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ALKYLATION OF ACIDS WITH ALKYL ORTHOCARBOXYLATES

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This invention relates to the alkylation of certain acids and to the preparation of alkyl esters thereof, and more particularly to the alkylation of sulfonic and phosphonic acids with alkyl orthocarboxylates.

In the past alkylations of sulfonic and phosphonic acids have been carried out by several different methods. These have included the reaction of the appropriate sulfonyl or phosphonyl halide with an appropriate sodium alkoxide in alcohol solution, by reacting the sulfonyl halide or phosphonyl halide with the appropriate alcohol in the presence of an acid acceptor such as pyridine or other tertiary amine, the reaction of the silver salt of the sulfonic or phosphonic acid with alkyl iodide, the reaction of the appropriate sulfonic or phosphonic acid with a diazoalkane and, the reaction of the appropriate sulfonic or phosphonic acid with a ketene acetal. None of these methods have been fully suitable for the preparation of esters of such acids carrying groups sensitive to strong alkylating agents or severe alkylating conditions. For example, in attempting to alkylate ethylenesulfonyl chloride to its ethyl ester by means of sodium ethoxide one finds the alcohol adding across the vinyl group as well as substituting on the sulfonic acid group, thus lowering the yields to uneconomic levels. The use of diazoalkanes as alkylating agents is dangerous due to the possibility of explosive decomposition. Furthermore, the preparation of the alkyl esters by means of ketene acetal is very difficult and expensive in that ketene acetal is most difficult to prepare and must be employed immediately to prevent polymerization thereof before further reaction. These and other prior methods of alkylation have involved several steps which have been difficult and expensive to carry out and involve losses of the desired products. A direct synthesis of alkyl esters of sulfonic and phosphonic acids under mild conditions has thus been desired by the art.

Accordingly, the primary object of the present invention is the provision of a method of directly alkylating sulfonic and phosphonic acids under mild reaction conditions. A further object is the provision of a method to directly alkylate sulfonic and phosphonic acids which does not alkylate other substituent groups sensitive to strong alkylating agents. A still further object is the provision of such a method which is economical and direct and does not involve several separate reactions. A further object is the provision of such a method which employs readily available and economical reagents. Other objects will be apparent from the description of the invention hereinafter.

It has now been found that the objects of this invention can be accomplished by a method of alkylation which comprises reacting an acid selected from the group consisting of sulfonic acids and phosphonic acids with a trialkyl orthoester of a monocarboxylic acid of from one to five carbon atoms and recovering the resulting ester.

Trialkyl orthocarboxylates suitable as alkylating agents in the process of the instant invention are the lower trialkyl orthoesters of monocarboxylic acids of from one to five carbon atoms. Such orthoesters include trimethyl orthoformate, triethyl orthoformate, tri-n-propyl orthoformate, tri-i-propyl orthoformate, tri-n-butyl orthoformate, tri-i-butyl orthoformate tri-n-amyl orthoformate, tri-i-amyl orthoformate, tri-n-hexyl orthoformate, tricyclohexyl orthoformate, trimethyl orthoacetate, triethyl orthoacetate, tri-n-propyl orthoacetate, tri-i-butyl orthoacetate, tri-n-amyl orthoacetate, tricyclohexyl orthoacetate, trimethyl orthopropionate, triethyl orthopropionate, tri-i-propyl orthopropionate, tri-n-butyl orthopropionate, tri-i-amyl orthopropionate, tricyclohexyl orthopropionate, trimethyl ortho-n-butyrate, triethyl ortho-n-butyrate, tri-i-propyl ortho-n-butyrate, tri-n-butyl ortho-n-butyrate, tri-n-amyl ortho-n-butyrate, trimethyl ortho-n-valerate, triethyl ortho-n-valerate, tri-n-propyl ortho-n-valerate, tri-i-butyl ortho-n-valerate, tri-i-amyl ortho-n-valerate, tricyclohexyl ortho-n-valerate, and the like.

