Patented July 16, 1940 2,208,328

UNITED STATES PATENT OFFICE

2,208,328

NITRILES OF ACRYLIC ACIDS

Joy G. Lichty, Stow, Ohio, assignor to Wingfoot Corporation, Wilmington, Del., a corporation of Delaware

No Drawing. Application October 26, 1938, Serial No. 237,061

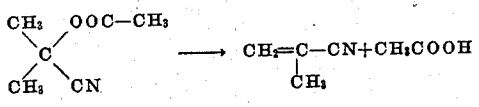
10 Claims. (Cl. 260—464)

This invention relates to an improved method of preparing nitriles of acrylic acids and, more particularly, to improved catalysts for the pyrolysis of cyanoalkyl esters and cyanoalkyl carbinols for the purpose of obtaining acrylo nitriles.

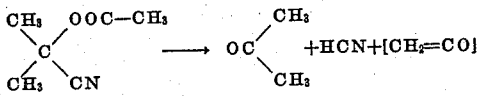
Cyanoalkyl esters and carbinols, such as the cyanoalkyl esters of fatty acids, may be subjected to pyrolysis to yield nitriles of various acrylic acids, such as acrylo nitrile and methacrylo nitrile. The method is subject to the disadvantage that excessive temperatures polymerizes the monomeric acrylo nitriles, even in the presence of inhibitors and, also, the reaction may partly proceed in a different manner which does not yield the desired product. The present method employs temperatures and catalysts which tend to prevent polymerization of the product and induce the reaction to proceed largely in the desired direction. Accordingly, by the use of the process herein described, it is possible to pyrolyze cyanoalkyl esters and cyanoalkyl carbinols, such as the cyanoalkyl esters of fatty acids, and particularly the alpha cyanoalkyl esters of lower fatty acids and the beta cyano carbinols to obtain nitriles of acrylic acids in much better yields than have been obtainable by the methods heretofore employed.

To illustrate, cyano isopropyl acetate may be pyrolyzed to yield methacrylo nitrile, but the pyrolysis may also produce acetone, hydrogen cyanide and, possibly, ketene, in accordance with the following equations:

(I)



(II)



The tendency of the reaction to proceed in the direction indicated by Equation II may be measured by the amount of HCN which is found in the reaction product.

Various catalysts and temperature conditions were tried out to determine the conditions most favorable to the reaction indicated by Equation I. The apparatus used consisted of a Pyrex glass tube one inch in diameter by 16 inches long, 12 inches of this tube being heated by means of a resistance coil. The exit end of the tube was equipped with a thermocouple and an exit tube leading to a condenser. The tube was charged with the catalyst, heated to the desired temperature and the cyanoalkyl acyl compound added through a dropping funnel. The temperature and rate of flow desired were established and maintained for a period of time and a sample of the product was then taken.

The extent of the reaction was then determined by titration of an aliquot part of a 10-gram sample dissolved in neutralized alcohol, to determine the amount of acetic acid present. This gives a measure of the extent to which both Reactions I and II, above, have proceeded, when cyano isopropyl acetate is the substance under investigation, since the ketene probably produced in Reaction II goes over to acetic acid. At the same time, estimation of the amount of HCN produced measures the extent to which the route indicated by Equation II has been followed. The difference between the two determinations indicates how much of the cyanoalkyl compound is being converted to an acrylonitrile.

It was found that the reaction could be successfully conducted at temperatures ranging from 350° to 600° C. but best results were obtained between 350° and 450° C., a temperature of 400° C. being selected as the optimum average temperature for the reason that, while pyrolysis may be satisfactorily conducted at higher temperatures, the product polymerizes and cuts down the yield of useful monomer. Best results with respect to yield and purity were obtained when the catalyst was elementary copper, elementary nickel, salts of copper or salts of nickel, such as copper sulfate, copper acetate, cuprous chloride, nickel sulfate, nickel acetate, nickel chloride, elementary copper in connection with iodine in the ester to be pyrolyzed, and elementary nickel in connection with iodine in the ester to be pyrolyzed. Quartz is also effective as a catalyst when used in conjunction with iodine in the ester. Heat is supplied to the reaction by heating the catalyst, or the solid portion thereof where iodine is present, to the specified temperature.

