137. *The Reaction of Acrylonitrile with Aliphatic Alcohols.*

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It has already been shown that acrylonitrile reacts smoothly with ethyl alcohol in the presence of sodium ethoxide to form β-ethoxypropionitrile. The reaction of acrylonitrile with aliphatic alcohols, containing 1—10 carbon atoms, in the presence of various alkaline catalysts, has been studied, and three new methods of preparing β-alkoxypropionitriles are described. The following new compounds have been prepared: β-iso*propoxy-*, β-n-*butoxy-*, β-*amyloxy-*, β-n-*octyloxy-*, β-*2-ethylhexyloxy-*, and β-*decyloxy-propionitriles.*

β-Alkoxypropionitriles are high-boiling mobile liquids possessing good solvent properties. By hydrolysis with hot aqueous caustic alkalis or with concentrated hydrochloric acid, they yield the corresponding β-alkoxypropionic acid.

Recently Bruson *et al.* (*J. Amer. Chem. Soc.*, 1942, **64**, 2457, 2850; 1943, **65**, 18, 23; 1944, **66**, 56) have recorded the reaction of acrylonitrile with various compounds containing reactive methylene, amino-, or hydroxy-groups. In the last category the reaction with phenols, alicyclic alcohols, unsaturated alcohols, and glycols has been described by others (D.R.P. 670,357; *Chem. Abs.*, 1939, **33**, 2907; U.S.PP. 2,280,790, 2,280,791, 2,280,792; *Chem. Abs.*, 1942, **36**, 5588, 5589; Langley and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 2326). Koelsch (*ibid.*, 1943, **65**, 437) prepared β-ethoxypropionitrile by reaction of ethyl alcohol with acrylonitrile, using alcoholic sodium ethoxide as catalyst, and Harrison and Diehl (*Org. Synth.*, 1943, **23**, 33) obtained this nitrile by the reaction of sodium cyanide with β-ethoxyethyl bromide, but the latter authors' yield is lower, and their product less pure, than is obtained by the reactions described below. Kilpi (*Z. physikal. Chem.*, 1914, **86**, 672) prepared β-methoxy- and β-ethoxy-propionitriles by the action of phosphoric oxide on the β-alkoxypropionamides.

Examination of the conditions of reaction of acrylonitrile with aliphatic alcohols of the range C_1 to C_{10} has shown three other methods of reaction to be valuable.

(1) The alcohol is dissolved in 2% aqueous sodium hydroxide and shaken with acrylonitrile (1 mol.) until reaction is complete. The non-aqueous layer then contains the β-alkoxypropionitrile, which is obtained by fractionally distilling the neutralised and dried liquid. This method is of most value with the lower alcohols.

(2) Acrylonitrile (1 mol.) is added with stirring and, if necessary, external cooling to a 0·5% solution of potassium hydroxide in the alcohol. With butyl alcohol and higher homologues the mixture is then heated

on the water-bath at 80° until no more acrylonitrile refluxes. The product, when worked up, affords the β-alkoxypropionitriles in 80—90% yield when alcohols containing not more than five carbon atoms are used.

(3) Acrylonitrile (1 mol.) is stirred into a 0·05% solution of metallic sodium in the alcohol, with cooling if necessary, the subsequent procedure being as in (2). This method is applicable to all alcohols up to decyl alcohol. Cetyl alcohol failed to react under these conditions, and also when sodium and aluminium ethoxides were used as catalysts, being recovered unchanged in each case.

The β-alkoxypropionitriles are miscible with most organic solvents, including alcohol, acetone, ether, and benzene. All except β-methoxy- and β-ethoxy-propionitriles are miscible with light petroleum (b. p. 60—80°), but even these two compounds give completely homogeneous solutions on warming. All are insoluble in water. They are high-boiling, mobile liquids with a characteristic odour, and are excellent solvents for many difficultly soluble organic chemicals and high polymers. For example, polyvinyl acetate is soluble, and polyvinyl chloride and the co-polymer of vinyl chloride and vinyl acetate are very soluble in each of the β-alkoxypropionitriles prepared. The polymethacrylates dissolve in all these solvents, especially on warming. Secondary cellulose acetate shows a graded solubility; it dissolves slowly in cold β-methoxy- and β-ethoxy-propionitriles, and, on heating in β-iso*propoxy*-, β-n-*butoxy*-, and β-*amyloxy-propionitriles*, from which it separates out on cooling. In the higher members of the series, secondary cellulose acetate is only swollen, even on boiling. Nitrocellulose is swollen by all these compounds, whereas nylon and rubber are insoluble. The polyvinylacetals, such as "Formvar" and "Butvar" (Shawinigan Chemicals Ltd.), are only slightly dissolved in the boiling nitriles. The higher members of the series dissolve cellulose acetate-butyrate and also ethyl cellulose, but they are not satisfactory plasticisers owing to their persistent odour.

