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Abstract

Full Text

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ON THE INTERACTION OF LACTAMS WITH DIACETYLENE

The previously studied interaction of lactams with acetylene made it possible to synthesize substances of interest both practically and theoretically—vinyl lactams of the general formula $CH_2 = CH - N(CH_2)_nCO$ (1). It seemed of interest to study the reaction of lactams with diacetylene, which would make it possible to obtain valuable unsaturated compounds with conjugated systems of multiple bonds in combination with such heteroatoms as oxygen, nitrogen, and sulfur. At the same time, it was of interest to compare the activity of acetylene and diacetylene in their reaction with lactams.

There is no information in the literature on the interaction of lactams with diacetylene. In the present work, the addition of lactams to diacetylene was studied using pyrrolidone as an example. It was found that the reaction proceeds considerably more readily than with acetylene and is carried out at 20–35° and atmospheric pressure. The catalyst is the sodium salt of pyrrolidone. The reaction is conducted in dioxane or benzene; in the latter the process proceeds considerably faster. As the main reaction product, a crystalline substance with m.p. 96.8–97.2° (I) was isolated, corresponding in molecular weight and elemental composition to monopirrolidonylbutenine. In a number of experiments it was also possible to isolate a small amount of an isomeric compound II with m.p. 78.5–79°. The data of the IR spectra* of I and II, indicating the presence of the groups $C = O$, $C = C$, and $C \equiv C$ and the absence of the group $C = C = C$, ruled out possible structures of the lactim

$$((CH_2)_3 - N = C - O - C_4H_3),$$

allene, or butadiyne type

$$((CH_2)_2 - NH - CO - CH - CH = C = C = CH_2)$$

or

$$((CH_2)_3 - NH - C(OH)C \equiv C - C \equiv CH).$$

Table 1

Absorption frequencies of I and II in the IR spectrum, in cm^{-1}

	845	948	–	1020	1036	1070	1342	1420	1470	1500	1640	1715	2120
I	845	948	–	1020	1036	1070	1342	1420	1470	1500	1640	1715	2120
II	844	946	998	1024	–	1068	1344	1408	1468	1490	1638	1728	2120
Groups (2)	= CH	C = CH									C = C	C = O	C ≡ C

On the other hand, the almost complete coincidence of the absorption frequencies gave grounds to assume that I and II have the same structure. The identity of the hydrogenation product of I with *N*-*n*-butylpyrrolidone (IV), obtained by the known method (3,4) from *n*-butylamine and γ-butyrolactone, proves that I has the structure 1-*N*-(α-pyrrolidonyl)-1-buten-3-yne. This result is confirmed by the formation, on boiling I with 5% sulfuric acid, triacetylbenzene (III), whose formation upon hydrolysis of 1-substituted 1-buten-3-ynes according to the scheme:

[reaction scheme]

(IIIa) (IIIb) (III)

is well known in the literature [5,6].

The differences between I and II—in particular, the lower melting point, better solubility in most solvents, and instability of II—may be due to cis–trans isomerism or to dimorphism of the crystalline forms. Attempts to isomerize I into II with iodine in sunlight over 2 days and II into I under ultraviolet irradiation for 8 h were unsuccessful. In view of these facts, and especially in view of the complete coincidence of the UV spectra of I and II, which is unlikely for geometrical isomers [7], the more probable reason for their difference is monotropic molecular dimorphism.

In order to isolate the intermediate products—2-butyn-1-al (IIIa) or 3-butyn-1-al (IIIb)—and to prevent their trimerization, the hydrolysis reaction of I and II was carried out under milder conditions; moreover, the carbonyl compound formed was converted into a 2,4-dinitrophenylhydrazone (DNPH) by adding 2,4-dinitrophenylhydrazine (DNP) directly to the reaction mixture. In this way an unknown 2,4-DNPH, $C_{14}H_{15}N_5O_5$ (VI), m.p. 223.5–224°, was isolated. In the hydrolysis of I, it was also possible to isolate a small amount of the 2,4-DNPH of 2-butyn-1-al (VII). The investigation showed that (VI) is a derivative of 1-*N*-(α-pyrrolidonyl)-1-buten-3-one (V), formed as a result of hydration of 1-*N*-(α-pyrrolidonyl)-1-buten-3-yne at the triple bond. Ketone V was isolated upon hydration of I under mild conditions without introducing 2,4-dinitrophenylhydrazine into the reaction medium. The presence of a large exaltation of molecular refraction and of a large absorption maximum in the UV spectrum of the ketone indicates a high degree of conjugation in its molecule.