All sulfonic and phosphonic acids may be alkylated by the process of the instant invention. The process has been found most useful in the alkylation of those of such acids that carry substituents which are sensitive to the usual alkylating agents and conditions. Thus, such acids as ethylenesulfonic acid, 2-propene-1-sulfonic acid, isethionic acid (2-hydroxyethanesulfonic acid), 2-haloethanesulfonic acids, 1,2-ethanedisulfonic acid, p-phenolsulfonic acid, beta-styrenesulfonic acid, 2-propene-1-phosphonic acid, 1-hydroxyethanephosphonic acid, 1-hydroxy-1-methylethanephosphonic acid, and 1-hydroxy-1-phenylmethanephosphonic acid can be easily alkylated to their esters by this process. The instant process avoids substituting the normally sensitive substituent groups such as vinyl, and introducing side reactions such as the splitting out of water from isethionic acid. The process can produce esters which cannot be produced by normal methods such as the alkyl ester of 1,2-ethanedisulfonic acid which cannot be prepared from the disulfonyl chloride and sodium alkoxide because of decomposition of the acid chloride. In addition, the process of the instant invention has also been found useful to prepare high yields of the lower alkyl esters of sulfonic acids such as methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, butanesulfonic acid, 3,3-dimethylbutanesulfonic acid, p-toluenesulfonic acid, benzenesulfonic acid, p-chlorobenzenesulfonic acid, cyclohexanesulfonic acid, alpha-toluenesulfonic acid, cyclopentanesulfonic acid, 1-octanesulfonic acid, and the like. The instant process has also been found useful to prepare the lower alkyl esters of phosphonic acids such as methanephosphonic acid, ethanephosphonic acid, n-hexanephosphonic acid, benzenephosphonic acid, beta-toluenephosphonic acid, p-chlorobenzenephosphonic acid, 3-nitrobenzenephosphonic acid, phosphorous acid, and the like.

The conditions under which the process of the instant invention is carried out are unexpectedly advantageous because of their comparative mildness in contrast to the severe conditions or strong reagents usually required for alkylations. It has been found that the alkylation of sulfonic and phosphonic acids in general can be accomplished at temperatures of from about 0° C. to 200° C. in reasonable periods of time. With many of such acids the reaction can be carried out without additional heating because of its exothermic nature. With some of the weaker acids the reaction is accomplished by heating the reaction mixture to a temperature higher than the boiling point of the alkyl carboxylate used with continuous reflux from an associated condenser. Although yields are increased by the use of an excess of the orthocarboxylate alkylating agents, such is not necessary, since it has been found that when reacted in less than equi-

molar quantities of the alkyl carboxylates good yields are realized.

The application of the process of the instant invention is illustrated by the following examples. It is to be understood that the invention is not limited to any specific reagents or conditions as set forth herein, but is commensurate with the entire specification and the appended claims.

Example I

There was added 13.2 grams (0.09 mole) of triethyl orthoformate to 11 grams (0.1 mole) of ethylenesulfonic acid. Heat was immediately evolved and the flask was immersed in an ice water bath. When the reaction mixture had turned a deep red-brown color a Claisen distillation head was fitted to the flask and ethyl formate and some ethanol distilled off at a head temperature of 55° C. Vacuum was applied to distill off unreacted triethyl orthoformate and by-product ethanol. The reaction mixture was poured into water and formed a two-phase system. The mixture was extracted three times with ether, the ether extract was washed with distilled water, and dried over calcium chloride. The dried ether extract was distilled after adding anhydrous potassium carbonate to yield 4.84 grams (0.0356 mole) of ethyl ethylenesulfonate for a 40 percent yield. The product boiled at 73.5–74° C. and analyzed 35.61 percent carbon and 5.86 percent hydrogen compared to a theoretical content of 35.28 percent carbon and 5.85 percent hydrogen.

Example II

In the same manner as in Example I above 30.15 grams (0.2 mole) of triethyl orthoformate was added to 8.0 grams (0.05 mole) of benzenephosphonic acid and the reaction mixture heated together for about 4 hours during which time a distillate of ethyl formate was taken off at 54° C. At the end of this time vacuum was applied to the flask to strip off the remaining ethanol and the unreacted triethyl orthoformate. The product was distilled under a vacuum of 0.1 mm. of mercury to give 8.86 grams of ethyl benzenephosphonate boiling at 80–84° C. for a yield of approximately 83 percent. The product had a refractive index at 25° C. of 1.4937 as compared to literature value for the refractive index at that temperature of 1.4935.

Example III

There were reacted 8.24 grams (0.1 mole) of phosphorous acid with 39.2 grams (0.265 mole) of triethyl orthoformate by heating together for about four hours. During this time ethyl formate distilled at 54° C. After removing the ethanol and unreacted triethyl orthoformate under vacuum, the product was distilled at 6.5 mm. of mercury at a head temperature of 55° C. to yield 9.24 grams of diethyl hydrogen phosphite, representing a yield of 76 percent. The product possessed a refractive index at 20° of 1.4039 as compared to the literature value for that index of 1.4080.

