SYNTHESIS OF ALLENIC THIOETHERS OF THE PYRIDINE SERIES

REACTION OF α-PICOLYLLITHIUM AND 2,6-LUTIDYLLITHIUM WITH ALKYLTHIOVINYLACETYLENES

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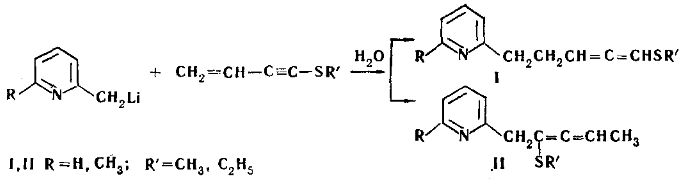
UDC 547.825.07

α-Picolyllithium and 2,6-lutidyllithium add to alkylthiovinylacetylenes to form adducts which, after demetallation with water, form allenic thioethers of the pyridine series.

It has been previously established that alkyllithium compounds add to alkylthiovinylacetylenes to form adducts which, after treatment with water, form allenic thioethers, during which the radical of the organolithium compound is fixed to the terminal carbon atom of the vinyl group [1]. The reaction of organolithium compounds of the heterocyclic series with alkylthiovinylacetylenes has not been described. We have studied the reaction of α-picolyllithium and 2,6-lutidyllithium with methyl- and ethylthiovinylacetylenes. This reaction resulted in the formation of one-to-one adducts which, after decomposition with water under an inert gas, give allenic thioethers of the pyridine series (see Table 1).* We unambiguously solved the problem of the nature of the multiple bonds and their position in the compounds obtained on the basis of a study of their IR spectra, in which one observes intense absorption bands of the unsymmetrical valence vibrations of the allenic grouping at 1940 cm^{-1} and absorption bands at 860 cm^{-1}, which correspond to deformation vibrations of the CH of the syn-disubstituted allenes. Absorption bands at 2100-2300 cm^{-1} (acetylenic bond) and 1610-1650 cm^{-1} (dienic system of bonds) were absent in the IR spectra of all of the addition products. Characteristic absorption bands for the valence vibrations of the pyridine ring at 1595 cm^{-1} were also clearly observed in the IR spectra.

The compounds that we obtained could have structure I or II depending on the site of entry of the α-picolyllithium and 2,6-lutidyllithium.



I, II $R = H, CH_3$; $R' = CH_3, C_2H_5$

We chose between these two formulas on the basis of the results of ozonization of the compound obtained by hydrolysis of the adduct of methylthiovinylacetylene ($R' = CH_3$) and α-picolyllithium (R = H). In the process, in accordance with formula I, only β-(α-pyridyl)propionic acid [2] was isolated, and acetic acid, which could form from II, was completely absent.

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* Table omitted in Russian original — Publisher.

Admiral S. O. Makarov Leningrad Higher Naval Engineering School. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 354-355, March, 1971. Original article submitted February 16, 1970.

EXPERIMENTAL

Addition of α-Picolyllithium and 2,6-Lutidyllithium to Alkylthiovinylacetylenes. An ether solution (1 : 1) of 0.07 mole of alkylthiovinylacetylene [4] was added in the course of 30 min with constant stirring at room temperature to an ether solution of organolithium compound obtained from 0.1 mole of substituted pyridine [3] under argon. A rise in temperature was observed. At the end of the reaction the contents of the flask were filtered from the unchanged lithium residues and decomposed with cold water under argon. The separated ether layer together with the ether extract was dried with calcined magnesium sulfate. The ether and volatile substances were removed by distillation, and the products were vacuum distilled. The compounds of the type I obtained (see Table 1) are slightly colored, viscous liquids with a disagreeable odor which are slightly soluble in water and quite soluble in the usual organic solvents (ether and alcohol). The products become yellow and resinify on standing in air but are stable under argon.

Ozonization of 2-[5-(Methylthio)penta-3,4-dienyl]pyridine (I, R = H, R' = CH_3). The compounds (2 g) were ozonized in 40 ml of ethyl chloride. After decomposition of the ozonide with 3% hydrogen peroxide and the usual workup, the ozonolysis products were extracted with ether by means of prolonged extraction. The extract was dried with calcined magnesium sulfate to give 0.8 g (60%) of β-(α-pyridyl)propionic acid [2].

LITERATURE CITED

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*Journal title incomplete in Russian original – Publisher.