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## Abstract

## Full Text

## CHEMISTRY

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# ON THE REACTIVITY OF NITROGEN-CONTAINING ETHYNYLVINYL COMPOUNDS

In our laboratory, the influence of various heteroatoms situated in direct proximity to multiple bonds on the reactivity of the latter is being studied systematically ([1–3]). The present investigation concerns the determination of the influence of a nitrogen atom on the activity of the triple bond in compounds of the general structure $R_2NCH = CH—C \equiv CH$. The reactivity of the triple bond in the indicated compounds was revealed by the hydration reaction.

As is known, acetylene and vinylacetylene are hydrated under rather severe conditions, on heating in the presence of Kucherov' s catalyst or in the gas phase at 325–400° over cadmium tungstate, zinc oxide, or a cadmium–calcium –phosphate catalyst, with formation of the corresponding ketones ([4]):

$$CH \equiv C—CH = CH_2 \xrightarrow{H_2O} CH_3COCH = CH_2.$$

Analogous conditions are also necessary for the hydration of homologs of vinylacetylene with a terminal vinylacetylene group, vinylalkylacetylenes and their derivatives ([5]).

Under milder conditions (boiling with 80% HCOOH), hydration proceeds for vinylacetylene hydrocarbons with substituents at the last and middle carbon atoms of the vinyl group $R—CH = C(R)—C \equiv CH$ ($R$ = alkyl).

The tendency toward hydration of the triple bond increases strongly in the following enyne derivatives $(Alk)_2NCH_2CH_2OCH = CH—C \equiv CH$ (I) and $(Alk)_2NCH = CH—C \equiv CH$ (II).

It was shown ([1,2]) that these compounds, under the influence of 10% sulfuric acid for I and 2% sulfuric acid for II, and on heating to 60–70°, form triacetylbenzene; i.e., under these conditions hydration of the triple bond occurs, accompanied by hydrolysis of the compounds obtained and cyclization of the formylacetone formed into triacetylbenzene.

$$(C_2H_5)_2NCH_2CH_2OCH = CH—C \equiv CH$$
$$\xrightarrow[H^+]{H_2O} [CH_3COCH_2CHO] \longrightarrow \text{triacetylbenzene}$$
$$(Alk)_2NCH = CH—C \equiv CH$$

$$\text{Alk} = CH_3 \text{ (IIa)};\ C_2H_5 \text{ (IIb)};\ C_4H_9 \text{ (IIc) and } C_5H_{11} \text{ (IId)}$$

A detailed study of the hydration reaction of these compounds led to still more interesting results. It turned out that water adds to $N, N$-dialkylamino-1-buten-1-ynes-3 (IIa) and (IIb) in the cold, in the absence of a catalyst, and with good yield $N, N$-dialkylaminovinylmethyl ketones (III). Triacetylbenzene was not isolated under these conditions,

$$\underset{\text{(IIa) and (IIb)}}{(Alk)_2NCH{=}CH{-}C{\equiv}CH} \xrightarrow{H_2O} \underset{\text{(IIIa) and (IIIb)}}{(Alk)_2NCH{=}CH{-}CO{-}CH_3}.$$

Hydrolysis of the vinyl ketones (III), accompanied by formation of triacetylbenzene, is observed only in the presence of acid catalysts (for example, 2% $H_2SO_4$). The structure of the vinyl ketones obtained, (IIIa) and (IIIb), was confirmed by IR spectra, which showed the presence of a carbonyl group conjugated with a double bond (1606 and 1661 $cm^{-1}$ for (IIIa), and 1650 and 1680 $cm^{-1}$ for (IIIb)), as well as by the color reaction for methyl ketones (7). Formation of a vinyl ketone had been observed earlier in the case of 1-$N$-($\alpha$-pyrrolidonyl)-but-3-yne, but under harsher conditions, namely under the action of 5% sulfuric acid and heating at 40° (8):

$$\text{pyrrolidone-}N{-}CH{=}CH{-}C{\equiv}CH \xrightarrow[H^+]{H_2O}$$
$$\longrightarrow \text{ pyrrolidone-}N{-}CH{=}CH{-}CO{-}CH_3.$$

**Fig. 1.** IR spectra of

$$(C_2H_5)_2NCH{=}CH{\equiv}CH \quad (1),$$
$$(C_2H_5)_2NCH{=}CH{-}C(=O){-}CH_3 \quad (2).$$

In the case of $N, N$-dialkylamino-1-buten-1-yn-3-ols (IIv and IIg), hydration likewise proceeds in the cold, but at a lower rate than for ethynylvinylamines (IIa) and (IIb). The ketone formed, on the other hand, is hydrolyzed more readily, as a result of which one of the reaction products proved to be the corresponding dialkylamine. The presence of a substance with a carbonyl group,

present as an impurity in the unreacted starting ethynylvinylamine (IIg), was shown by the IR spectrum (1687 $cm^{-1}$). Formylacetone, which does not exist in the free state and is unable under these conditions to cyclize to triacetylbenzene, evidently resinified:

$$R_2NCH{=}CH{-}C{\equiv}CH \xrightarrow{H_2O} [R_2NCH{=}CH{-}CO{-}CH_3] \rightarrow R_2NH{+}[CH_3COCH_2CHO]$$

$$R = C_4H_9 \text{ (IIv) and } C_5H_{11} \text{ (IIg).}$$

A study of the reaction with water of 1-($\beta$-diethylamino)-ethoxybut-1-en-3-yne (I) showed that under analogous conditions (in the cold, in the absence of a catalyst) it is neither hydrated nor hydrolyzed and is isolated unchanged. The experimental data on the hydration of ethynylvinylamines (II) and ethynylvinyl ethers (I), together with the previously obtained results (1, 2) on the addition to them of alcohols and amines at the triple bond, indicate the greater reactivity of ethynylvinylamines in comparison with their oxygen analogues. Dialkylaminobutenynes (II) react with aliphatic alcohols and amines, as well as with water, under milder conditions than do $\beta$-dialkylaminoethoxybutenynes (I).