Example IV

In the same manner as in Example I above 20 grams (0.13 mole) of triethyl orthoformate was added to 9.5 grams (0.05 mole) of p-toluenesulfonic acid. Heat was immediately evolved and upon its subsidence the reaction mixture was warmed on a water bath to distill off ethyl formate and ethanol boiling between 54 and 79° C. When all distillation had ceased vacuum was applied to the system and the excess triethyl orthoformate was removed by another distillation. The reaction mixture was then poured into water and extracted three times with ether. The ether layer was washed once with dilute potassium bicarbonate solution and the ether evaporated. The crude product thus obtained amounted to 9.8 grams (0.049 mole) of ethyl p-toluenesulfonate representing a yield of 98 percent of theoretical and melting at 30–31° C. as compared to a recorded melting point in the literature of 32° C.

Example V

Methanesulfonic acid was produced by refluxing 43 grams of methanesulfonyl chloride together with 7 grams of water for 2 hours at which time a single phase had resulted. The hydrogen chloride gas was removed under vacuum and the contents of the flask transferred to a distillation flask. The pressure was reduced to 2 mm. of mercury and a small quantity of unreacted methanesulfonyl chloride recovered. The distillation was stopped when the first drop of acid distilled at 147° C. in order to prevent decomposition and the reaction residue was isolated as the desired methanesulfonic acid.

In the same manner as in Example IV above there was reacted 15.8 grams (0.16 mole) of the crude methanesulfonic acid obtained above with 60 grams (0.4 mole) of triethyl orthoformate. The reaction proceeded in the same manner as described in Example IV above. Upon isolation and washing of the ether extract said extract was dried overnight over calcium chloride and potassium carbonate and the ether distilled from the extract. There was then distilled a total of 5 grams of ethyl methanesulfonate representing a yield of 25 percent based on the crude methanesulfonic acid employed boiling at 80–81° C. at 8 mm. pressure.

Example VI

In the same manner as Example IV above there was reacted 5.5 grams (0.05 mole) of p-toluenesulfonic acid monohydrate with 15 grams (0.11 mole) of trimethyl orthopropionate. The resulting mixture was heated in the same manner as described in Example IV above and the by-products distilled. The reaction mixture residue was poured into water, extracted three times with ether, the ether extract washed with potassium bicarbonate solution, and the ether evaporated. In this manner there was realized 8.8 grams of methyl p-toluenesulfonate which was practically water white in color and represented an 88 percent yield of the desired product. The crude product melted at 26–27° C. Upon recrystallization from ethyl ether and ligroin the melting point of the product was 27–28° C. as compared with the recorded value in the literature of 28° C.

Example VII

There was added to 17.4 grams (0.1 mole) of p-phenolsulfonic acid 16 grams (0.115 mole) of triethyl orthoformate. The reaction mixture was heated on a water bath to approximately 54° C. in order to distill ethyl formate. Two separate phases persisted in the reaction mixture but one decreased upon distillation of the by-product. After a period of 60 minutes there was added 27 grams (0.18 mole) of additional triethyl orthoformate and distillation continued. At the end of an additional period of 50 minutes a small layer still persisted. A third portion of 21 grams (0.13 mole) of triethyl orthoformate was added. After distillation of by-product from the third addition the reaction mixture constituted a homogeneous solution. After the removal of the excess triethyl orthoformate and ethanol at reduced pressure the reaction mixture residue was poured into water and extracted 3 times with ether. Titration of the extracted water layer indicated the presence of 55 percent of the starting p-phenolsulfonic acid. The crude ethyl p-phenolsulfonate remaining after evaporation of the ether was an oil weighing 6 grams and representing a yield of 30 percent. This rather viscous oil was characterized by converting to the benzoyl derivative by means of the Schotten-Baumann reaction with benzoyl chloride and sodium hydroxide. There was obtained 9 grams of ethyl O-benzoyl-p-phenolsulfonate which possessed a melting point of 54–55° C. Recrystallization of the crude benzoyl derivative from ethyl ether and ligroin yielded a material having a melting point of

61–61.5° C. as compared to a recorded value in the literature of 62° C.

From the above examples it is apparent that the process of the instant invention is useful in preparing alkyl esters of sulfonic and phosphonic acids, including both saturated and unsaturated aliphatic and aromatic acids. Furthermore, the instant process is of unique utility in the direct preparation of alkyl esters of such acids bearing substituent groups sensitive to other means of alkylation such as the ethylenesulfonic and p-phenolsulfonic acids of the above examples.