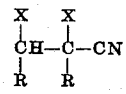
Results obtained using these catalysts within the preferred range of temperatures, namely, 350°–400° C., as applied to the pyrolysis of cyano isopropyl acetate to yield methacrylo nitrile, gave the following results:

Catalyst	Percent pyrolysis		
	350° C.	400° C.	Average at 400° C.
Copper wire	26.0	72.7, 74.0	73.3
CuCl pumice	26.0	63.9, 66.5	65.2
Quartz ester contains 1% I_2	29.8	66.8, 66.8	66.8
Copper wire ester contains 1% I_2	32.4	76.5, 74.3	75.4
Quartz	7.6	40.2, 38.4	39.3

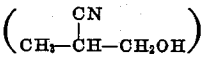
It will be noted that the results obtained with the improved catalysts were high, nearly ¾ of

the theoretically possible yield of methacrylo nitrile being obtained from the pyrolysis of cyano isopropyl acetate. The formation of hydrogen cyanide and acetone was not appreciable, indicating that Reaction II does not proceed to any great extent. Also, it will be observed that quartz alone gave a yield of not much more than half that obtained with the catalysts of the invention at the specified temperature.

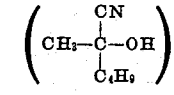
The method, employing the improved catalysts, can be applied to the pyrolysis of other cyanoalkyl esters and cyanoalkyl carbinols, the process being generally applicable to the treatment of compounds included by the formula



where R is an alkyl, aryl or aralkyl group or hydrogen and X is carboxy alkyl, hydroxyl or hydrogen and only one X being hydrogen, such as the cyanoalkyl esters of fatty acids, preferably the alpha cyanoalkyl esters of the lower fatty acids, i. e., those from formic acid up to and including butyric acid and the beta cyano carbinols. Examples are cyanoethyl acetate, cyanoisopropyl acetate, cyanobutyl acetate, cyano secondary butyl acetate, alpha-phenyl-alpha-cyanoethyl acetate, cyanoethyl formate, cyanobutyl propionate, cyanoisopropyl butyrate, etc. There may be obtained by this method acrylo nitrile, methacrylo nitrile, ethacrylo nitrile, alpha phenyl acrylonitrile, propyl acrylo nitrile, butyl acrylo nitrile, amyl acrylonitrile, hexyl acrylonitrile and similar acrylonitriles. Cyanoalkyl carbinols which may be pyrolyzed in the same manner are beta cyanomethyl carbinol ($CN—CH_2—CH_2—OH$), beta cyano n-propyl alcohol



alpha cyanomethyl butyl carbinol



and the like.

While there has been described above a preferred embodiment of the invention, it will be understood that the same is not limited thereto but that the conditions of pyrolysis can be modified and various cyanoalkyl esters and cyanoalkyl carbinols other than those mentioned can be treated, it being intended to include by such expressions compounds wherein the alkyl chain is substituted by various radicals, such as other alkyl groups and aryl groups. However, the temperatures to be employed should preferably be those indicated above and the catalysts used will be those mentioned. It is intended, then, that the patent shall cover, by suitable expression in the appended claims, all features of patentable novelty residing in the invention.

What I claim is:

1. A method of preparing nitriles of acrylic acids which comprises heating a compound from the group consisting of cyanoalkyl esters and cyanoalkyl carbinols in contact with iodine as a catalyst at a temperature between about 350° and 600° C.

2. A method of preparing nitriles of acrylic acids which comprises heating a compound from the group consisting of cyanoalkyl esters and cyanoalkyl carbinols in contact with iodine and a metal chosen from the group consisting of copper and nickel as a catalyst at a temperature between about 350° and 600° C.

3. A method of preparing nitriles of acrylic acids which comprises heating a cyanoalkyl ester of a fatty acid in contact with iodine as a catalyst at a temperature between about 350° and 600° C.

4. The method as in claim 3 wherein the ester is a cyanoalkyl ester of a lower fatty acid.

5. A method of preparing nitriles of acrylic acids which comprises heating a cyanoalkyl ester of a fatty acid in contact with iodine and a metal chosen from the group consisting of copper and nickel as a catalyst at a temperature between about 350° and 600° C.

6. The method as in claim 5 wherein the ester is a cyanoalkyl ester of a lower fatty acid.

7. A method of preparing methacrylonitrile which comprises heating cyanoisopropyl acetate in the presence of iodine and a metal chosen from the group consisting of copper and nickel at a temperature between about 350° and 600° C.

8. The method as in claim 7 wherein the temperature is between about 350° and 450° C.

9. A method of preparing nitriles of acrylic acids which comprises passing an alpha cyanoalkyl ester of a lower fatty acid containing iodine into contact with copper at a temperature between about 350° and 600° C.

10. A method of preparing methacrylo nitrile which comprises passing cyanoisopropyl acetate containing about one percent of iodine over elementary copper at a temperature between about 350° and 450° C.

JOY G. LICHTY.