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Abstract

Full Text

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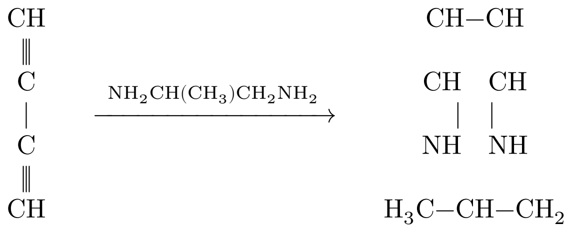
INTERACTION OF DIACETYLENE WITH BIFUNCTIONAL COMPOUNDS

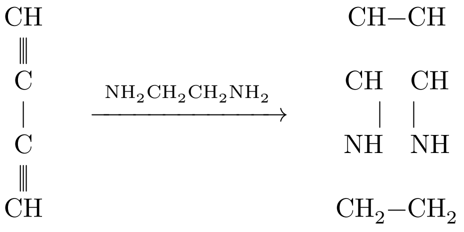
Diacetylene readily reacts with alkylamines and β-(dialkylamino)ethanols, forming the corresponding ethynylvinyl and divinyl derivatives ([1],[2]). It seemed of interest to study the interaction of diacetylene with compounds containing simultaneously two reactive functional groups: primary amino or hydroxyl groups.

In the present work we investigated the reactions of diacetylene with alkylenediamines and ethanolamine, the possibility of which we had indicated earlier ([3], [4]).

Using 1,2-propylenediamine and ethylenediamine as examples, it was shown that the reaction of diacetylene with alkylenediamines proceeds exothermically, considerably more vigorously than that between diacetylene and alkylamines, and leads to the formation of cyclic compounds: diaza-1,4-methyl-2-cyclooctadiene-5,7 (I) and diaza-1,4-cyclooctadiene-5,7 (II).



$$\begin{array}{c} CH \\ ||| \\ C \\ | \\ C \\ ||| \\ CH \end{array} \xrightarrow{NH_2CH(CH_3)CH_2NH_2} \begin{array}{c} CH{-}CH \\ \\ CH \quad CH \\ | \quad\;\; | \\ NH \quad NH \\ \\ H_3C{-}CH{-}CH_2 \end{array} \qquad (I)$$



$$\begin{array}{c} CH \\ ||| \\ C \\ | \\ C \\ ||| \\ CH \end{array} \xrightarrow{NH_2CH_2CH_2NH_2} \begin{array}{c} CH{-}CH \\ \\ CH \quad CH \\ | \quad\;\; | \\ NH \quad NH \\ \\ CH_2{-}CH_2 \end{array} \qquad (II)$$

The IR spectrum of the compounds obtained, which are the product of addition of one molecule of diamine to one molecule of diacetylene, showed the presence

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

of a diene grouping (1540 cm^{-1} and 1634 cm^{-1}) and of the –NH–group (3450 cm^{-1}). The absorption band characteristic of a triple bond was absent. These data agree with a negative qualitative test for mobile acetylenic hydrogen and with the results of determining the percentage content of active hydrogen. The analysis indicates the presence of two active hydrogen atoms in the substance under study, which is characteristic only of the closed system shown above.

Construction of Briegleb models of the cis- and trans-products of addition of one molecule of diamine to one molecule of diacetylene (in the event that cyclization had not occurred) showed that ring closure could have taken place only in the case of formation of the cis-isomer (Figs. 1 and 2). These data confirm the previously observed (^{5}) stereodirection of the addition reaction of alkylamines to diacetylene, which follows the rule of "trans-addition."

