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Direction of Addition Reactions of Electrophilic and Nucleophilic Reagents to Unsymmetrical Homologs of Diacetylene

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In a series of communications from our laboratory, the principal regularities in addition reactions of electrophilic, nucleophilic, and radical reagents to unsaturated hydrocarbons of various structures containing several multiple bonds, in particular to enyne and dienyne hydrocarbons, were described ([1]). Continuing these studies, we undertook an investigation of the direction of addition of the same reagents to diacetylene hydrocarbons of different structures. The present communication considers the direction of addition of typical electrophilic reagents, bromine and hydrogen bromide, and typical nucleophilic reagents, sodium methylate and sodium ethyl mercaptide, to a representative unsymmetrical diyne with conjugated triple bonds—ethyldiacetylene (hexadiyne-1,3).

In the literature there is only an indication concerning the order of addition of alcoholates to methyl- and ethyldiacetylenes; enyne ethers with an alkoxy group at the terminal carbon atom were obtained ([2]). The direction of addition of 1 mole of bromine or hydrogen bromide to diacetylene has been established ([3]). Alcoholates and mercaptides add to diacetylene with formation of enyne ethers

$$\mathrm{HC \equiv C{-}CH = CH{-}OR}$$

([4]) and cis-thioethers

$$\mathrm{HC \equiv C{-}CH = CH{-}SR}$$

([5]).

Amines add in an analogous manner as well ([6,7]).

As a result of the addition of 1 mole of bromine to ethyldiacetylene, the formation of 3 dibromides could be expected:

$$\mathrm{CHBr = CBr{-}C \equiv C{-}C_2H_5}\ \text{(I)},\quad \mathrm{HC \equiv C{-}CBr = CBr{-}C_2H_5}\ \text{(II)},$$

Fig. 1. IR transmission spectra: 1 —hexadiyne-1,3; 2 —products of addition of bromine to it; 3 —the same, of hydrogen bromide; 4 —hexadiyne-2,4 (5% solution in CCl_4); 5 —cis-ethyl (buten-1-yn-3-yl) sulfide.

Figure 1: Fig. 1. IR transmission spectra: 1 —hexadiyne-1,3; 2 —products of addition of bromine to it; 3 —the same, of hydrogen bromide; 4 —hexadiyne-2,4 (5% solution in CCl_4); 5 —cis-ethyl (buten-1-yn-3-yl) sulfide.

$$\mathrm{CHBr = C = C = CBr{—}C_2H_5}\ \text{(III)}.$$

In fact, a mixture of dibromides (I) and (II) was obtained, with predominance of (I); moreover, polybromides were present in significant amount in the reaction mixture even with an excess of hydrocarbon.

The structure of the dibromides was established from IR spectra and NMR spectra; the quantitative ratio was determined from NMR spectra and chromatographically.

In the IR spectrum of the mixture of dibromides there remain the bands, present in the spectrum of the hydrocarbon (Fig. 1, *1, 2*), of monosubstituted (3290, 2092 cm^{-1}) and disubstituted (2210 cm^{-1}) triple bonds, and there also appear intense bands of a double bond (1628, 1577 cm^{-1}) and, evidently, of valence CH vibrations in the CHBr group (3086 cm^{-1}). Bands of dibromide (III) with a cumulated structure (in the region of 2000 cm^{-1}) (^{8}) were not detected.

In the NMR spectrum (Fig. 2, *2*), along with the signals of the ethyl group, a signal of the hydrogen in the CHBr-group, strongly shifted toward low field, was observed (2.2 m.d., standard H_2O). It should be noted that dibromide (II), formed by addition of bromine at the disubstituted triple bond, contains no ethylenic hydrogen atoms. The intensity of the signal under consideration makes it possible to assert that dibromide (I) is the principal product of the reaction. Judging from the chromatogram, the amounts of dibromides (I) and (II) are in the ratio 3 : 1.

