

An Improved Laboratory Preparation of Alkyl Cyanides

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Widely used laboratory manuals (1), (3), describe refluxing an aqueous solution of sodium cyanide with methanol and n-butyl bromide for 25-30 hours and carefully distilling off the methanol before isolation of n-butyl cyanide. The use of a higher boiling solvent and a much shorter reflux period has been studied. A yield equal to those in the above references (65-70%) has been obtained by refluxing for only two hours with cellosolve. The addition of small amounts of potassium iodide increase the yield. Very much lower yields were obtained when butyl bromide was replaced by butyl chloride, with or without the addition of an iodide. Yields of n-propyl cyanide are somewhat lower than those for n-butyl cyanide. These modifications have been used with advantage for several years by students in organic preparation courses.

Experimental

Two balls of 96% sodium cyanide (51 g.) (1 mole) and 2.0 g. potassium iodide are dissolved in 65 ml. of water by heating under reflux and 130 ml. cellosolve and the alkyl halide (118 g. n-butyl bromide) added. Reflux vigorously for two hours using a bulb condenser, add 200 ml. of water and distil until no more water insoluble material passes over. Separate the upper layer and wash it in turn with equal volumes of 40% calcium chloride solution, water, cold 50% sulfuric acid (to remove the isonitrile formed in the reaction) and saturated sodium bicarbonate solution. After drying with anhydrous calcium chloride, distil using a Vigreux column. The product is collected at 138-140°/737 mm. The yield is 67 and 68% in two runs and with the forerun redried and redistilled the yield is increased to 74-75%. The product has a refractive index at 25° C. of 1.3955. The literature value (2) is 1.3950.

n-Butyl cyanide from n-Butyl bromide

g. moles RBr	g. KI	% xs NaCN	hrs. reflux	% yield n-BuCN
0.89	2	10	3.3	63
0.69	2	50	3.3	58
0.91	2	10	4.6	69
0.91	None	10	4.6	54
0.88	2	16	2.0	67
0.88	2	16	2.0	68

n-Butyl cyanide from n-Butyl chloride

g. moles RCl	g. KI	% xs NaCN	hrs. reflux	% yield	recovery BuCl	corrected % yield
1.45	5	10	4	12	61	30
1.41	5	10	12	28	26	38
0.88	None	10	9	20	50	40

n-Propyl cyanide from n-Propyl bromide

g. moles RBr	g. KI	% xs NaCN	hrs. reflux	% yield n-PrCN
0.95	3	10	2.5	55
0.90	3	10	3.7	48
0.95	3	5	3.7	52

Yields were taken after two or three fractional distillations of product boiling 113-117° at 738 mm. The refractive index at 25° was 1.3815-1.3826 compared with a literature value (2) of 1.3820.

Literature Cited

1. ADAMS, R., and JOHNSON, J. R. 1949. Laboratory Experiments in Organic Chemistry. The MacMillan Co., Fourth Ed., p. 403.
2. TIMMERMANS, J. 1950. Physico-Chemical Constants of Pure Organic Compounds. Elsevier Publishing Co.
3. VOGEL, A. I. 1951. A Textbook of Practical Organic Chemistry. Longmans, Green and Co. Second Ed., p. 401.