Taking into account the greater reactivity of alkylamines compared with β-(dialkylamino)ethanols (^{1},^{2}) in the reaction with diacetylene, it could be assumed that ethanolamine would interact

Fig. 1. Cis-$NH_2CH_2CH_2NHCH{=}CH{-}C{\equiv}CH$

with diacetylene at the amino group, analogous to the reaction with primary amines. Indeed, the reaction of diacetylene with ethanolamine, as with alkylenediamines, proceeds exothermically at two triple bonds, but in this case no cyclic system is formed; rather, the product is the addition of two ethanolamine molecules to a diacetylene molecule, containing a diene grouping (1555 cm^{-1} and 1620 cm^{-1}).

$$2NH_2CH_2CH_2OH + CH{\equiv}C{-}C{\equiv}CH \rightarrow HOCH_2(CH_2NHCH{=}CH{-}CH{=}CHNHCH_2CH_2OH. \quad \text{(III)}$$

It should be noted that the reaction of diacetylene with alkylenediamines and ethanolamine is another example of the influence of the nitrogen atom on the reactivity of the triple bond in nitrogen-containing ethynylvinyl compounds (^{6}). Moreover, the mutual influence of the triple bond and the primary amino group is so great that aminobutenynes cannot be isolated, as in the case of the reaction of diacetylene with secondary amines (^{2}). Under the same mild conditions, intramolecular interaction or addition of a second molecule of the amino-containing compound then takes place.

Fig. 2. Trans-$NH_2CH_2CH_2NHCH{=}CH{-}C{\equiv}CH$

Experimental Part

Reaction of diacetylene with alkylenediamines. In a three-necked flask equipped with a stirrer, a condenser, a thermometer, and a gas-inlet tube, 40 g of 1,2-propylenediamine are placed (b.p. 119°; n_D^{20} 1.4478). With cooling (ice water), 10 g of diacetylene diluted with gaseous nitrogen are passed through the 1,2-propylenediamine. Distillation of 46 g of the reaction mixture gives 29.9 g of the starting diamine, 0.2 g of an intermediate fraction, 11.8 g of diaza-1,4-methyl-2-cyclooctadiene-5,7 (I), and 3.5 g of resin. Yield of (I) 70%. B.p.

148°/10 mm; n_D^{20} 1.5709.

Found, %: C 67.51; H 9.72; N 22.63; active hydrogen 1.64
$C_7H_{12}N_2$. Calculated, %: C 67.69; H 9.74; N 22.56; active hydrogen 1.62

Similarly, from the reaction mixture obtained by the interaction of diacetylene (6.2 g) with ethylenediamine (24 g), distillation gives 15.8 g of the starting diamine, 0.1 g of an intermediate fraction, 6.4 g of diaza-1,4-cyclooctadiene-5,7 (II), and 7.2 g of resin. Yield of (II) 55%. B.p. 136°/6 mm; n_D^{20} 1.5549.

Found, %: C 65.27; H 9.34; N 25.02
$C_6H_{10}N_2$. Calculated, %: C 65.41; H 9.15; N 25.43

Both substances obtained (I and II) are yellow oils.

Interaction of diacetylene with ethanolamine.
Into the previously described apparatus are placed 10 g of ethanolamine (b.p. 170–171°, n_D^{20} 1.4537), and, while cooling with ice water, 10 g of diacetylene diluted with gaseous nitrogen is passed through it; after this the mixture is stirred until crystallization begins. The crystallized reaction mixture is treated with dioxane. The precipitate is filtered off. From the filtrate, distillation gives 2.6 g of the starting aminospirit (b.p. 165–167°; n_D^{20} 1.4529).

The solid substance (III), in an amount of 7.2 g, is recrystallized several times from dioxane and dried. The resulting N-(β-hydroxyethyl)-diamino-1,4-butadiene-1,3 (III) is a hygroscopic white powder. Yield of (III) 70%. M.p. 115–116°.

Found, %: C 56.04; H 9.23; N 16.05
$C_8H_{16}O_2N_2$. Calculated, %: C 55.78; H 9.36; N 16.26

Because of the insolubility of N-(β-hydroxyethyl)-diamino-1,4-butadiene-1,3 (III) in carbon tetrachloride, it was not possible to determine, with the aid of IR spectra, the presence of amino and hydroxyl groups in (III), since in the IR spectrum of the pure substance (III), taken in Vaseline oil, the absorption bands of the amino and hydroxyl groups merge into one very intense absorption band at 3275 cm^{-1}. Our attempts to determine the presence of hydroxyl groups by chemical methods proved unsuccessful because of the simultaneous presence in (III) of other functional groups and the greater reactivity of the compound caused by this.

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