The IR spectrum confirms structure V: 1750 cm^{-1} very strong (amide $C = O$), 1682 cm^{-1} medium ($C = O$, conjugated with $C = C$), 1632 cm^{-1} and 1608 cm^{-1} very strong ($C = C$), 1464 cm^{-1} weak ($-CH_2-$), 1396 cm^{-1} medium, broad (CH_2 in the chain $CH_2 - CO - N$), 1342 cm^{-1} medium, 1242 cm^{-1} strong, 1210 cm^{-1} [2].

Fig. 1. UV absorption spectra (in C_2H_5OH).
1 $-$1-*N*-(α-pyrrolidonyl)-1-buten-3-yne (I), 2 $-$1-*N*-(α-pyrrolidonyl)-1-buten-3-yne (II), 3 $-$1-*N*-(α-pyrrolidonyl)-1-buten-3-one (V), 4 $-$1-*N*-(α-pyrrolidonyl)-4-phenylthio-1,3-butadiene (VIII).

The surprising ease of hydration of the triple bond of *N*-pyrrolidonylbutenyne, somewhat comparable with the ease of hydration of phenylacetylene [8,9], is apparently associated with interaction of the $C = O$ group of the lactam ring with the vinylacetylene chain through the nitrogen atom. This circumstance made it possible to synthesize a representative of a previously unknown series of unsaturated ketones with a lactam ring as substituent at the double bond. It should also be noted that the double bond of *N*-pyrrolidonylbutenyne is less active in the hydrolysis reaction than the alkoxybutenines (5), analogous to the greater passivity noted earlier (10) of the double bond of N-vinyllactams in the hydrolysis reaction in comparison with simple vinyl ethers.

1-N-(-Pyrrolidonyl)-1-buten-3-yne, like the alkoxybutenynes (4), in the presence of the radical initiator azobisisobutyronitrile (AIBN), adds one molecule of thiophenol with formation of 1-N-(-pyrrolidonyl)-4-phenylthio-1,3-butadiene (VIII). This is indicated by the negative reaction with Ilosvay' s reagent (absence of the $C \equiv CH$ group) and by the UV-spectrum data, which point to a greater length of the conjugated chain. In the case of radical addition of thiophenol at the double bond, the conjugation chain would be interrupted. Judging from the broad melting-point interval, analytically pure VIII is a mixture of isomers, which could not be separated by crystallization.

[reaction scheme]

Experimental Part

Diacetylene was obtained from 1,4-dichloro-2-butyne (3) and purified by passage through 10% NaOH and a column with $CaCl_2$. The amount of diacetylene entering the reaction was determined from the increase in weight.

1-N-(-Pyrrolidonyl)-1-buten-3-yne (I and II). To a weighed portion of Na-pyrrolidone, prepared from 2.3 g of pyrrolidone and 0.2 g of sodium in 3 ml of benzene, 100 ml of benzene was added; 6.64 g of diacetylene was absorbed at 5° (in a stream of nitrogen), and a solution of 6.35 g of pyrrolidone in 4 ml of benzene was added dropwise at 30-35°. The mixture was left at 30-35° for 2 h and at 20° for 2 days. The product was treated with benzene; the precipitate was filtered off and washed with benzene and ether. From the filtrate, 11.4 g of crystals was isolated, from which fractional crystallization (dibutyl ether, 70°) gave 1-N-(-pyrrolidonyl)-1-buten-3-yne: 5.16 g of form I, m.p. 92–95°, yield 41%, and 1.9 g of form II, m.p. 78–85°, yield 15.2%. Repeated recrystallizations gave I with m.p. 96.8–97.2° (from dioxane or benzene) and II with m.p. 78.5–79° (from benzene).

I. Found, %: C 70.85; 70.75; H 6.57; 6.53; N 10.63; 10.58
II. Found, %: C 70.98; 70.95; H 6.62; 6.70; N 10.37; 10.24
C_8H_9NO. Calculated, %: C 71.09; H 6.70; N 10.36

Mol. wt. (cryoscopic in C_6H_6): 126.4 for I and 119 for II, calc. 135. A mixed sample of I and II melts at 84–89°. With Ilosvay' s reagent, I and II in dioxane solution give a yellow precipitate, and with ammoniacal $AgNO_3$ solution—a white precipitate.

