Chemistry of Heterocyclic Compounds, Vol. 36, No. 7, 2000

FORMATION OF 3-(1,3-DIYNYL)-4-(2-YNYL)-SUBSTITUTED PYRIDINES IN REACTIONS OF 1-LITHIO-1,3-DIYNES WITH BENZONITRILE

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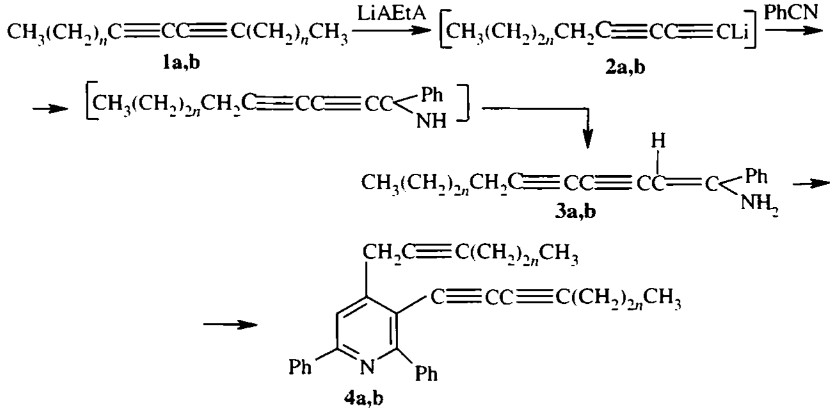
Keywords: benzonitrile, diacetylene enamines, 3-(1,3-diynyl)-4-(2-ynyl)pyridines, 1-lithio-1,3-diynes.

In studying the reaction of 1-lithio-1,3-diynes with benzonitrile, we have observed that the diacetylene enamines formed undergo ring closure, yielding 3-(1,3-diynyl)-4-(2-ynyl)-substituted pyridines.

1-Lithio-1,3-diynes **2** were obtained when disubstituted acetylenes **1** were treated with a three-fold excess of lithium 2-aminoethylamide (LiAEtA) and were used *in situ* in subsequent reactions with benzonitrile.



1–4 a *n* = 2, **b** *n* = 3

The first step, the "acetylene lightning reaction", occurs in 10 min at 16-18°C in a mixture of solvents 1:1:1 THF–benzene–hexane and an amide concentration of 1.4 mol/l. After the first step is completed, a solution of benzonitrile in THF is added to the reaction mixture and it is stirred at room temperature. According to TLC data for the reaction mixture, the second step occurs over a period of 1-1.5 h.

Under the reaction conditions, the initially formed imine is isomerized in the presence of base and is converted to diacetylene enamine.

(*Z*)-1-Phenylundec-1-ene-3,5-diynamine (**3a**) was isolated in the reaction with 1-lithiodeca-1,3-diyne (**2a**) in 60% yield, calculated based on the starting deca-4,6-diyne (**1a**). The presence of an amino group in compound **3a** is confirmed by the presence of two bands in the IR spectrum in the 3380-3490 cm-1 region. In the ^{1}H NMR spectrum, upfield we observe signals from protons of the alkyl substituent: a two-proton triplet at 2.37 ppm (2H,

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 993-995, July, 2000. Original article submitted June 15, 2000.

$J = 7$ Hz) corresponds to protons of the methylene group in the α position relative to the triple bonds; a singlet at 4.58 ppm, and a broad singlet at 5.12 ppm belong respectively to the proton at the double bond and the protons of the amino group. Downfield we see signals from protons of the phenyl ring. The ^{13}C NMR spectrum showed the presence of 5 signals from carbon atoms in the alkyl substituent, which indicates a shift of the triple bonds toward one methylene group compared with signals in the spectrum of compound **2a**; signals at 66.2, 75.0, 79.7, 85.7 ppm correspond to *sp*-hybridized atoms of the two triple bonds. Downfield we see signals from carbon atoms of the phenyl ring and signals from carbon atoms of the double bond of the enamine moiety (74.4, 158.2 ppm).

In the reaction of 1-lithiododeca-1,3-diyne with benzonitrile, we were unable to isolate enamine **3b** in pure form because during chromatographic separation on silica gel it was converted to 4-(dec-2-ynyl)-3-(undeca-1,3-diynyl)-2,6-diphenylpyridine (**4b**), the structure and composition of which were established on the basis of IR spectra, NMR spectra (^{1}H, ^{13}C, ^{13}C DEPT), and also mass spectra (M^+ 513) and elemental analysis data for C, H, and N. The yield of compound **4b** was 74%, calculated on the basis of the starting compound **1b**. We were able to detect formation of a reaction intermediate, enamine **3b**, with the help of IR spectra and ^{1}H NMR spectra of the reaction mixture before isolation.

Enamine **3a** in the presence of traces of HCl is quantitatively converted to analogously substituted 3-(nona-1,3-diynyl)-4-(oct-2-ynyl)-2,6-diphenylpyridine (**4a**), which was also completely characterized by spectral data. In the ^{1}H NMR spectra of the pyridines obtained, we observe triplet signals from protons of two methylene groups adjacent to the triple bond in the 2.3-2.4 ppm region, a singlet from protons of the methylene group between the triple bond and the pyridine ring in the 3.8-3.9 ppm region, and upfield we observe signals from protons of the two phenyl rings and a singlet from the proton of the pyridine ring at 8.05 ppm. In the ^{13}C NMR spectrum, the signals from 6 *sp*-hybridized carbon atoms confirm the presence of three triple bonds. Downfield we see signals from carbon atoms of the two phenyl rings and signals from carbon atoms of the pyridine ring (114.7, 117.7, 152.5, 155.6, 161.0 ppm).

This method allows us to obtain 3-(alka-1,3-diynyl)-4-(alka-2-ynyl)-substituted pyridines in good preparative yields in a single step from very simple and readily available starting compounds.

This research was done with the financial support of grants from the Russian Foundation for Basic Research No. 98-03-32744 and INTAS No. 97-31999.