120°C).**

Moreover thionyl chloride must be used in excess in order to offset the amount carried away by the HCl evolved and also that decomposed by the water formed in the reaction. Alternatively, a small amount of thionyl chloride can be added initially to the acid to offset its hygroscopicity. In this manner yields of about 60% were obtained.

An alternative procedure was tried by feeding thionyl chloride into a solution of perfluoro-n-butanesulfonic acid in 2,2,2-trifluoroethanol, but yields were never higher than 20%, probably because the temperature was too low (less than 102 °C).

Preparation of perfluoro-n-butanesulfonyl chloride

Using $SOCl_2$ or $POCl_3$ in order to transform perfluoro-n-butanesulfonic acid into its chloride always led to very low yields. With PCl_5 it was possible to obtain high yield (70-90%) by using amounts 2-3 times the stoichiometric value. A by-product was also found together with acyl chloride; its probable formula is $C_4F_9SO_2PO_2$ due to the following experimental data: MS m/e 347, 315, 283 ($M^+ - PO_2$), 251, 219 $(C_4F_9)^+$, 170, 131, 119, 100 $(C_2F_4)^+$, 85, 69 $(CF_3)^+$, 31; anal. found (calculated for $C_4F_9O_4SP$): F 48% (49.4%), S 10% (9.2%). Relative amounts of these compounds appeared to depend on the conditions of reaction, particularly on the amount of PCl_5. This method is described in [4], but lower yields (about 52%) are reported.

From perfluoro-n-butanesulfonyl chloride the corresponding fluoride can be easily prepared by a hot-treatment with KF in 1,4-dioxane, and both can be changed into the corresponding 2,2,2-trifluoroethyl ester by reacting them in the traditional way [1] with 2,2,2-trifluoroethyl alcohol.

EXPERIMENTAL

Waste alkaline perfluoro-n-butanesulfonate purification

In a 2000 ml three-necked flask, fitted with mechanical stirrer, condenser, thermometer and electric heating, 900 g of waste alkaline perfluoro-n-butanesulfonate and 1000 ml of methylene chloride were placed. The suspension was stirred vigorously for 30 minutes at reflux temperature (40 °C); the stirrer was stopped and the solvent settled. This procedure was repeated three times with fresh solvent in order to remove organic materials. The residue obtained by a final filtration (796 g) was then stirred three times with 1000 ml of hot methano in the same apparatus; alkaline perfluorosulfonate dissolved in the solvent. After filtering and removing of the solvent, methanolic solution gave 481 g of pure (98%) sodium perfluoro-n-butanesulfonate.

Preparation of perfluoro-n-butanesulfonic acid

Usual method. 200 g (0.61 mol) of pure sodium perfluoro-n-butanesulfonate were placed in a 1000 ml 'Pyrex' glass flask equipped with electric heating; 200 g of 96% sulfuric acid and 370 g of 25% oleum were added. The mixture was distilled at 15 mm Hg: 127 g of pure (92%) perfluoro-n-butanesulfonic acid was recovered at 120-130 °C (molar yield: 63.8%).

New method. A solution of 400 g (1.22 mol) of pure sodium perfluoro-n-butanesulfonate in 1000 ml of methanol was placed in a 2000 ml three-necked 'Pyrex' glass flask fitted with magnetic stirrer, electric heat, condenser, thermometer and gas inlet. The solution was stirred magnetically and hydrogen chloride was then bubbled through at 50 °C: NaCl began to precipitate. After 1 hour the stirrer was stopped and the solid removed by filtration; 50 g of NaCl were recovered. After concentrating the solution by solvent distillation, 12 g of NaCl were recovered. Finally, complete removal of methanol gave 390 g of a residue containing 10 g of NaCl and 321 g of perfluoro-n-butanesulfonic acid (82% pure, molar yield: 87.7%).

Preparation of 2,2,2-trifluoroethyl-perfluoro-n-butanesulfonate

100 g (0.27 mol) of 82% perfluoro-n-butanesulfonic acid obtained in this manner were placed in a 500 ml three-necked "Pyrex" glass flask fitted with magnetic stirrer, electric heat, condenser and thermometer. The temperature of the stirred acid was raised to 130 °C; 40 g (0.4 mol) of 2,2,2-trifluoro-ethanol dissolved in 60 g (0.5 mol) of thionyl chloride were added dropwise from a separating funnel. The reaction mixture was kept at reflux; the feed ratio of the alcoholic solution **was regulated so that the temperature remained at the highest** possible value (about 120 °C). After the addition was complete, the reaction mixture was distilled; the distillate was added to a ice-water mixture and a layer of ester was separated. 73 g (0.19 mol) of ester dried over sodium sulfate were finally obtained (molar yield: 70.4%).

Preparation of perfluoro-n-butanesulfonyl chloride

110 g (0.53 mol) of PCl_5 were placed in a 500 ml four-necked "Pyrex" glass flask equipped with **mechanical stirrer, electric** heat, condenser and thermometer. 100 g (0.27 mol) of 82% perfluoro-n-butanesulfonic **acid (obtained as described in b)** were added dropwise from a separating funnel under mechanical stirring. An exothermic reaction evolving HCl occurred. After completing the acid feed, the reaction mixture was stirred for 1 hour at about 100 °C. Distillation gave 78.4 g (0.23 mol) of 98% perfluoro-n-butanesulfonyl chloride (molar yield: 86.6%) at 98-102 °C, and 8.8 g of a by-product at 127-130 °C; MS analysis of this last compound gave a molecular ion of 346 m/e and fragmentation in good agreement with the formula $C_4F_9SO_2PO_2$.

Perfluoro-n-butanesulfonyl chloride formation was confirmed by treating the fraction distilled at 98-102 °C with KF in 1,4-dioxane. Pure perfluoro-n-butanesulfonyl fluoride was obtained in a yield higher than 95% and then converted into the corresponding 2,2,2-trifluoroethyl ester by reaction with 2,2,2-trifluoroethanol.

The analogous treatment carried out with the fraction distilled at 127-130 °C only gave potassium perfluoro-n-butanesulfonate; moreover, chloride ions were not found in the reaction mixture.

CONCLUSIONS

The reported experimental results show the possibility of a suitable re-use of waste alkaline perfluorosulfonates from alkylation reactions employing perfluorosulfonate esters. In particular, alkaline perfluorosulfonates can be easily converted in high yield into the corresponding acid from which the 2,2,2-trifluoroethyl ester, recyclable in the same alkylation process, can be directly prepared. Alternatively perfluoro-n-butanesulfonic acid can be changed into the corresponding chloride or fluoride, from which 2,2,2-trifluoroethyl ester can also be prepared. Because the procedures involved are simple and easy to carry out, this method could have important industrial applications, with economic and environmental benefits.

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