Russian Journal of Organic Chemistry, Vol. 41, No. 8, 2005, pp. 1232–1233. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 8, 2005, p. 1254.
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SHORT COMMUNICATIONS

Synthesis of 2-Vinyloxybenzonitrile

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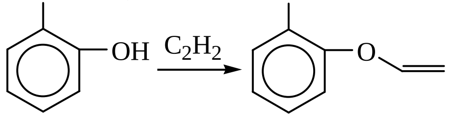
Received January 5, 2005

Vinyloxynitriles are of interest as monomers and reagents. They are prepared either by transvinylation of hydroxynitriles with vinyl ethers or by cyanoethylation of monovinyl ethers of polyhydric alcohols with acrylonitrile [1].

The benzaldehyde oxime is known to easily undergo dehydration into benzonitrile in a 91–92% yield at heating to 120–140°C for 3 h with KOH in DMSO [2]. These are the same conditions as used in catalytic vinylation of alcohols with acetylenes in DMSO [3].

We suggested that vinylation of 2-hydroxybenzaldehyde oxime (**I**) with acetylene in DMSO in the presence of KOH would result in formation of 2-vinyloxybenzonitrile (**II**). However only at rising the process temperature to 200–210°C in the reaction mixture were found traces of the expected compound **II** by means of GLC. The reaction mixture suffered strong tarring apparently due to the known processes catalyzed by bases of hydroxy groups addition to cyano groups [4].

As a result of a search for catalyst and solvent we found that oxime **I** vinylated with acetylene in the presence of anhydrous cadmium(II) acetate in 1-methyl-2-pyrrolidone at 190–195°C afforded a fair yield (46%) of vinyl ether **II**.



I **II**

2-Vinyloxybenzonitrile (II). A mixture of 200 ml of N-methylpyrrolidone, 27.4 g (0.2 mol) of oxime **I**, and 2.7 g of anhydrous cadmium(II) acetate was saturated with acetylene at a pressure 15 at and was heated for 6 h to 190–195°C. The reaction mixture was poured into 750 ml of water and extracted with ethyl ether (3×100 ml). The extract was dried with K_2CO_3 and distilled. Yield of compound **II** 13.4 g (46%), bp 111–114°C (10 mm Hg), d_4^{20} 1.0668, n_D^{20} 1.5420. IR spectrum, ν, cm^{-1}: 770, 1495, 1590, 1600, 1620, 1640, 2230, 3045, 3080, 3110. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.63 d.d (1H, *cis*-HC=CO, $^2J_{gem}$ 2.1, $^3J_{cis}$ 6.0), 4.91 d.d (1H, *trans*-HC=CO, $^2J_{gem}$ 2.1, $^3J_{trans}$ 13.6), 6.63 d.d (1H, OCH=C, $^3J_{cis}$ 6.0, $^3J_{trans}$ 13.6), 7.07 d.d (1H, Ar-H, C^{3}H, $^3J_{C^3H-C^4H}$ 9.4, $^4J_{C^3H-C^5H}$ 0.9), 7.12 d.t (1H, Ar-H, C^{5}H, $^3J_{C^4H-C^5H}$ 7.6, $^3J_{C^5H-C^6H}$ 7.6, $^4J_{C^3H-C^5H}$ 0.9), 7.53 d.d.d (1H, Ar-H, C^{4}H, $^3J_{C^4H-C^5H}$ 7.6, $^3J_{C^3H-C^4H}$ 9.4, $^4J_{C^4H-C^6H}$ 1.7), 7.53 d.t (1H, Ar-H, C^{6}H, $^3J_{C^5H-C^6H}$ 7.6, $^4J_{C^4H-C^6H}$ 1.7). ^{13}C NMR spectrum, δ, ppm: 98.392 (CH_2), 103.262 (C^1), 115.609 (NC), 116.044 (C^3), 123.178 (C^5), 133.777 (C^4), 134.356 (C^6), 146.398 (OCH), 158.158 (C^2). Found, %: C 74.32; H 4.90; N 9.45. C_9H_7NO. Calculated, %: C 74.47; H 4.86; N 9.65.

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker DPX-400 (400 and 100 MHz respectively) in $CDCl_3$ at 26°C, internal reference HMDS. IR spectrum was recorded on a spectrophotometer Specord 75-IR from thin film. The purity of the initial compound **I** and of obtained substance **II** was controlled by GLC on chromatograph LKhM-80, detector katharometer, steel column 3×3000 mm, stationary phase 3% OV-17 on Inerton Super (0.160–0.200 mm), oven temperature programmed from 60 to 280°C at a rate 4 deg/min, carrier gas helium.

In the synthesis was used commercial N-methylpyrrolidone, freshly prepared oxime **I** of purity no less than 99.5% (GLC), and commercial acetylene of 99% purity.

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