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As a result of the addition of 1 mole of hydrogen bromide to ethyldiacetylene, the formation of 6 hydrobromides could be expected:

$$\begin{gathered}\mathrm{CHBr = CH - C \equiv C - C_2H_5}\ (I), \quad \mathrm{CH_2 = CBr - C \equiv C - C_2H_5}\ (II),\\ \mathrm{HC \equiv C - CBr = CH - C_2H_5}\ (III), \quad \mathrm{HC \equiv C - CH = CBr - C_2H_5}\ (IV),\\ \mathrm{CH_2 = C = C = CBr - C_2H_5}\ (V), \quad \mathrm{CHBr = C = C = CH - C_2H_5}\ (VI).\end{gathered}$$

In actuality, the addition of hydrogen bromide, like that of bromine, proceeded predominantly at the monosubstituted triple bond, with formation of hydrobromide (I).

In the IR spectrum of the adduct (Fig. 1, 3) there were bands of both terminal (3298 cm^{-1}) and disubstituted (2215 cm^{-1}) acetylenic bonds. There was no band characteristic of a cumulated system in the spectrum. The presence of the already-mentioned band at 3086 cm^{-1} (the CHBr= grouping) indicated the presence of hydrobromide (I) in the mixture; at the same time, the absence of a band near 890 cm^{-1}, characteristic of the $\mathrm{CH_2}$= grouping in the spectra of compounds of the type $\mathrm{R-C\equiv C-CHlg=CH_2}$ (^{9}), showed that there was no hydrobromide (II) in the mixture.

In the region of 960 cm^{-1} there were only weak bands; on the contrary, in the region of 700 cm^{-1} there was an intense band. Thus, hydrobromide (I) was formed–

predominantly in the cis form, evidently as a result of trans addition of HBr. The indicated structure of the main product of the hydrobromination of ethyldiacetylene was confirmed by the NMR spectrum. In the latter a signal was observed that is characteristic of the grouping –CH=CH–(4 peaks (^{10}), Fig. 2, 3).

The content of the main product, hydrobromide (I), was determined chromatographically to be about 88%. Argentometric determination of hydrobromides with a terminal acetylenic group gave an overestimated value (about 30%).

When ethyldiacetylene was treated with sodium methylate under the conditions used for this reaction by Herbertz (^{2}), isomerization of ethyldiacetylene to dimethyldiacetylene occurred, together with slow addition of the alcohol to the latter.

Addition of ethyl mercaptide to ethyldiacetylene likewise proceeded at the monosubstituted triple bond, with formation almost exclusively of the cis thio ether

$$\mathrm{C_2H_5—C\equiv C—CH=CH—SC_2H_5}.$$

The content in the reaction products of a compound with a terminal triple bond, and also of the trans isomer of the named ether, did not exceed 4-5%. The amount of diadduct was negligible. In the IR spectrum of the enyne thio ether obtained there were only bands characteristic of a disubstituted triple bond (2207 cm^{-1}) and of double bonds (1552, 1590 cm^{-1}) (Fig. 1, 5).

In the NMR spectrum of the substance (Fig. 2, 5), along with overlapping bands of two ethyl groups, there were 4 peaks characteristic of the above-mentioned ethylene grouping.

In the chromatogram of the substance, the intensity of the main peak was about 95% of the total absorption. One of the weak peaks present in the chromatogram

Fig. 2. NMR spectra: 1 —decadiene-1,3; 2 —products of addition of bromine to it; 3 —the same —of hydrogen bromide; 4 —hexadiyne-2,4; 5 —cis-ethyl (buten-1-yn-3-yl) sulfide

Figure 2: Fig. 2. NMR spectra: 1 —decadiene-1,3; 2 —products of addition of bromine to it; 3 —the same —of hydrogen bromide; 4 —hexadiyne-2,4; 5 —cis-ethyl (buten-1-yn-3-yl) sulfide

may be assigned to the isomer with a terminal acetylenic group; the other, possibly, belongs to an impurity of the trans form of the main substance.

