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Abstract

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STRUCTURE AND SOME PROPERTIES OF THE PRODUCTS OF THE INTERACTION OF DIACETYLENE WITH ALKYLAMINES

In studying the interaction of diacetylene with primary and secondary alkylamines (¹), we found that the principal reaction products are, respectively, *N*-alkyldiamino-1,4-butadienes-1,3 and *N*, *N*-dialkylamino-1-buten-1-ynes-3. Continuing work in this direction, we succeeded in isolating the geometric isomers of *N*, *N*-diethylamino-1-buten-1-yne-3 (I and II) from the reaction mixture obtained in the interaction of diacetylene with diethylamine

$$\mathrm{HC \equiv C - C \equiv CH + HN(C_2H_5)_2 \rightarrow (C_2H_5)_2N \quad CH = CH \quad C \equiv CH} \; +$$

$$+ \, \mathrm{(C_2H_5)_2N}$$

$$\mathrm{CH = CH} \qquad \begin{matrix}\mathrm{(I)}\\ \mathrm{(II)}\end{matrix}$$

$$\mathrm{C \equiv CH}$$

Confirmation of the cis- and trans-structure of the isomers of *N*, *N*-diethylamino-1-buten-1-yne-3 (I and II) is provided by their chemical transformations and by spectral-analysis data. First of all it should be noted that isomer I, on heating, is converted into isomer II.

From comparison of the ultraviolet spectra of both substances (Fig. 1) it is seen that the spectrum of isomer II has a higher intensity than the spectrum of isomer I. Investigation of the infrared spectra of substances I and II (Table 1) showed that in the spectrum of isomer I there are no absorption bands in the region 800–1000 cm^{-1}, whereas for isomer II an intense absorption band at 945 cm^{-1}, characteristic of the trans configuration, is observed. In the spectrum of substance I an intense absorption band at 692 cm^{-1} is observed, which may be assigned to the CH deformation vibration of the cis isomer. In the spectrum of substance II the corresponding band is absent in this region. In addition, the infrared spectra of isomers I and II, recorded on an instrument of high resolving power*, showed that the double-bond band is split into two

Fig. 1

Figure 1: Fig. 1

components, the components having different intensities in the different substances. Since substances I and II can be only geometric isomers or positional isomers $(C_2H_5)_2NCH = CH - C \equiv CH$ and $CH_2 = CN(C_2H_5)_2 - C \equiv CH$, the absence in the infrared spectra of both substances of absorption bands in the regions 885-895 cm^{-1} and 3075-3095 cm^{-1}, which are characteristic of a terminal double bond, is proof of cis-trans isomerism. Positional isomerism is also rejected on the basis of investigation of the products of addition to I and II of amines (III), alcohols (IV), and mercaptans (V), which were the corresponding 1,4-substituted butadienes-1,3

Fig. 1

* Spectrophotometer UR-10.

$$
\begin{array}{ccc}
 & \xrightarrow{C_5H_{11}NH_2} & \begin{array}{c}(C_2H_5)_2NCH = CH - CH = CHNHC_5H_{11}\\ \text{(III)}\end{array} \\
(C_2H_5)_2NCH = CH - C \equiv CH & \xrightarrow{C_4H_9OH} & \begin{array}{c}(C_2H_5)_2NCH = CH - CH = CHOC_4H_9\\ \text{(IV)}\end{array} \\
 & \xrightarrow{C_2H_5SH} & \begin{array}{c}(C_2H_5)_2NCH = CH - CH = CHSC_2H_5\\ \text{(V)}\end{array}
\end{array}
$$

As a result of the interaction of *n*-amylamine and isomers I and II under analogous conditions, formation of 1,4-amino-substituted butadienes (III) was observed; these had identical physicochemical constants, picrates, and similar IR spectra. The formation of one and the same butadiene III from substances I and II, if they were positional isomers, is unlikely. On the contrary, the comparative ease of mutual conversion of cis-trans isomers is well known.

Table 1

Absorption-band frequencies, cm^{-1} substance I	Absorption-band frequencies, cm^{-1} substance II	Assignment of individual absorption bands to functional groups and bonds	Absorption-band frequencies, cm^{-1} substance I	Absorption-band frequencies, cm^{-1} substance II	Assignment of individual absorption bands to functional groups and bonds
692 s.	–	C=C (cis)	1308 m.	1303 m.	–
804 m.	908 w.	–	1357 m.	1362 m.	CH_3
–	945 s.	C=C (trans)	1374 m.	1381 m.	–
1000 m.	1010 m.	–	1398 } m.	–	–
1064 w.	1037 m.	–	1425 } m.	1409 m.	–
1100 m.	1082 m.	–	1449 m.	1452 m.	CH_3
1203 s.	1120 s.	–	1463 m.	1465 m.	CH_2
1215 w.	1196 s.	–	1618 s.	1616 s.	C=C (conjugated)
1256 s.	1264 s.	–	2075 s.	2078 s.	C C (conjugated)
1277 w.	1282 w.	–			

Note. s. –strong band, m. –band of medium intensity, w. –weak band.

