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# REACTION OF 2-PICOLYLLITHIUM AND 6-METHYL-2-PICOLYLLITHIUM WITH VINYL(tert-BUTYL)ACETYLENE

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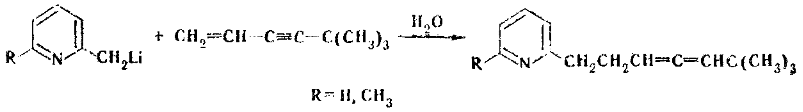
UDC 547.821.4'315.1.07:543.422.4

The possibility of obtaining pyridylallene hydrocarbons with normal structure with a branched grouping in the side chain on the basis of vinyl(alkyl)acetylene hydrocarbons with iso structures and, respectively, 2-picolyl- and 2,6-lutidyllithium is demonstrated.

The reaction of 2-picolyllithium with vinyl(alkyl acetylene hydrocarbons with normal structures may serve as a convenient method for preparation of pyridylallene hydrocarbons [1-3].

In order to extend the possibility of the utilization of this reaction in the synthesis of pyridine, furan, and thiophene derivatives and also to study the effect of groupings with iso structures attached to the triple bond of vinyl(alkyl)acetylenes on the direction of addition of heterocyclic lithium compounds to them we studied the reaction of 2-picolyl-, 2,6-lutidyl-, 2-pyridyl-, 2-furyl-, and 2-thienyllithium with vinyl(tert-butyl)acetylene. Our experiments showed that of all of the above-indicated heterocyclic lithium compounds, only 2-picolyllithium and 2,6-lutidyllithium add to the multiple bonds of vinyl(tert-butyl)acetylene in a ratio of 1:1 to give adducts, the demetallation of which with water in a stream of argon gives, respectively, 2-(6,6-dimethylhepta-3,4-dienyl)pyridine and 6-methyl-2-(6,6-dimethylhepta-3,4-dienyl)pyridine.



The IR spectra of the compounds obtained in this research contain intense absorption bands of unsummetrical stretching vibrations of the CH=C=CH grouping at 1965-1970 $cm^{-1}$, but absorption bands of the stretching vibrations of an acetylenic bond (2100-2300 $cm^{-1}$) and a 1,3-diene grouping (1610-1760 $cm^{-1}$) are completely absent; this excludes the formation in these reactions of acetylenic and 1,3-diene isomers (products of 1,2 and 3,4 addition). Characteristic absorption bands of stretching vibrations of a puridine ring at 1589-1600 $cm^{-1}$ are also observed in the IR spectra. We established the site of fixation of the groupings in 2-(6,6-dimethylhepta-3,4-dienyl)pyridine on the basis of data on its ozonization; in this case we isolated only 3-(2-pyridyl)propionic and trimethylacetic acids, and the copious liberation of carbon dioxide was observed in the decomposition of the ozonide, which additionally confirmed the presence of an allene system of bonds in the compound obtained. Taking into account the monotypical character of the indicated reactions, a similar conclusion regarding the site of fixation of the grouping can also be extended to 6-methyl-2-(6,6-dimethylhepta-3,4-dienyl)pyridine. 2-Pyridyl-, 2-furyl-, and 2-thienellithium do not add under similar conditions to the multiple bonds of both vinyl(tert-butyl)acetylene and vinyl(alkyl)acetylenic hydrocarbons with normal structures [vinyl(methyl)- and vinyl(ethyl)acetylene] in the same way as ω-styryl- and phenylacetylenyllithium [4]. Thus the direction of addition of 2-picolyllithium to vinyl(tert-butyl)acetylene does not differ from the direction of its addition to

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S. O. Makarov Leningrad Higher Engineering Nautical School, Leningrad. Translated from Khimiya Geterotsiklicheskikh Soedinenni, No. 11, pp. 1521-1522, November, 1982. Original article submitted December 28, 1981.

0009-3122/82/1811-1181$07.50

vinyl(alkyl)acetylenic hydrocarbons with normal structures, whereas 2,6-lutidyllithium adds to vinyl(tert-butyl)acetylene in the same way as 2-picolyllithium.

As a result of this research we have demonstrated the possibility of obtaining pyridylallenic hydrocarbons with normal structures with a branched grouping in the side chain on the basis of vinyl(alkyl)acetylenic hydrocarbons with iso structures and, respectively, 2-picolyl- and 2,6-lutidyllithium.

## EXPERIMENTAL

The IR spectra of the compounds obtained were recorded with an IKS-22 spectrometer.

2-Picolyllithium was prepared from 2.3 g (0.025 mole) of 2-picoline by metallation with previously prepared phenyllithium (from 0.4 g of lithium and 4 g of bromobenzene) in absolute diethyl ether and in an argon atmosphere at room temperature [5]. 2,6-Lutidyllithium was obtained from 2.7 g (0.025 mole) of 2,6-ludidine by metallation with previously prepared phenyl=lithium in the same was as 2-picolyllithium [5]. 2-Pyridyl-, 2-furyl-, and 2-thienyllithium were prepared by known methods [5].

2-(6,6-Dimethylhepta-3,4-dienyl)pyridine. An ether solution (in a ratio of 1:1) of vinyl(tert-butyl)acetylene (0.023 mole) [6] was added to the ether solution of 2-picolyllithium, obtained as described above, in the course of 30 min at –10° with continuous stirring in a stream of argon. The reaction was accompanied by a rise in the temperature of the mixture. At the end of the reaction, the reaction mixture was filtered to remove the residual unchanged lithium compound, and the filtrate was decomposed slowly with external cooling with cold water in a stream of argon (in the case of decomposition in air the pyridylallenic hydrocarbons were contaminated with hydroxy and carbonyl compounds). The ether solution was separated from the aqueous layer and combined with the ether extracts after two extractions with ether, and the combined ether solution was dried with magnesium sulfate. The ether and highly volatile substances were removed by distillation, and the residue was distilled in vacuo to give 3.3 g (70%) of 2-(6,6-dimethylhepta-3,4-dienyl)pyridine with bp 105°C (1.5 mm), $d_4^{20}$ 0.9091, and $n_D^{20}$ 1.5072. Found: C 83.6; H 9.6; N 6.9%. $C_{14}H_{19}N$. Calculated: C 83.5; H 9.5; N 7.0%.

6-Methyl-2-(6,6-dimethylhepta-3,4-dienyl)pyridine. This compound was obtained in 70% yield (based on the starting hydrocarbon) from 2,6-lutidyllithium and vinyl(tert-butyl)acetylene by a similar method. The product had bp 115-116° (1 mm), $d_4^{20}$ 0.9104, and $n_D^{20}$ 1.5080. Found: C 83.7; H 9.8; N 6.4%. $C_{15}H_2N$. Calculated: C 83.7; H 9.8; N 6.5%.

The reaction products that we obtained were slightly colored liquids with an unpleasant odor and were only slightly soluble in water but quite soluble in ordinary organic solvents (ether, alcohol). They turned yellow upon prolonged standing in air but were stable in a stream of argon.

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