REACTIONS OF 1,3-ALKADIYNES (n > 4) WITH SECONDARY AMINES*

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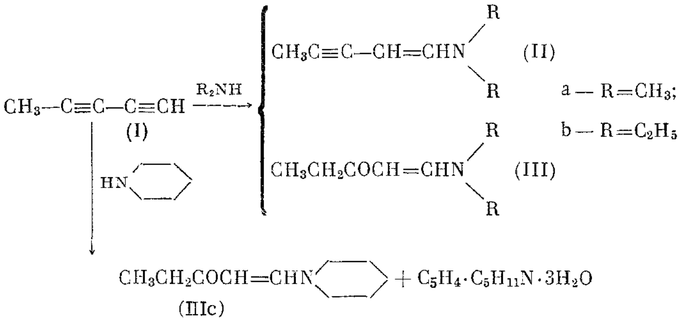
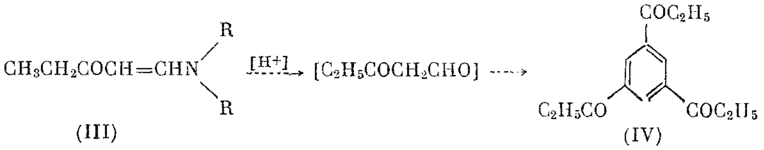
The nucleophilic addition of amines to butadiyne [1,2] and to some diynic alcohols and glycols [3-6] has been studied fairly thoroughly, but the addition of amines to 1,3-alkadiynes with more than four carbon atoms in the chain has not been studied. We here report a study of this question.

We have found that in the reaction of 1,3-pentadiyne (I) with 30% aqueous solutions of dimethyl- and diethyl-amines at room temperature mixtures are formed of the N,N-dialkyl-1-penten-3-ynylamines (II) and 1-(dialkylamino)-1-penten-3-ones (III).



The performance of this reaction at higher temperatures or for a long time at room temperature leads to the formation of only the 1-(dialkylamino)-1-penten-3-ones (III). This indicates that in presence of the secondary amine the enamine (II) is readily converted into (III), and this was confirmed by a special experiment. According to the IR and UV spectra the keto group in the 1-(dialkylamino)-1-penten-3-ones (III) is conjugated with the double bond, and their structure as products of the addition of the amino group at the terminal carbon was confirmed by the conversion of (III) by acid hydrolysis into 1,3,5-tripropionylbenzene (IV) [7]:



Also, on reaction with p-nitrophenylhydrazine in acetic acid the 1-(dialkylamino)-1-penten-3-one (IIIb) gives, in accordance with its structure, a mixture of the known 3- and 5-ethyl-1-p-nitrophenylpyrazoles [8].

It is known that the nucleophilic addition of alcohols and thiols to diynes and polyynes usually leads to the formation of cis isomers [9, 10], although sometimes a mixture of both geometric isomers is formed [9]. The IR spectra of our products (IIa) and (IIb) contain absorption bands at 690 and 931 cm^{-1} and is indicative of the presence of both the cis and the trans isomer in these products with a predominance of the former. When the products were heated, ready isomerization of cis into trans was observed, and as a result it was not possible to determine the percent composition of the reaction products with the aid of gas-liquid chromatography.

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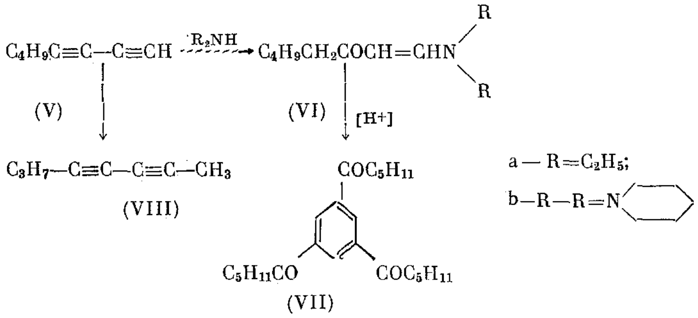
Unlike N,N-dialkyl-1-buten-3-ynylamines [1], our N,N-dialkyl-1-penten-3-ynylamines (IIa) and (IIb) are not hydrated when shaken with water for 24 h, and when heated in aqueous solutions they resinify. However, on acid hydrolysis their simultaneous hydration occurs, which leads to the formation of (IV); simultaneously there is considerable resinification. It is interesting that in the reaction of 1,3-pentadiyne (I) with a 30% aqueous solution of piperidine an enamine of type (II) is not formed, and the main product is 1-piperidino-1-penten-3-one (IIIc) together with a crystalline substance of m.p. 68°. When heated with water, the latter is readily converted into (IIIc), and preliminary data indicate that it has the composition $C_5H_4 \cdot C_5H_{11}N \cdot 3H_2O$.