Other advantages accrue from the use of the process of the instant invention. It is possible to recover unreacted starting materials of the alkylation process which are suitable for reuse in this or other processes. The trialkyl orthocarboxylates are distilled at a sufficiently different temperature range to insure good separation from the by-products of the alkylation reaction and these recovered trialkyl orthocarboxylates are suitable for further use, including reuse in the instant process. Also, the unreacted acids used in the process are recoverable for subsequent additional and further uses. For example, in the recovery procedures illustrated in the above examples the unreacted sulfonic acids remaining in the aqueous layer after extraction of the alkyl esters produced are easily recovered by evaporation or distillation of the water and are of such quality that they can be reused. Numerous other advantages of the instant invention will be apparent to those skilled in the art.

The principal products of the process of the instant invention, the alkyl esters of the sulfonic and phosphonic acids, are suitable for a great variety of uses. Some of the esters are excellent plasticizing agents for the plasticization of synthetic resins. Others, including the alkyl ethylenesulfonates, are themselves polymerizable to such resinous products. Many of the sulfonates possess utility as surface active agents in the nature of detergents and the like.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A process for alkylating acids which comprises reacting an acid selected from the group consisting of sulfonic acids and phosphonic acids with a trialkyl orthoester of a monocarboxylic acid of from one to five carbon atoms in which each alkyl group contains from one to six carbon atoms inclusive and recovering the alkyl ester of the said acid selected from the group consisting of sulfonic acids and phosphonic acids so produced.

2. The process of claim 1 wherein the trialkyl orthoester is a trialkyl orthoformate in which each alkyl group contains from one to six carbon atoms inclusive.

3. The process of claim 1 wherein the trialkyl orthoester is a trialkyl orthoacetate in which each alkyl group contains from one to six carbon atoms inclusive.

4. The process of claim 1 wherein the trialkyl orthoester is a trialkyl orthopropionate in which each alkyl group contains from one to six carbon atoms inclusive.

5. The process of claim 1 wherein the trialkyl orthoester is a trialkyl orthobutyrate in which each alkyl group contains from one to six carbon atoms inclusive.

6. The process of claim 1 wherein the trialkyl orthoester is a trialkyl orthovalerate in which each alkyl group contains from one to six carbon atoms inclusive.

7. The process of claim 1 wherein the acid is ethylenesulfonic acid.

8. The process of claim 1 wherein the acid is methanesulfonic acid.

9. The process of claim 1 wherein the acid is p-toluenesulfonic acid.

10. The process of claim 1 wherein the acid is p-phenolsulfonic acid.

11. The process of claim 1 wherein the acid is benzenephosphonic acid.

12. A process for alkylating acids which comprises heating until reacted an acid selected from the group consisting of sulfonic acids and phosphonic acids with a trialkyl orthoester of a monocarboxylic acid of from one to five carbon atoms in which each alkyl group contains from one to six carbon atoms inclusive, distilling off by-products of the said reaction and unreacted alkyl orthoester, and recovering the alkyl ester of the said acid selected from the group consisting of sulfonic acids and phosphonic acids so produced.

13. A method for producing ethyl ethylenesulfonate which comprises reacting ethylenesulfonic acid with triethyl orthoformate, distilling off ethyl formate, ethanol, and unreacted triethyl orthoformate, and recovering the ethyl ethylenesulfonate thus produced.

14. A method for producing ethyl methanesulfonate which comprises reacting methanesulfonic acid with triethyl orthoformate, distilling off ethyl formate, ethanol, and unreacted triethyl orthoformate, and recovering the ethyl methanesulfonate thus produced.

15. A method for producing ethyl p-phenolsulfonate which comprises reacting p-phenolsulfonic acid with triethyl orthoformate, distilling off ethyl formate, ethanol, and unreacted triethyl orthoformate, and recovering the ethyl p-phenolsulfonate thus produced.

16. A method for producing ethyl benzenephosphonate which comprises reacting benzenephosphonic acid with triethyl orthoformate, distilling off ethyl formate, ethanol, and unreacted triethyl orthoformate, and recovering the ethyl benzenephosphonate thus produced.

17. A method for producing methyl p-toluenesulfonate which comprises reacting p-toluenesulfonic acid with trimethyl orthopropionate, distilling off methyl propionate, methanol, and unreacted trimethyl orthopropionate, and recovering the methyl p-toluenesulfonate thus produced.

No references cited.