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Abstract

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Chemistry

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On the Conditions for the Addition of Aromatic Amines to Acrylonitrile

(Presented by Academician I. N. Nazarov, 26 XI 1956)

It is known that the addition of aromatic amines to acrylonitrile can be carried out in the presence of acidic catalysts (acetic acid, its salts with amines, acetic anhydride, salts of inorganic acids with aromatic and aliphatic amines ((^{1-5}))).

When aromatic amines are boiled with acrylonitrile without a catalyst, addition does not occur; unchanged substances are isolated from the reaction mixture ((^{6})).

In studying this reaction we attempted to obtain β-phenylaminopropionitrile by heating the components in a sealed tube at (165–170^{ }); however,

Table 1

β-Arylaminopropionitriles
(X–) (-NH–CH_2–CH_2–CN)

X	b.p., °C/(P) mm	m.p., °C	Yield, %	Source	N %, found	N %, calculated
H	199–200/35–37	49–50	19	((^{2}))	–	–
CH(_3)	204–206/32	104	25	((^{9,3}))	–	–
Cl	199–200/7–8	74–75	53	((^{2,10}))	–	–
OC(_2)H(_5)	225/22	74,5–75	62,1	–	14,58	14,78 14,73
OCH(_3)	219–223/21	62	69,5	((^{11,10}))	–	–

the addition product could not be obtained—the starting components were isolated from the mixture. Using, instead of the base of the aromatic amine, its hydrochloride when boiling with acrylonitrile, we confirmed the negative results of Zimmermann-Craig et al. ((^{6})).

However, we found that heating the indicated components in an aqueous medium leads to the formation of β-phenylaminopropionitrile ((^{7})). We also established that ammonium chloride does not exert a catalytic influence when aniline is boiled with acrylonitrile in an anhydrous medium; in the presence of water, (NH_4Cl) catalyzes this reaction and β-phenylaminopropionitrile is obtained in a yield of about 60%.

The data presented made it possible to suppose that a necessary condition in the reaction of addition of aromatic amines to acrylonitrile is the presence of a proton in the reaction mixture. Therefore we considered it possible to carry out the addition of an aromatic amine to acrylonitrile without adding acidic catalysts in water, which, itself being an ionic medium, contains protons.

The experiments we carried out fully confirmed this assumption. It turned out that aromatic amines do indeed add to acrylonitrile when heated in water. We carried out experiments with five aroma-

aromatic amines (aniline, *p*-toluidine, *p*-chloroaniline, *p*-anisidine, *p*-phenetidine) under identical conditions, and in all cases obtained the corresponding β-arylaminopropionitriles (Table 1).

The yield of β-arylaminopropionitriles apparently depends on the solubility of the starting amines in water. We assume that the reaction mechanism consists in the formation of an intermediate carbonium ion, which itself may be the alkylating agent (^{8}).

The method for obtaining β-arylaminopropionitriles by cyanoethylation of aromatic amines in an aqueous medium may have practical significance and makes this class of compounds readily accessible.

Experimental Part

Addition of aromatic amines to acrylonitrile in water without a catalyst. An aromatic amine (0.05 mole) was heated with acrylonitrile (0.1 mole) in water (5 ml) at boiling for 11.5 h. The reaction mixture was extracted with benzene. The benzene solution was washed with water and dried with potassium carbonate. After removal of the volatile products, the residue was distilled in vacuo.

The following aromatic amines were used: aniline, *p*-toluidine, *p*-chloroaniline, *p*-anisidine, *p*-phenetidine. The results of the experiments are given in Table 1.

Reaction of aniline with acrylonitrile in an anhydrous medium. a. Aniline, 9.3 g (0.10 mole), and acrylonitrile, 6.0 g (0.11 mole), were heated in a sealed tube for 8.5 h at 165–170°. After distillation of the mixture the following

fractions were obtained: 1) 5.0 g, b.p. 76° (acrylonitrile); 2) 8.5 g, b.p. 122° at 90 mm (aniline); 3) 0.4 g, b.p. up to 115° at 3 mm; a yellowish oil distilled with decomposition and contains aniline. The oil obtained could not be crystallized.

b. Aniline, 4.7 g (0.05 mole), acrylonitrile, 2.8 g (0.05 mole), and ammonium chloride, 1.4 g (0.026 mole), were heated at boiling for 7.5 h. After the usual treatment of the reaction mixture and removal of the volatile products from the residue, fractionation in vacuo gave only aniline (3.2 g), b.p. 73° at 3-4 mm.

Reaction of aniline with acrylonitrile in an aqueous medium in the presence of NH_4Cl. In an experiment analogous to that described in paragraph "b," but carried out in the presence of water (5 ml), two fractions were isolated from the residue after removal of the readily volatile products: 1) 0.9 g, b.p. up to 100° at 7 mm —aniline; 2) 4.3 g, 58.9% of theory, b.p. 173-175° at 7 mm, m.p. 49° (from alcohol) —β-phenylaminopropionitrile.

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Note: Figure translations are in progress. See original paper for figures.