On hydrolysis of the β-alkoxypropionitriles with hot 5% sodium hydroxide or concentrated hydrochloric acid, the β-alkoxypropionic acids are obtained. These are colourless liquids with a high b. p. and an objectionable odour. They have already been prepared by several methods.

EXPERIMENTAL.

β-Methoxypropionitrile.—To a solution of methyl alcohol (32 g., 1 mol.) in 50 c.c. of 2% aqueous sodium hydroxide, acrylonitrile (53 g., 1 mol.) was added, and the mixture shaken until a slight evolution of heat ceased. The upper layer was separated, neutralised with acetic acid, dried (sodium sulphate), and distilled. The nitrile (76 g., 90%) was obtained as a clear, colourless liquid, b. p. 164°.

β-Ethoxypropionitrile.—This was obtained by the same procedure but by use of ethyl alcohol (46 g., 1 mol.); it was a clear, colourless liquid, b. p. 172° (90 g., 90%).

*β-*iso*Propoxypropionitrile.*—Potassium hydroxide (0·3 g.) was dissolved in *iso*propyl alcohol (60 g., 1 mol.), and acrylonitrile (53 g., 1 mol.) added slowly with stirring. When evolution of heat ceased, the mixture was heated on the water-bath for 1 hour to complete the reaction. Distillation yielded the *nitrile* (96 g., 85%) as a colourless liquid, which became brown on standing, even in the dark; b. p. 179° (Found : N, 12·3. $C_6H_{11}ON$ requires N, 12·4%).

*β-*n*-Butoxypropionitrile.*—Similarly prepared, this *nitrile* (106 g., 88%) distilled as a clear, colourless liquid, which changed to a pale yellow on standing; b. p. 206° (Found : N, 10·85. $C_7H_{13}ON$ requires N, 11·0%).

β-Amyloxypropionitrile.—Sodium (0·05 g.) was dissolved in B.D.H. purified amyl alcohol (88 g., 1 mol.) and acrylonitrile (53 g., 1 mol.) added slowly. After procedure as before, distillation yielded *β-amyloxypropionitrile* (128 g., 92%) as a colourless liquid, which did not darken on standing; b. p. 218° (Found : N, 9·81. $C_8H_{15}ON$ requires N, 9·9%).

*β-*n*-Octyloxypropionitrile.*—Sodium (0·07 g.) was dissolved in *n*-octyl alcohol (130 g., 1 mol.) and mixed with acrylonitrile (53 g., 1 mol.). The mixture was heated on the water-bath for 1 hour at 40° and then at 80° until no further acrylonitrile refluxed. Distillation yielded *β-*n*-octyloxypropionitrile* (146 g., 80%) as a straw-coloured liquid; b. p. 150°/20 mm., 259°/760 mm. (Found : N, 7·7. $C_{11}H_{21}ON$ requires N, 7·7%). [Use of potassium hydroxide (Method 2) in place of metallic sodium gave only a 50% yield.]

β-2-Ethylhexyloxypropionitrile.—By the same procedure, 2-ethylhexyl alcohol (130 g., 1 mol.) afforded this *nitrile* (161 g., 88%) as a clear, colourless, mobile liquid; b. p. 100—110°/2 mm. (Found : C, 72·5; H, 11·7; N, 7·7. $C_{11}H_{21}ON$ requires C, 72·1; H, 11·5; N, 7·7%). Method 2 gave a lower yield (60%).

β-Decyloxypropionitrile.—This *nitrile* (73 g., 37%) was obtained from decyl alcohol (158 g., 1 mol.) by the usual method as a clear, colourless liquid; b. p. 283° (Found : N, 6·6. $C_{13}H_{25}ON$ requires N, 6·6%).

β-Ethoxypropionic Acid.—*β*-Ethoxypropionitrile (99 g., 1 mol.) was mixed with concentrated hydrochloric acid (120 c.c., 1·2 mols.) and heated under reflux for 1 hour. Ammonium chloride was filtered off, and the filtrate continuously extracted with ether. The ether was dried and evaporated, leaving *β*-ethoxypropionic acid (71 g., 60%) as a colourless, slightly oily liquid of penetrating odour; b. p. 218°.

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