Furthermore, the IR spectra of butadienes III, as well as of the products of addition to N,N-diethylamino-1-buten-1-yne-3 (I) of butyl alcohol (IV) and ethyl mercaptan (V), did not contain absorption bands corresponding to a terminal double bond, which excludes the presence of the latter in the initial isomers I and II.

Table 2

Solvent	Position of absorption bands, cm^{-1}
CCl_4	1624, 1578
$CHCl_3$	1620, 1573
Pure substance	1620, 1576

On the basis of the ratio of the boiling and freezing temperatures of isomers I and II and the intensity of the UV spectra of these substances, as well as the presence or absence of absorption bands in the region 800–1000 cm^{-1} in the IR spectra, we suppose that the principal product of the reaction of diacetylene with diethylamine (I) is the cis isomer with an admixture of the trans component, whereas the second product II contains predominantly the trans isomer. The possibility is not excluded that the latter is formed as a result of isomerization of the cis isomer during distillation.

Thus, the main direction of the reaction of diacetylene with diethylamine is addition with formation of cis-N,N-diethylamino-1-buten-1-yne-3 (I), which agrees with the results of the ionic interaction of thiols with diacetylene (^{2}), which proceeds stereospecifically and obeys the rule of "trans addition."

This also corresponds to the direction of the reaction of diacetylene with primary alkylamines, as was shown using *n*-butylamine as an example (^{1}). The principal product of the reaction of diacetylene with *n*-butylamine is N-butyl-

diamino-1,4-butadiene-1,3 (VI)

$$C_4H_9NHCH = CH - CH = CHNHC_4H_9$$

with a cis-cis arrangement of the substituents relative to the double bonds. The structure of butadiene VI was confirmed by diene synthesis and by spectral-analysis data. The ease with which VI enters into diene synthesis is somewhat at variance with its cis-cis configuration. Construction of a Brigueleb model of cis-cis-butadiene VI showed that a planar structure is unfavorable for this molecule; apparently, in the real molecule there is a deviation from coplanarity with a small angle of deformation. In this case, entry into diene synthesis becomes possible at a lower activation energy than for ordinary cis-cis forms.

We also established that the indicated N-butyl-diamino-1,4-butadiene-1,3 (VI) does not contain the possible tautomeric form with a $> C = N-$ bond. Owing to the limited literature data on the spectra of substances containing a $> C = N-$ bond (3), the mere absence of the $> C = N-$ frequency in the IR spectrum of butadiene VI could not serve as confirmation of the absence of this bond in the substance under study. Therefore we studied the IR spectra of butadiene VI in polar and nonpolar solvents, which should exert a substantially different influence on the position of the absorption bands of the $> C = N-$ and $> C = C <$ bonds, significant for the first and small for the second. From Table 2 it is seen that the change in the position of both absorption bands is insignificant and does not exceed the error of measurement ($\pm 5\ \text{cm}^{-1}$).

In addition, the Raman spectrum of butadiene VI, in the event that a $> C = N-$ bond were present, should have shown two absorption bands, since the frequency of the $> C = N-$ bond is sufficiently intense in the spectrum of combination scattering of light. In the case of the diene

Table 3

Characteristics of the compounds obtained

Compound	Yield, calculated on the initial reaction product, %	B.p., or m.p., °C/mm	n_D^{20}	d_4^{20}	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N	Spectroscopic data*: absorption frequencies of multiple bonds, cm^{-1} C C	Spectroscopic data*: absorption frequencies of multiple bonds, cm^{-1} C=C	Frequencies of groups connected by a double bond, cm^{-1}, cis	Frequencies of groups connected by a double bond, cm^{-1}, trans
$(C_2H_5)_2NCH=CH-C\equiv CH$ cis (I)	70	80°/15 (not recrystallized), 89°/15 (from heptane), m.p. −60°	1.5170	0.8570	78.26	10.61	11.37	77.99	10.63	11.37	2075	1618	692	–
$(C_2H_5)_2NCH=CH-C\equiv CH$ trans (II)	15		1.5236		77.44	10.61	11.81	77.99	10.63	11.37	2078	1616	–	945
$(C_2H_5)_2NCH=CH-CH=NC_5H_{11}$ (III)	80	149°/760	1.4696	0.8515	74.19	12.13	13.06	74.22	12.45	13.31	–	1579, 1615	–	–
$(C_2H_5)_2NCH=CH-CH=CH-OC_4H_9$ (IV)	30–40	134°/4.5	1.5075	0.8816	72.89	11.43	7.08	73.04	11.74	7.09	–	1576, 1606	–	–
$(C_2H_5)_2NCH=CH-CH=CH-SC_2H_5$ (V)	50–60	101–102°/3		0.9219	64.88	10.24	S – 17.20	64.80	10.33	S – 17.30	–	1588, 1567, 1624	–	–
$C_4H_9NHCH=CH-CH=NC_4H_9$ (VI)	80	117°/8	1.5032	0.8540	73.20	12.21	14.59	73.40	12.32	14.26	–	1578	730	–