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The data given on the direction of addition of bromine, hydrogen bromide, and mercaptides to ethyldiacetylene show that this direction is not consistent with the presumed polarization of the conjugated system of the hydrocarbon in question under the influence of the ethyl radical (dipole moment of ethyldiacetylene about 1.1 *D*)*:

$$C_2H_5—C \equiv C—C \equiv CH.$$

All the reagents investigated, irrespective of their nature, add according to one and the same scheme, and in all cases the electropositive particle adds to the most electronegative atom of the system**. Consequently, the usual arguments concerning the influence of polarization of molecules of unsaturated compounds on the direction of addition in heteropolar reactions are inapplicable in the case of alkyldiacetylenes.

* Measured by K. S. Mingaleva.

** According to Bol' man' s data, bromine can add to diacetylene also by a nucleophilic mechanism. For hydrogen bromide, an electrophilic mechanism has been demonstrated ([12]).

Experimental Part

Ethyldiacetylene was obtained by alkylation of diacetylene in liquid ammonia ([2]).

Bromination. To a solution of 13.1 g of hydrocarbon (twofold excess) in 100 ml of chloroform at −40° and with vigorous stirring, 13 g of bromine in 100 ml of chloroform was added. On distillation of the residue after removal of the solvent and of the starting hydrocarbon, about 3.5 g of dibromides, 5.6 g of tetrabromide, and 8.4 g of higher-boiling products were obtained. For the dibromides the following was found: b.p. 55-62° (1-2 mm), d_4^{20} 1.7625, n_D^{20} 1.5790.

Found, %: Br 67.16; 67.37
$C_6H_6Br_2$. Calculated, %: Br 67.17

Hydrobromination. To 10 g of hydrocarbon (one-and-a-half-fold excess) in 70 ml of ether, a solution of 6.24 g of HBr in 80 ml of ether was added at −50°. After the mixture had stood for 12 hours, it was brought to room temperature and distilled. About 2.5 g of monohydrobromides and about 4 g of dihydrobromides were obtained. Residue 0.8 g. For the monohydrobromides the following was found: b.p. 58-59° (20 mm), d_4^{20} 1.3068, n_D^{20} 1.5190.

Found, %: Br 50.35; 50.47
C_6H_7Br. Calculated, %: Br 50.25

Addition of methyl alcohol. A solution of 11.6 g of hydrocarbon and 11.9 g of KOH in 128 ml of methyl alcohol was heated in sealed glass tubes for 3 hours at 135-145°. Distillation of the reaction mass gave 4.3 g of products with b.p. 75-95° (80 mm) and 2.7 g of residue. From the distillate (directly and upon cooling), about 1.3 g of crystals separated, m.p. 65-66° (from petroleum ether at −70°), which corresponds to dimethyldiacetylene ([13]) (IR spectrum—Fig. 1, curve 4; NMR spectrum—Fig. 2, curve 4).

Found, %: C 91.89; H 7.98
C_6H_6. Calculated, %: C 92.25; H 7.74

On hydrolytic cleavage of the residue, judging from the IR and NMR spectra, not an aldehyde but a ketone was obtained.

Addition of ethyl mercaptan. To a boiling solution of 8 g of hydrocarbon and 0.8 g of KOH in 20 ml of methyl alcohol, 24 g of ethyl mercaptan was added over 1.5 hours. After heating for 1 hour, the mixture was diluted with a saturated solution of $CaCl_2$; the upper layer was washed with the same solution and dried over ignited $CaCl_2$. Vacuum distillation gave 6.8 g (62%) of cis-ethylbut-1-en-3-ynyl sulfide. B.p. 66-67° (2.5 mm), d_4^{20} 0.9299, n_D^{20} 1.5380.

Found, %: C 68.29; 68.29; H 8.79; 8.47; S 22.57; 22.88
$C_8H_{12}S$. Calculated, %: C 68.51; H 8.63; S 22.86

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