We have shown previously [11] that, under the conditions for the nucleophilic addition of an alcohol, 1,3-octadiyne (V) is isomerized into 2,4-octadiyne (VIII). It was of interest to determine whether the addition of a secondary amine to (V) can be effected. It was found that at room temperature the addition of the amine does not occur, but (V) is slowly isomerized. However, when the latter was boiled for 2 h with a 50% aqueous solution of diethylamine a mixture was formed of the isomerization product (VIII) and 1-(diethylamino)-1-octen-3-one (VIa), the structure of which was confirmed by spectral data and by its conversion on acid hydrolysis into 1,3,5-trihexanoylbenzene (VII).



It was also shown that under these conditions the amine does not add to 2,4-actadiyne (VIII). The addition of piperidine to 1,3-octadiyne (V) goes still more readily. The result is analogous to that obtained in the case of (I): 1-piperidino-1-octen-3-one (VIb) is formed together with a crystalline product of m.p. 72°, whose structure is being studied.

EXPERIMENTAL

Reaction of 1,3-Pentadiyne (I) with Dimethylamine. A mixture of 2 g of (I) and 30 ml of 30% aqueous dimethylamine solution was shaken for 10 h. The reaction mixture was extracted with chloroform, and the chloroform solution was dried with potassium carbonate. In the fractionation we isolated 0.8 g of (I), 0.4 g of N,N-dimethyl-1-penten-3-ynylamine (IIa) [B.p. 65–67° (12 mm); n_D^{20} 1.5400; λ_{max} 273 mμ (ε 12100, in alcohol); ν 692, 945, 1575, 1630, 2218 cm^{-1}. Found %: C 77.35, 77.47; H 10.28, 10.09; N 13.14, 13.31. $C_7H_{11}N$. Calculated %: C 77.01; H 10.16; N 12.83], and 0.4 g of 1-(dimethylamino)-1-penten-3-one (IIIa); b.p. 120–122° (10 mm); n_D^{20} 1.5460; λ_{max} 303 mμ (ε 250,000, in alcohol); ν 1568, 1618, 1663 cm^{-1}. Found %: C 66.21, 66.05; H 10.34, 10.37; N 11.18, 11.36. $C_7H_{13}ON$. Calculated %: C 66.10; H 10.30; N 11.01.

Reaction of 1,3-Pentadiyne (I) with Diethylamine. In a similar way from 3 g of (I) and 60 ml of 50% aqueous diethylamine solution we obtained 2 g of (I), 0.2 g of N,N-diethyl-1-penten-3-ynylamine (IIb) [B.p. 70–71° (10 mm); n_D^{20} 1.5092; λ_{max} 275 mμ (ε 13,000, in alcohol); ν 690, 931, 1570, 1626, 2210 cm^{-1}. Found %: C 78.84, 78.72; H 10.80, 10.42; N 10.08, 10.13. $C_9H_{15}N$. Calculated %: C 78.77; H 11.02; N 10.21.], and 0.3 g of 1-(diethylamino)-1-penten-3-one (IIIb); b.p. 129–130° (10 mm) n_D^{20} 1.5330; λ_{max} 305 mμ (26,000, in alcohol); ν 1562, 1618, 1665 cm^{-1}. Found %: C 69.08, 68.92; H 10.84, 10.91; N 9.06, 9.10. $C_9H_{17}ON$. Calculated %: C 69.63; H 11.04; N 9.02.

When a mixture of 2.7 g of (I) and 30 ml of 50% aqueous diethylamine solution was boiled for 2 h, we obtained 3.5 g of (IIIb).

Transformations of 1-(Diethylamino)-1-penten-3-one (IIIb). 0.8 g of (IIIb) was heated with 10 ml of 10% sulfuric acid at 70° for 30 min. The white flocs which came down were extracted with ether, and the extract was dried with magnesium sulfate. In the fractionation we obtained 0.4 g (78%) of 1,3,5-tripropionylbenzene (IV), b.p. 135° (0.4 mm), m.p. 96° (water); ν 1540, 1598, 1698 cm^{-1}. Found %: C 73.21, 74.04; H 7.62, 7.59. $C_{15}H_{18}O_3$. Calculated %: C 73.14; H 7.36.

