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3,262,967

PROCESS FOR THE PREPARATION OF α-FLUOROACRYLATES

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This invention relates to the preparation of α-fluoroacrylates. More particularly, the invention relates to the preparation of esters of α-fluoroacrylic acid in good yield and purity directly obtained from fluoroacetates.

In the past, it has been difficult, if not impractical, to obtain esters of α-fluoroacrylic acid from lower alkyl fluoroacetates in good yield and purity. One successful method for preparing α-fluoroacrylates is disclosed and claimed in U.S. Letters Patent No. 3,075,002 to J. A. Sedlak, issued on January 22, 1963. This patent discloses a process for preparing α-fluoroacrylates by reacting a lower alkyl fluoroacetate in the presence of a strong base, such as an alkali metal alkoxide, followed by reaction with an aldehyde, such as formaldehyde or paraformaldehyde. Unfortunately, the yield obtained, although good in view of the direct nature of the process, is not satisfactory for commercial exploitation. If a process could be found in which α-fluoroacrylates are obtained in good yield and purity that finds acceptance commercially, such a process would be highly desirable.

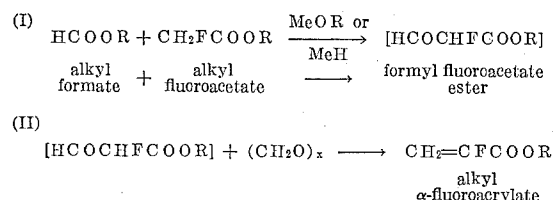
It is, therefore, a principal object of the present invention to prepare certain unsubstituted α-fluoroacrylates in good yield and purity. Other objects and advantages will be readily ascertained from a consideration of the following detailed description.

It has been found unexpectedly that esters of α-fluoroacrylic acid of the structure:



wherein R is a lower alkyl radical, such as methyl, ethyl, propyl, butyl or hexyl, can be obtained in a straightforward manner in good yield and purity. The reaction is readily accomplished by admixing an alkyl formate with an alkyl fluoroacetate in the presence of a strong base and reacting the so-formed product with an aldehyde. In so-proceeding, the over-all yield of unsubstituted α-fluoroacrylates is increased from approximately 15% when an alkyl formate is omitted to about 35%, or more, when the alkyl formate is present.

The stepwise reaction may be written as follows:



wherein Me is an alkali metal, such as sodium or potassium, R is lower alkyl, and x is unity or higher. Although equimolar proportions are indicated in the over-all reaction, a mol excess of each of the reactants can be employed without adversely affecting the yield.

In general, the alkyl formates herein employed are: methyl formate, ethyl formate, propyl formate and butyl formate. The lower alkyl fluoroacetates contemplated are: the methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl- and heptyl-fluoroacetates, as well as their isomers.

The formaldehyde reactant can be utilized in any convenient form. Thus, monomeric formaldehyde conveniently obtained from one of its polymers, paraform-

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aldehyde, by heating the latter and collecting the resultant formaldehyde vapor, can be directly introduced into the reaction product resulting from the initial addition of the formate to the fluoroacetate in the presence of a strong base. Alternatively, polymeric formaldehyde can be directly employed during reaction without initially generating formaldehyde vapor.

Illustrative strong bases that can be employed for the process of the invention are, for example, sodium hydride, potassium hydride, sodium methoxide, sodium ethoxide and sodium propoxide. It is convenient to incorporate an inert solvent such as tetrahydrofuran, ether, benzene, petroleum ether, dimethyl sulfoxide, tetramethylene sulfone and equivalents thereof.

It is found that a reaction time from at least one hour to about forty-eight hours is sufficient to effect completion of the over-all reaction. At the end of this time, the reaction mass is neutralized in any suitable manner and next worked up with an inert organic solvent, such as methylene chloride, pentane or benzene, to extract the so-neutralized product which product is next distilled to separate the solvent from the desired α-fluoroacrylate. Prior to work-up, however, the temperature employed in the process of the invention is about 125° C., or below. Temperatures between about zero and 75° C. are best for optimum recovery of the desired product.

To facilitate a further understanding of the invention, the following examples are presented primarily for purposes of illustrating certain more specific details of the invention. Except as defined in the claims, the scope of the disclosure herein is not to be taken as limitative. Parts given are by weight, unless otherwise noted.

Example 1

In a dry atmosphere, a solution of 45.0 parts of methyl fluoroacetate in 88.4 parts of methyl formate is added dropwise during six and one-half hours to a mixture of 39.7 parts of sodium methoxide and 200 parts of tetrahydrofuran stirred in an ice bath. During addition, the temperature does not exceed 4° C. After the addition is completed, the mixture is stirred at room temperature for sixteen hours.

