Patented Nov. 11, 1947

2,430,569

UNITED STATES PATENT OFFICE

2,430,569

METHOD OF THE PRODUCTION OF NEUTRAL ESTERS OF PHOSPHORIC ACID

David C. Hull and Albert H. Agett, Kingsport, Tenn., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application December 8, 1943, Serial No. 513,471

11 Claims. (Cl. 260—461)

1

This invention relates to the preparation of neutral esters of phosphoric acid by reacting an alkyl meta phosphate or pyrophosphate with an acetal.

Neutral esters of phosphoric acid have of late years assumed importance such as for plasticizers, spinning lubricants and the like. Various methods have been suggested for preparing these esters such as by reacting alcohol and phosphorous oxychloride, ethylene oxide and trichloride, hydroquinone and phosphorous oxychloride or phenols and either phosphorous pentachloride or P_2O_5. These various methods which have been suggested heretofore have involved either the use of expensive starting materials or difficulty and expense in refining the products obtained. Also, in many cases side reactions have occurred cutting down the yields.

One object of our invention is to provide a method of preparing phosphoric acid esters in an economical manner. This economy is realized by the use of less expensive starting material, by obtaining the product in good yield, and by recovering the product merely by vacuum distillation in a form sufficiently pure for use commercially.

We have found that the reaction of an alkyl meta phosphate or pyrophosphate with an acetal at an elevated temperature results in neutral esters of phosphoric acid which are of value for the various uses to which such compounds are put at the present time. The reaction may either be carried out without a catalyst or may be promoted by the use of an esterification catalyst if desired.

The alkyl or aryl meta phosphate or pyrophosphate or their mixture employed as the starting materials for our process may be prepared, for instance, by reacting P_2O_5 with an ether, the latter not being present in more than a theoretical amount or by treating triethyl phosphate with P_2O_5 to convert it to the meta phosphate or pyrophosphate. The alkyl meta phosphate or the pyrophosphate or their mixture and the acetal are mixed together and subjected to a temperature of at least 65° C. for several hours so as to form the desired product. Instead of ethyl meta phosphate or pyrophosphate, other alkyl meta phosphates or pyrophosphates may be employed such as those in which the alkyl group is methyl, normal or isopropyl or normal or isobutyl. If desired, an aryl meta phosphate or pyrophosphate may be employed such as phenyl or cresyl meta phosphate or pyrophosphate.

The acetal employed may be any of the compounds of this type, a simple and effective compound which may be employed being ethyl butyral. However, other acetals such as ethyl propional, methyl butyral, or in fact any of the acetals particularly those prepared from an aldehyde having 4 or more carbon atoms may be employed.

2

As the acetals are not decidedly low boiling ordinarily the reaction in accordance with our invention may be carried out at atmospheric pressure and it is preferred to carry out the reaction under moderate temperature conditions. Nevertheless it is to be understood that higher temperatures are not precluded, the only criterion being that the temperature be limited so as to not generate pressures which would be destructive of equipment or materials. We have found that the reaction of the acetal and a metaphosphate or pyrophosphate takes place readily and, therefore, a wide temperature latitude is permissible. In practical operation a temperature of 80° C. is ordinarily preferred. However, temperatures ranging from 0° C. up to 200° C. are useful in the carrying out of our process, the most suitable temperatures in this range being a matter of selection depending on the reaction materials employed, particularly the acetals chosen.

The alkyl meta phosphate or pyrophosphate employed as a starting material is preferably prepared immediately prior to use and the reaction mass containing that material is employed in the reaction. For instance, ethyl meta phosphate and pyrophosphate may be prepared by reacting P_2O_5 and diethyl ether, the latter being present in no more than theoretical amount. However, if desired, triethyl phosphate may be prepared in accordance with the method described in Hull and Snodgrass application, Serial No. 513,472, now United States Patent 2,407,279, dated Sept. 10, 1946, filed of even date and the ethyl meta phosphate may be prepared therefrom by reacting the triethyl phosphate with P_2O_5. If desired, the triethyl phosphate used may be prepared by reactions known in the prior art. The time employed for the reaction is not critical depending upon the vigorousness of the treatment and whether or not a catalyst is employed. Any commonly known esterification catalyst may be used to promote the reaction providing it is compatible with the constituents of the reaction mass. Some of the catalysts which may be mentioned as suitable are sulfuric acid, phosphoric acid, zinc chloride, iodine, ferric chloride, etc. The following example illustrates the preparation of a neu-

tral ester of phosphoric acid in accordance with our invention.