* IR spectra were recorded on a double-beam IKS-14 spectrophotometer.

for a structure $> C = C - C = C <$, one of the frequencies may be absent from the Raman spectrum owing to an alternative prohibition. Indeed, only one line in the region of 1600 cm^{-1} was observed in the spectrum. The presence of a

$> C = N-$ bond (absorption frequency 1684 cm^{-1} in the IR spectrum) was observed in the second substance, formed in a small amount as a result of the reaction of diacetylene with *n*-butylamine. Its investigation is continuing.

Experimental Part

Reaction of diacetylene with diethylamine. According to the procedure described earlier (^{1}), from 45 g of diethylamine (b.p. 55°; n_D^{20} 1.3870) and 7 g of diacetylene there were obtained 34.2 g of the starting diethylamine, 9.4 g of diethylethynylvinylamine (I) (b.p. 72–75°/11 mm), 3.4 g of a fraction with b.p. 75–79°/11 mm, and 4.5 g of resin. The higher-boiling fractions, combined from several experiments, were distilled in vacuo (15 mm) on a column, as a result of which substance II was isolated, with b.p. 89°/15 mm and m.p. −46°. On heating I (b.p. 75°/12 mm; n_D^{20} 1.5176) for 4 hr at 100–120°, a fraction was obtained with b.p. 75–82°/12 mm and n_D^{20} 1.5189, representing a mixture of substances I and II. The physicochemical constants and analyses of substances I and II are given in Table 3.

Reaction of diethylethynylvinylamine (II) with *n*-amylamine. A mixture of 1.5 g of diethylethynylvinylamine (II) and 4.5 g of *n*-amylamine (b.p. 104°; n_D^{20} 1.4123) was heated in vacuo (70–80 mm) for 13 hr. As a result of distillation of the reaction products, 2.6 g of the starting *n*-amylamine, 2.2 g of III, and 0.4 g of resin were isolated. Butadiene III (n_D^{20} 1.4996) is identical with N,N-diethyl-N′-amyldiamino-1,4-butadiene-1,3, obtained by us earlier (^{1}) from the principal fraction of N,N-diethylamino-1-buten-1-yne-3 (I). The picrate of butadiene III melted at 78°. A mixed melting point of the picrates of the butadienes obtained by the reaction of isomers I and II with *n*-amylamine showed no depression.

Addition of diethylamine to I proceeds upon more prolonged heating (80 hr) and with a lower yield (10%) of the corresponding butadiene.

Reaction of diethylethynylvinylamine (I) with butyl alcohol. A mixture of 8.5 g of diethylethynylvinylamine (I) and 11 g of butyl alcohol was heated with stirring to 90–100° for 5 hr, kept for a day, and then distilled in vacuo. The following were isolated: unreacted butyl alcohol, 9.3 g, and diethylethynylvinylamine, 3.8 g; a fraction with b.p. 123–154°/23 mm, 3.2 g; and 2.1 g of resin. From the indicated fraction, by distillation on a column, butoxy-N,N-diethylamino-1,4-butadiene-1,3 (IV) was isolated (see Table 3).

Reaction of diethylethynylvinylamine (I) with ethyl mercaptan. A mixture of 12.4 g of diethylethynylvinylamine (I) and 12.4 g of ethyl mercaptan was heated with stirring to 80–90° for 9 hr, kept for a day, and then distilled in vacuo. There were isolated 8.5 g of ethyl mercaptan, 1.2 g of the starting amine, 9.5 g of a fraction with b.p. 110–127°/5 mm, and 3.7 g of resin. Upon redistillation of the fraction, ethylmercapto-N,N-diethylamino-1,4-butadiene-1,3 (V) (see Table 3) was isolated, as well as a higher-boiling fraction, whose IR spectrum showed the presence of an ethylenic bond. The fraction is being investigated.

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