This can be explained by the structural features of the compounds indicated above and, apparently, primarily by the influence on the distribution of electron density along the conjugation chain of the nitrogen atom, whose lone pair of electrons is included in the $\pi$-electron interaction of this same molecule, which is consistent with physical methods of investigation (9). On the basis of the foregoing, it follows naturally that biosynthesis, which, as is known, proceeds under extremely mild conditions, is carried out not only owing to the action of the corresponding biocatalysts, but also because under natural conditions compounds of this kind are synthesized.

molecules, the mutual influence of whose atoms ensures that the reaction proceeds under the mildest conditions.

## Experimental Part

**Synthesis of N,N-diethylaminovinyl methyl ketone (IIIb).** A mixture of 9.7 g of diethylethynylvinylamine (b.p. 83°/22 mm; $n_D^{20}$ 1.5177) and 6 g of water is sealed in an ampoule and shaken on a shaker at room temperature for 10 h. The solution is extracted with benzene, the benzene is evaporated in vacuo, and the residue, amounting to 8.8 g, is distilled in vacuo. This gives 8.2 g (75% of theory) of vinyl ketone (IIIb) and 0.4 g of resin.

The isolated vinyl ketone (IIIb) has the following constants: b.p. 155°/10 mm; $n_D^{20}$ 1.5693; $d_4^{20}$ 0.9404.

| | | | |
|---|---|---|---|
| Found, %: | C 67.92, 67.92; | H 10.61, 10.51; | N 10.08, 10.02 |
| $C_8H_{15}NO$. Calculated, %: | C 68.04; | H 10.70; | N 9.92 |

The constants and analysis of vinyl ketone (IIIb) are given for the higher-boiling fraction, since the compound indicated apparently forms in isomeric forms that correspond exactly, by analysis, to the formula $C_8H_{15}O$. N,N-Diethylaminovinyl methyl ketone (IIIb) is also formed on prolonged standing (4–5 months) at room temperature of a solution of 2 g of ethynylvinylamine (IIb) in a large excess (75 g) of diethylamine. Ketone (IIIb) is isolated by distillation in vacuo in an amount of 1.5 g (yield 60%).

**Color reaction for vinyl ketone (IIIb).** To 0.1 ml of a solution of vinyl ketone (IIIb) in methanol is added 0.5 g of a freshly prepared mixture consisting of 0.03 parts by weight of sodium nitroprusside, 5 parts by weight of ammonium acetate, and 5 parts by weight of sodium carbonate. After some time an intense blue coloration is observed, characteristic of butenones.

**Synthesis of N,N-dimethylaminovinyl methyl ketone (IIIa).** Into a three-necked flask equipped with a stirrer, a bubbling tube, and a thermometer are placed 180 g of a 33% aqueous solution of dimethylamine. At room temperature, 10.5 g of diacetylene diluted with gaseous nitrogen is passed through the solution. The reaction is exothermic (50°). The solution is stirred for 5 h and then left to stand for 24 h. The reaction product is salted out of the aqueous solution with potassium hydroxide, separated, and distilled in vacuo. This gives 10 g of N,N-dimethylaminovinyl methyl ketone (IIIa) with b.p. 120–121°/10 mm, $n_D^{20}$ 1.5593; $d_4^{20}$ 0.9655.

| | | | |
|---|---|---|---|
| Found, %: | C 63.48, 63.35; | H 9.72, 9.68; | N 12.73, 12.68 |
| $C_9H_{11}NO$. Calculated, %: | C 63.68; | H 9.79; | N 12.38 |

The isolated ketone apparently consists predominantly of the trans isomer (974 $cm^{-1}$).

**Interaction of N,N-diamylamino-1-buten-1-yne-3 (IIg) with water.** A mixture of 7 g of N,N-diamylamino-1-buten-1-yne-3 (IIb) (b.p. 139°/7 mm; $n_D^{20}$ 1.4992) and 5 ml of water in a sealed ampoule is shaken on a shaker at room temperature for 11 h. The upper layer, amounting to 6.6 g, is distilled in vacuo, as a result of which 0.9 g of diamylamine with b.p. 81°/9 mm and $n_D^{20}$ 1.4271 is isolated (literature data: $n_D^{20}$ 1.4272), 0.5 g of an intermediate fraction, 3.7 g of the starting ethynylvinylamine (IIg) with b.p. 150–152°/9 mm and $n^{20}$ 1.4943, containing an admixture of ketone (the IR spectrum of the substance contained an absorption band characteristic of a carbonyl group conjugated with a double bond, 1687 $cm^{-1}$), and 1.3 g of resin. The lower aqueous layer, amounting to 5.4 g, is extracted with benzene. After removal of the benzene, it was not possible to distill the insignificant residue. A similar result was obtained in the interaction of N,N-dibutylamino-1-buten-1-yne-3 (IIc) with water.

**Interaction of 1-($\beta$-diethylamino)-ethoxybutene-1-yne-3 (I) with water.** A mixture of 6 g of the ethynylvinyl ether (I) (b.p. 110°/18 mm; $n_D^{20}$

1.4832) and 5 ml of water is shaken in a sealed ampoule at room temperature for 12 h. The upper layer, amounting to 5.35 g, is distilled in vacuo, as a result of which 5 g of the initial ethynylvinyl ether (b.p. 102°/8 mm and $n_D^{20}$ 1.4822) and 0.15 g of resin are obtained. Nothing could be isolated by extraction from the lower aqueous layer.

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