Hydrogenation of I. To a suspension of 5.9 g of Raney nickel saturated with hydrogen (50 ml) in 20 ml of dioxane, a solution of 2.72 g of I in 40 ml of dioxane was added; with shaking (23°; 748 mm), 1136 ml of hydrogen was absorbed (theoretical 1042 ml), giving 1.82 g of N-*n*-butylpyrrolidone (IV). Yield 64.5%. B.p. 101–101.5°/6 mm, 69–70°/2 mm, n_D^{20} 1.4656, d_4^{20} 0.9599, MR_D found 40.703. N-*n*-Butylpyrrolidone, obtained by the interaction of *n*-butylamine and γ-butyrolactone ([5,6]), had b.p. 100.5–102.5°/5.5 mm, 68.5–70°/2 mm, n_D^{20} 1.4655, d_4^{20} 0.9595, MR_D found 40.707, calculated 40.66.

Hydrolysis of 1-N-(-pyrrolidonyl)-1-buten-3-yne. 1) 0.23 g of I in 2.7 ml of 5.5% sulfuric acid was boiled for 10 min; the precipitate was filtered off at 10°, washed with water, and dried, giving 0.1 g of 1,3,5-triacetylbenzene, m.p. 154–156°. Yield 30%. A mixed sample with authentic 1,3,5-triacetylbenzene (m.p. 161–162°) melted at 156.5–159°.

2) 4 g of I and 100 ml of 5% sulfuric acid in the presence of hydroquinone were heated for 1 h at 50–70°; the solution was neutralized with 10% sodium bicarbonate at 10°, saturated with solid ammonium sulfate, and extracted with chloroform. From the extract were obtained: fraction I, b.p. 80–156°/2 mm, $n_D^{21.5}$ 1.5210, 0.22 g; fraction II, 156–157°/2 mm, $n_D^{21.5}$ 1.5604, solidification point 12°, 2.35 g of 1-N-(-pyrrolidonyl)-1-buten-3-one (V). Yield 51%. The purified sample of V had b.p. 147–147.5°/1.5 mm, solidification point 16°, n_D^{25} 1.5565, d_4^{25} 1.1364, MR_D found 43.35; for $C_8H_{11}NO_2F$, MR_D calculated 40.44.

Found, %: C 62.17; 62.16; H 7.08; 7.26; N 9.19; 9.03
$C_8H_{11}NO_2$. Calculated, %: C 62.72; H 7.23; N 9.14

2,4-Dinitrophenylhydrazone of ketone (VI). Bright red, m.p. 223.5–224° (from chloroform).

Found, %: C 50.44; 50.30; H 4.56; 4.35; N 20.91; 20.69
$C_{14}H_{15}N_5O_5$. Calculated, %: C 50.45; H 4.54; N 21.01

3) 0.4 g of I was dissolved in 4 ml of 5% sulfuric acid at 70° (30 min), and to the mixture were added 0.2 g of 2,4-dinitrophenylhydrazine, 2 ml of conc. sulfuric acid, 2 ml of water, and 4 ml of 96% ethanol. The precipitate filtered off after one day was washed with water, alcohol, and ether, giving 0.25 g of VI, m.p. 211-216°. Yield 74%. A pure sample had m.p. 222.5-223.5° (from chloroform) and gave no depression of the m.p. in a mixed sample with VI obtained in experiment 2. From the acidic mother liquor, by precipitation with water and extraction with ether, 0.11 g of yellow crystals, m.p. 111-112°, was isolated; from these, by crystallization in 96% ethanol, 0.031 g of the 2,4-dinitrophenylhydrazone of 2-butyn-1-al (VII), m.p. 132-134°, was obtained. Yield 13.6%. Literature data (10): m.p. 136°. A mixed sample of VII with authentic 2,4-DNPH of 2-butyn-1-al (m.p. 134.5-135°) melted at 132.5-135°. 4) 0.4 g of II was dissolved in 4 ml of 5% sulfuric acid at 45° (30 min), DNPH was added to the solution, and, analogously to experiment 3, VI, m.p. 222-223°, was obtained. Yield 98% based on DNPH. A mixed sample with the samples of VII obtained in experiments 2 and 3 gave no depression of the m.p.

1-N-(-Pyrrolidonyl)-4-phenylthio-1,3-butadiene (VIII). To a solution of 2.02 g of I and 0.01 g of AIBN in 10 ml of dioxane was added 1.79 g of thiophenol; the mixture was left for a week at 20°, dioxane was distilled off in vacuo, and by crystallization of the solid residue (3.68 g), 1.45 g of VIII, m.p. 94-102.5° (from 96% ethanol), was obtained. Yield 39.5%. After recrystallization from dibutyl ether and heptane, VIII had m.p. 98-102.5°.

Found, %: C 68.83; 69.03; H 6.26; 6.19; S 13.00; 13.07
$C_{14}H_{15}NOS$. Calculated, %: C 68.53; H 6.16; S 13.07

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