REACTION OF METHYLDIACETYLENE WITH ALIPHATIC ALCOHOLS UNDER ALKALINE CATALYSIS CONDITIONS

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Previously we had shown that monosubstituted diacetylenes when heated with either methyl or ethyl alcohol in the presence of alkaline catalysts easily form cis-ethynyl vinyl ethers [1, 2]. However, it was indicated [3] that when diacetylene is reacted with alcohols the configuration of the formed products depends on the nature of the alcohol and the reaction conditions.

In order to ascertain if the rule of "trans-addition" is retained in the monosubstituted diacetylene series we studied the addition of a number of aliphatic alcohols on the example of methyldiacetylene (I).

$$CH_{3}C \equiv C - C \equiv CH \xrightarrow{ROH} CH_{3}C \equiv C - CH = CHOR$$
(I)
(II)
(II)
(II)
(II)
(II)
(II)

Here only the cis-isomers (II) were obtained. The formation of the trans-isomer was also not observed when (I) was heated with MeOH in an aprotic solvent like dioxane. Apparently, the trans-addition rule [4] is obeyed well under the employed conditions as the result of the coordinated attack by the alkoxyl ion and the alcohol (solvent), without the formation of the carbanion with a delocalized charge [5]. By means of special experiments it was shown that isomerization is not observed when the reaction products are heated at $130-140^{\circ}$ for 3-4 h. The purity of the obtained products was checked by GLC. The structure of the obtained cis-ethynyl vinyl ethers was confirmed by the NMR spectra, which were taken on a Varian DA-60-IL instrument (Table 1), and by the data of the IR spectra (strong band at 736 cm⁻¹).

EXPERIMENTAL METHOD

General Method for Preparation of Ethynyl Vinyl Ethers (II). A mixture of 2 g of methyldiacetylene (I), 20 ml of the alcohol (or 10 ml of alcohol and 10 ml of dioxane) and 0.1 g of KOH was heated in an ampul for 2 h on the steam bath, neutralized by the passage of CO_2 , diluted with water, extracted with ether, and dried over K_2CO_3 . After distilling off the solvent the obtained ethynyl vinyl ethers were subjected to distillation. The yields and physicochemical data are given in Table 2.

TABLE 1. Chemical Shifts and Spin–Spin Coupling Constants for $CH_3C \equiv C-CH = CH-OR$ (ô, ppm, relative to HMDS, in CCl_4 , J, Hz)

R		δ _H β	δ _{CH3}		⁸ −OR	1. feloren	$^{J}\mathrm{H}_{\alpha}\mathrm{H}_{\beta}$	J CH $_{a},~{ m H}_{eta}$	$^{J}{ m CH}_{a}, { m H}_{\alpha}$
	δ _H α			-OCH2	-(CH ₂) _n	-CH3			
CH3 C2H5 C3H7 C4H9 C5H11	$ \begin{array}{c} 6,02\\ 6,04\\ 6,03\\ 6,03\\ 6,02 \end{array} $	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	1,86 1,85 1,84 1,86 1,86	$\left \begin{array}{c}3,64 \\ 3,78\\3,78\\3,76\\3,76\\3,76\\3,76\end{array}\right $	1,52 1,48 1,37	1,22 0,92 0,92 0,92 0,92	6,45 6,5 6,5 6,5 6,5 6,5	2,8 2,6 2,6 2,6 2,6 2,6	0,8 0,8 0,8

*Refers to the OCH₃ group,

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		Bp, °C(p in	Found, %		Calculated,%			
R	%	mm of Hg) nD	с	н	C	H	α _{max} , nm ε(in alcohol)	v, cm ⁻¹
CH3	77,5	59-60 (40)	74,60	8,40	74,97	8,391	237	736, 1636,
C ₂ H ₅	80,5	67 (20) 1 4892	76,18	9,13	76,32	9,15	237 16600	736, 1636,
C ₃ H ₇	76,4	72 (11)	77,19	9,76	77,37	9,74	237	736, 1638,
C ₄ H ₉	76,0	83 (10) 1,4792	78,14	10,17	78,21	10,21,	237	736, 1634,
C5H11	74,5	98 (11) 1,4760	78,82	10,48	78,89	10,51	237 16600	736, 1634, 2220

TABLE 2. Properties of Obtained Ethynyl Vinyl Ethers $CH_3C \equiv C - CH = CHOR$

CONCLUSIONS

The reaction of methyldiacetylene with aliphatic alcohols (heating on the steam bath in the presence of KOH) leads only to the cis-ethynyl vinyl ethers.

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