Example

295 grams of freshly prepared ethyl meta phosphate was mixed with 400 grams of ethyl butyral and the mass was heated at 80° C. with stirring for 5 hours. The mixture was allowed to stand overnight. The mass was then vacuum distilled and a neutral ester of phosphoric acid was thereby obtained in a yield of 52.3% based on the amount of ethyl meta phosphate used.

The neutral esters of phosphoric acid obtained may be employed for plasticizers, spinning lubricants, anti-static agents, catalysts, surface active agents, and the like. By our method phosphoric acid esters are obtained in a more pure state than by methods previously described in the prior art. Also, the phosphoric acid esters prepared in accordance with our procedure may be separated from the reaction ingredients by vacuum distillation thus avoiding the necessity of expensive purifying procedures.

We claim:

1. The method of preparing triethyl phosphate which comprises treating ethyl metaphosphate with ethyl butyral.

2. The method of preparing triethyl phosphate which comprises treating tetraethylpyrophosphate with ethyl butyral.

3. The method of preparing a neutral ester of orthophosphoric acid which comprises treating an ester of the group consisting of alkyl metaphosphates and alkyl pyrophosphates, the alkyl being of 1–4 carbon atoms, with an acetal of 6–8 carbon atoms at 0–200° C.

4. The method of preparing a neutral ester of orthophosphoric acid which comprises treating an alkyl metaphosphate, the alkyl being of 1 to 4 carbon atoms with an acetal of 6–8 carbon atoms at 0–200° C.

5. The method of preparing a neutral ester of orthophosphoric acid which comprises treating an alkyl pyrophosphate, the alkyl being of 1–4 carbon atoms with an acetal of 6–8 carbon atoms at 0–200° C.

6. The method of preparing a neutral ester of orthophosphoric acid which comprises treating an ester of the group consisting of ethyl metaphosphates and ethyl pyrophosphates with an acetal of 6–8 carbon atoms at 0–200° C.

7. The method of preparing a neutral ester of orthophosphoric acid which comprises treating an ester of the group consisting of alkyl metaphosphates and alkyl pyrophosphates, the alkyl being of 1–4 carbon atoms with ethyl butyral at 0–200° C.

8. The method of preparing a neutral ester of orthophosphoric acid which comprises treating an ester of the group consisting of alkyl metaphosphate and alkyl pyrophosphate, the alkyl being of 1–4 carbon atoms with ethyl propional.

9. The method of preparing a neutral ester of orthophosphoric acid which comprises treating an ester of the group consisting of alkyl metaphosphate and alkyl pyrophosphate, the alkyl being of 1–4 carbon atoms with methyl butyral.

10. A method of preparing a neutral ester of orthophosphoric acid which comprises treating ethyl metaphosphate with an acetal of 6–8 carbon atoms at 0–200° C.

11. A method of preparing a neutral ester of orthophosphoric acid which comprises treating tetra ethyl pyrophosphate with an acetal of 6–8 carbon atoms at 0–200° C.

DAVID C. HULL.
ALBERT H. AGETT.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,052,029	Harris	Apr. 25, 1936
2,325,597	Farrington	Aug. 3, 1943

FOREIGN PATENTS

Number	Country	Date
481,557	Great Britain	Mar. 7, 1938

OTHER REFERENCES

Chemical Abstracts, vol. 31, 1937, pp. 2166–2167 (abstract of article by Wagner-Jauregg et al. in Berichte).

Feiser et al., Organic Chemistry, page 32 (1944), Heath & Co., publishers, Boston.

Science News Letter, March 22, 1947, page 188.