A mixture of 0.24 g of (IIIb) and 0.28 g of p-nitrophenylhydrazine in 30 ml of acetic acid was boiled for 30 min. On dilution of the reaction mixture with an equal amount of water we isolated 0.25 g of an orange-yellow crystalline product. From this by fractional crystallization we isolated 3-ethyl-1-p-nitrophenylpyrazole, m.p. 121–122° (50% acetic acid); and 5-ethyl-1-p-nitrophenylpyrazole, m.p. 111–112° (50% acetic acid); these were identical in melting points and UV spectra to the samples described earlier [8].

Hydration of N,N-Diethyl-1-penten-3-ynylamine (IIb). A mixture of 0.2 g of (IIb) and 10 ml of 50% aqueous diethylamine solution was left for two days at room temperature. After the usual treatment we obtained 0.15 g of (IIIb), identical in its chromatogram to the substance described above. Gas-liquid chromatography was conducted on a column of length 2.5 m containing 1% of Silicone F on Chromosorb W at 120°.

A mixture of 0.6 g of (IIb) and 10 ml of 10% sulfuric acid was stirred for two days and extracted with ether; the ethereal solution was dried with magnesium sulfate. In the fractionation we obtained 0.3 g of (IV).

Reaction of 1,3-Pentadiyne (I) with Piperidine. A mixture of 0.9 g of (I) and 30 ml of 30% aqueous piperidine solution was boiled for 20 min and then extracted with ether; the extract was dried over magnesium sulfate. Ether was driven off, and we obtained a mixture of liquid and crystals. The crystals were filtered off, washed with hexane, and vacuum-sublimed at 60° (10 mm); m.p. 68° (in sealed capillary).* On fractionation of the liquid part we isolated 1 g of 1-piperidino-1-penten-3-one (IIIc); b.p. 110–111° (0.7 mm); n_D^{20} 1.5600; λ_{max} 307 mμ (ε 25,500, in alcohol); ν 1561, 1607, 1662 cm^{-1}. Found %: C 72.18, 72.30; H 10.18, 10.20; N 8.74, 8.78. $C_{10}H_{17}ON$. Calculated %: C 71.81; H 10.25; N 8.38.

Reaction of 1,3-Octadiyne (V) with Diethylamine. A mixture of 1.5 g of (V) and 30 ml of 50% aqueous diethylamine solution was boiled for 3 h. After the usual treatment we obtained 0.5 g of 2,4-octadiyne [11] and 1.5 g of 1-(diethylamino)-1-octen-3-one (VIa); b.p. 115° (0.5 mm); n_D^{20} 1.5130; λ_{max} 306 mμ (ε 27,200, in alcohol); ν 1558, 1606, 1659 cm^{-1}. Found %: C 73.06, 73.11; H 12.10, 11.84; N 7.49, 7.36. $C_{12}H_{23}N$. Calculated %: C 73.04; H 11.75; N 7.70.

1.6 g of (VIa) was stirred with 5 ml of 10% sulfuric acid for two days, the mixture was extracted with ether, and the extract was dried with magnesium sulfate. In the fractionation we obtained 0.9 g of 1,3,5-trihexanoylbenzene (VII); b.p. 135° (0.06 mm); n_D^{20} 1.5130; ν 1549, 1589, 1699 cm^{-1}. Found %: C 77.28, 77.10; H 10.01, 10.19. $C_{24}H_{36}O_3$. Calculated %: C 77.37; H 9.74.

Reaction of 1,3-Octadiyne (V) with Piperidine. A mixture of 3.5 g of (V) and 30 ml of 30% aqueous piperidine solution was boiled for 1 h. After the usual treatment we obtained 1-piperidino-1-octen-3-one (VIb); b.p. 125° (0.2 mm); n_D^{20} 1.5390; λ_{max} 308 mμ (ε 28,000, in alcohol); ν 1548, 1604, 1649 cm^{-1}. Found %: C 74.77, 74.91; H 10.91, 10.85; N 7.20, 7.33. $C_{13}H_{23}ON$. Calculated %: C 74.59; H 11.08; N 6.69. We also obtained 0.5 g of a crystalline substance of m.p. 72°, whose structure is being studied.

CONCLUSIONS

A study was made of some regular features of the addition of secondary amines to 1,3-alkadiynes with more than four carbons in the chain.

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*The structure of this product is being studied.