The mixture is cooled to ice bath temperature and 29.4 parts of paraformaldehyde are added. An immediate temperature rise to 8° C. occurs, but within ten minutes, the temperature returns to 0° C. After stirring for two hours in the ice bath, the cold reaction mixture is slowly poured into 325 parts of methylene chloride stirred with a solution of 25.6 parts of hydrochloric acid in 150 parts of water, the mixture being maintained below 20° C. during the neutralization. The organic layer is separated and washed with two portions of saturated aqueous dibasic sodium phosphate and one portion of saturated aqueous sodium chloride. Small amounts of hydroquinone and chloranil are added as inhibitors and the solution is dried at minus (—) 20° C. over anhydrous magnesium sulfate.

The methylene chloride and most of the tetrahydrofuran are removed by distillation, first at atmospheric pressure and then at reduced pressure. The product is distilled at 150 mm. Hg pressure to yield 25.2 parts of distillate having a boiling point of 22.9° C. to 48.0° C. at 150 mm. Hg. Vapor phase chromatographic analysis shows that the distillate consists of: 19.1 parts of CH₂=CFCOOCH₃, 0.6 part of CH₃FCOOCH₃ and 5.5 parts of tetrahydrofuran. The conversion of methyl fluoroacetate is 44.4 parts, or 99%, and the yield of methyl α-fluoroacrylate based on this conversion is 38%.

Example 2

The procedure of Example 1 is followed, except that only 15 parts of formaldehyde (as paraformaldehyde)

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are employed. Also, in the neutralization step 18 parts of hydrochloric acid are employed.

The product is distilled at 200 mm. Hg pressure to yield 26.7 parts of distillate possessing a boiling point in the range from 31° C. to 66° C. at 200 mm. Hg and consisting of: 15.9 parts of methyl α -fluoroacrylate, 7.0 parts of methyl fluoroacetate and 3.8 parts of tetrahydrofuran. The conversion of methyl fluoroacetate is 38.0 parts, or 84%, and the yield of methyl α -fluoroacrylate based on this conversion is 37%.

Example 3

In an anhydrous atmosphere, 45.0 parts of methyl fluoroacetate are added dropwise over two and three-quarter hours to a mixture of 11.8 parts of sodium hydride, 59.0 parts of methyl formate and 144 parts of tetrahydrofuran stirred in an ice bath. During addition, the temperature never exceeds 4° C. After addition is completed, the mixture is stirred at ice bath temperature for two and one-half hours and then at room temperature for an additional twelve hours.

The mixture is cooled to ice bath temperature and 14.7 parts of paraformaldehyde are added. After stirring for two hours in the ice bath, the reaction mixture is worked up as in Example 1, except that only 18 parts of hydrochloric acid are employed in the neutralization.

The product is distilled at 200 mm. Hg to yield 25.2 parts of distillate possessing a boiling point of 33.5° C. to 57.1° C./200 mm. Hg and consisting of: 19.6 parts of methyl α -fluoroacrylate, 1.7 parts of methyl fluoroacetate and 3.9 parts of tetrahydrofuran. The conversion of methyl fluoroacetate is 43.3 parts or 96%, and the yield of methyl α -fluoroacrylate based on this conversion is 40%.

We claim:

1. In an improved process for preparing unsubstituted α -fluoroacrylic acid esters having the structure:



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wherein R is a lower alkyl radical, prepared from the reaction between equimolar amounts of an ester of fluoroacetic acid having the structure:



wherein R is defined as above, and an aldehyde selected from the group consisting of monomeric formaldehyde and paraformaldehyde, at a temperature between about zero degrees and 125° C. in the presence of a strong base selected from the group consisting of alkali metal alkoxides and alkali metal hydrides, the improvement which comprises: admixing at least an equimolar amount of a lower alkyl formate with said fluoroacetic acid ester, reacting the latter mixture with said aldehyde, and thereafter recovering desired α -fluoroacrylate in good yield and purity.

2. A process according to claim 1, in which the reaction is carried out at a temperature of about 0° C.

3. A process according to claim 1, in which the base is sodium hydride.

4. A process according to claim 1, in which the lower alkyl formate is methyl formate, the fluoroacetate is methyl fluoroacetate and the base is sodium methoxide.

5. A process according to claim 1, in which the lower alkyl formate is ethyl formate, the fluoroacetate is ethyl fluoroacetate, and the base is sodium ethoxide.

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