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Abstract

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CHEMISTRY

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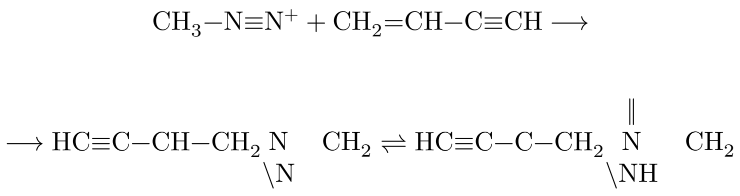
THE INTERACTION OF VINYLACETYLENE WITH DIAZOMETHANE

(Presented by Academician B. A. Arbuzov, 2 XII 1957)

In a number of works published by our laboratory, some basic regularities in the reactions of vinylacetylene hydrocarbons with electrophilic reagents have been described (^{1,2}). Of no less interest are the reactions of these hydrocarbons with nucleophilic reagents. The present article considers the results of experiments on the interaction of vinylacetylene with a typical nucleophilic reagent—diazomethane (^{3,4}).

Diazomethane readily reacts with acetylene to form pyrazole (^{5}). With ethylene it gives pyrazoline, but in poor yield (^{6}). With divinyl, depending on the ratio of the reagents and the reaction time, either 5-vinylpyrazoline or 5,5′-dipyrazolyl is formed (^{7}); with diacetylene, respectively, ethynylpyrazole or dipyrazolyl (^{8}). We found no data in the literature on the order of addition of diazomethane to vinylacetylene.

In view of the great tendency of the triple bond toward addition of nucleophilic reagents, it might have been expected that diazomethane would form vinylpyrazole with vinylacetylene. However, the experiments carried out showed that addition occurs only at the double bond, and that the reaction product is 3-ethynylpyrazoline in accordance with the scheme:



$$CH_3{-}N{\equiv}N^+ + CH_2{=}CH{-}C{\equiv}CH \longrightarrow$$

$$\longrightarrow HC{\equiv}C{-}CH{-}CH_2\;\underset{\backslash N}{N}\quad CH_2 \rightleftharpoons HC{\equiv}C{-}C{-}CH_2\;\underset{\backslash NH}{\overset{\|}{N}}\quad CH_2$$

The structure of the substance obtained was proved in the following way.

Fig. 1. Infrared transmission spectra: 1 —ethynylpyrazoline, 2 —pyrazoline

Figure 1: Fig. 1. Infrared transmission spectra: 1 —ethynylpyrazoline, 2 —pyrazoline

1. By the mercury method (⁹), 97.8% of acetylenic hydrogen (of the terminal acetylene grouping) was found in the compound.
2. In the infrared spectrum of the substance (see Fig. 1) there was a fairly intense band of the terminal conjugated acetylene grouping (2100 cm^{-1}), an intense band of CH vibrations of acetylenic hydrogen (3280 cm^{-1}), and a frequency around 1700 cm^{-1} characteristic of acetylenes (¹⁰). The characteristic frequencies of the vinyl group in the region 900—1000 cm^{-1} were absent from the spectrum. A fairly intense band at 1526 cm^{-1} corresponded to the double bond.
3. In order to decide the question of the position of the double bond in the ring, we recorded the infrared spectrum of pyrazoline. In this substance the double bond corresponds to the higher frequency 1585 cm^{-1}. Consequently, in the ethynylpyrazoline obtained by us there is conjugation of the double and acetylene bonds, since both of these bonds correspond to lowered values of the infrared frequencies.

Thus, as a result of the present investigation it was established that vinylacetylene reacts with diazomethane as a conjugated system, although it adds it only at the double bond. The order of addition corresponds to the proposed polarization of vinylacetylene and to the nucleophilic character of diazomethane.

Experimental Part

To an ethereal solution of diazomethane containing about 5 g of CH_2N_2 and cooled to —5°, liquid vinylacetylene (3.9 g) was added in the form of an ethereal solution (20 ml of ether) cooled to the same temperature.

The mixture was left in the dark at room temperature for 24 hours. The color of the solution became weaker, but decolorization did not occur (on longer standing the color intensifies).

Fig. 1. Infrared transmission spectra: **1** —ethynylpyrazoline,
2 —pyrazoline

The ethereal solution was filtered from flakes and freed from solvent by distillation on a water bath at a temperature of 40–50° (at the end of the distillation, it was carried out under the vacuum of a water-jet pump). The residue gave an oil (6.3 g), distilling in vacuum within a range of one degree. Yield 89.5% of theory. B.p. 54–55°/5 mm, d_4^{20} 1.019, n_D^{20} 1.4830.

Found, %: C 63.61; 63.67; H 6.44; 6.41; N 29.83
$C_5H_6N_2$. Calculated, %: C 63.80; H 6.47; N 29.70

A colorless transparent oil with a distinctive odor reminiscent of the odor of cocoa. On standing it evolves small bubbles of a colorless gas and gradually becomes colored first yellow, then red. It colors pine splint yellow-red. With Ilosvay' s reagent it forms a red precipitate; with an ammoniacal solution of silver oxide, a light-yellow precipitate.

Infrared spectrum (cm^{-1}): 899 v. s., 943 med., 1011 s, 1043 med., 1100 s, 1154 s, 1233 s, 1296 s, 1391 s, 1422 s, 1526 v. s, 1700 s, 2100 med., 2852 s, 2864 s, 2914 med., 2940 med., 2970 s, 3280 s, 3332 w.

Infrared spectrum of pyrazoline (cm^{-1}): 892 med., 940 s, 1028 med., 1115 med., 1158 s, 1204 s, 1258 med., 1290 s, 1328 s, 1404 s, 1433 s, 1585 s, 2869 s, 2950 s, 2975 s, 3090 med., 3322 med.

The infrared spectra were recorded on an IKS-12 spectrophotometer up to 5 μ with a LiF prism, and thereafter with a NaCl prism.

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Note: Figure translations are in progress. See original paper for figures.