Addition of Carboxylic Acids to Acrylonitrile

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Hydracrylonitrile acetate, propionate, *n*-butyrate, and isobutyrate were synthesized by addition of acetic, propionic, *n*-butyric, and isobutyric acids to acrylonitrile. A small amount of acrylamide was also obtained. NMR and infrared spectra of hydracrylonitrile acetate are given.

ACRYLONITRILE reacts by addition with a variety of compounds that possess a reactive hydrogen atom to yield β-substituted propionitrile derivatives. This reaction is known as cyanoethylation (*2*, *4*). Many reports have indicated the addition of over 1300 compounds to acrylonitrile, but carboxylic acids reportedly failed to add in the presence or absence of acid or base catalyst (*2*, *4*). According to the best of our knowledge there is no report of the cyanoethylation of carboxylic acids, which would have provided a simple route for synthesizing β-substituted esters of hydracrylonitrile.

Here we report the addition of some common carboxylic acids to acrylonitrile. Acetic, propionic, *n*-butyric, and isobutyric acids were added to acrylonitrile, giving the acetate, propionate, *n*-butyrate, and isobutyrate of hydracrylonitrile, respectively. A small amount of acrylamide was produced in every case. Reactions were conducted in a 50-ml. autoclave at about 160° C. for 11 hours.

The results are summarized in Table I.

$$CH_2{=}CHCN + RCOOH \rightarrow RCOOCH_2CH_2CN$$

$$R = CH_3,\ CH_3CH_2,\ CH_3CH_2CH_2,\ (CH_3)_2CH$$

Usually the addition to acrylonitrile proceeds at normal temperatures and in most cases violent reaction occurs, which is controlled by cooling and using inert solvents (*1*, *2*). Previous failures to add carboxylic acids may be attributed to the moderate conditions used, so the reaction was studied under somewhat drastic conditions. Several process parameters were studied and it was found that the reaction took place above 135° C. The optimum reaction conditions are given in Table I. Increase in reaction time increased the amount of the side product, acrylamide. A long reaction time may have helped in eliminating water from acetic acid, which in turn reacted with acrylonitrile to give acrylamide. A similar effect was noted with increase in reaction temperature. The yields of the adducts decreased sharply from acetic to isobutyric acid. Addition of sodium acetate as a catalyst gave some selectivity, since acetate ion concentration may have facilitated the nucleophilic attack, but the degree of selectivity was not appreciable in the present experiments, as the reaction was thought to be reversible at higher temperatures (*3*, *5*, *6*).

EXPERIMENTAL

NMR spectra were taken with a Model JNM-G-60 spectrometer (Japan Optics Laboratory Co.). Infrared spectra were taken with a Shimazu IR-27C spectrometer.

Hydracrylonitrile Acetate. To a 50-ml. autoclave was added 6 grams of acrylonitrile and the volume was made up to 40 ml. with acetic acid. Heating was continued for 11 hours at 155° to 160° C. After filtration, acetic acid was removed under reduced pressure. The fraction boiling at 115° to 120° C. (18 mm.) was redistilled to give pure hydracrylonitrile acetate (1), a colorless liquid boiling at 115° C. (18 mm.), which was identified by NMR, infrared, and gas chromatography by comparison with an authentic sample.

INFRARED SPECTRUM OF 1. 2900 cm.$^{-1}$ (weak), 2250.$^{-1}$ (weak), 1750 cm.$^{-1}$ (strong sharp), 1360 to 1380 cm.$^{-1}$ (medium), 1225.$^{-1}$ (strong), 1045 cm.$^{-1}$ (strong), 925 cm.$^{-1}$ (weak).

NMR OF 1 in $CdCl_3$ 5.75 (triplet $J = 6$ c.p.s., 2 protons), 7.30 (triplet $J = 6$ c.p.s., 2 protons) 7.90 (singlet, 3 protons).

The authentic sample was prepared by refluxing 10 ml. of ethylene cyanohydrine and 50 ml. of acetic anhydride for 5 hours in 100 ml. of pyridine. The solvent was removed under reduced pressure and hydracrylonitrile acetate was collected at 115° C. (18 mm.).

Acrylamide. The second fraction of the reaction products, collected at 130° to 135° C. (18 mm.), became a white solid in the flask and condenser. It was recrystallized with benzene. By NMR crystals were identified as acrylamide (12%), confirmed by infrared and gas chromatography by comparison with an authentic sample (m.p. 85° C.). There was no depression in the mixed melting point.

Table I. Addition of Carboxylic Acids to Acrylonitrile

Expt. No.	Acid	Temp., ° C.	Time, Hours	Catalyst	Product	Yield[a], %
1	CH_3COOH	155–60	11	None	$AcOCH_2CH_2CN$	40
					$CH_2{=}CHCONH_2$	12
2	CH_3COOH	155–60	15	None	$AcOCH_2CH_2CN$	40
					$CH_2{=}CHCONH_2$	19
3	CH_3COOH	155–60	11	CH_3COONa	$AcOCH_2CH_2CN$	44
					$CH_2{=}CHCONH_2$	8
4	CH_3CH_2COOH	160–70	11	None	$CH_3CH_2COOCH_2CH_2CN$	15
					$CH_2{=}CHCONH_2$	4
5	$CH_3CH_2CH_2COOH$	160–70	11	None	$CH_3CH_2CH_2COOCH_2CH_2CN$	12
					$CH_2{=}CHCONH_2$	3
6	$(CH_3)_2CHCOOH$	160–70	11	None	$(CH_3)_2CHCOOCH_2CH_2CN$	7
					$CH_2{=}CHCONH_2$	2

[a] Based on acrylonitrile used.

Hydracrylonitrile Propionate. To a 50-ml. autoclave was added 6 grams of acrylonitrile and the volume was made up to 40 ml. with propionic acid. Heating was continued at 160° C. for 11 hours. Unreacted acrylonitrile and propionic acid were removed under vacuum and the fraction boiling at 120° to 135° C. (18 mm.) was identified as a mixture of hydracrylonitrile propionate (15%) and acrylamide (4%), confirmed by their characteristic peaks on the infrared spectrometer and gas chromatograph.

Hydracrylonitrile *n*-Butyrate. The method was the same, but *n*-butyric acid was used. The fraction boiling at 130° to 135° C. (18 mm.) was found to be a mixture of hydracrylonitrile *n*-butyrate (12%) and acrylamide (3%), confirmed by infrared spectra and gas chromatography.

Hydracrylonitrile Isobutyrate. The same procedure was followed, using isobutyric instead of *n*-butyric acid. The fraction collected at 130° to 135° C. (18 mm.) was identified as a mixture of hydracrylonitrile isobutyrate (7%) and acrylamide (2%), confirmed by infrared spectra and gas chromatography.

Gas Chromatography of Adducts. The S.E. 30 and P.E.G. 20M columns were used for gas chromatography of the adducts. Quantitative analysis was done on the P.E.G. 20M at 180° C. and carrier gas at 10 ml. per minute.

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