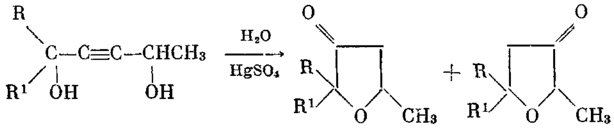
HYDRATION OF UNSYMMETRICAL ACETYLENIC γ-GLYCOLS

A. S. Medvedeva, L. P. Safronova,
I. D. Kalikhman, and V. M. Vlasov*

UDC 542.934:547.423

The addition of water to primary and secondary-tertiary acetylenic δ-glycols in the presence of $HgSO_4$ proceeds with the preferential formation of keto glycols in which the CO group is found α to the tertiary C atom [1-4]. By analogy with δ-diols, the structure of substituted tetrahydrofuranones, with the CO group in the 4 position, was adopted for the hydration products of secondary-tertiary acetylenic γ-glycols (II) and (III), and the primary-tertiary analogs [5].

However, a study of the hydration products of γ-glycols (I), (II), and (III) via NMR disclosed that, independent of the structure of the radicals on the tertiary C atom, a mixture of the isomeric tetrahydrofurans *a* and b is formed in an equal ratio:

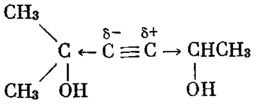


(I)—(III) (IVa)—(VIa) (IVb)—(VIb)

$R = R^1 = CH_3$ (I), (IV); $R = CH_3$, $R^1 = C_2H_5$ (II), (V); R, $R^1 = C_5H_{10}$ (III), (VI)

In the NMR spectra of the tetrahydrofuranones with different substituents in the 2 position [(IV), VI)], or in the 5 position (V), the nonequivalence of the A and B protons is caused by their cis- or trans-arrangement relative to the substituents; two groups of signals are observed in the spectrum of compound (V), which are characteristic for two isomers with a cis- and trans-arrangement of the substituents (Table 1).

The results of hydrating the unsymmetrical acetylenic γ-glycols can be explained if the electronic effects of the substituents are taken into account. As an example we will discuss the distribution of the electron density on the C atoms of the triple bond of glycol (I). The σ* constant of the $(CH_3)_2COH$ group, calculated via the principle of structure additivity [6], is −0.365; σ* of the $CH(OH)CH_3$ group is −0.450 [6]. Taking into account only the induction effects, the distribution of the electron density on the C atoms of the C≡C bond can be depicted in the following manner.



$$(CH_3)_2C(OH) \leftarrow \overset{\delta-}{C} \equiv \overset{\delta+}{C} \rightarrow CH(OH)CH_3$$

Since $-I_1 < -I_2$ the difference $I_2 - I_1$ is quite small, and the triple bond is not sufficiently polarized for the selective addition of water, as a result of which of tetrahydrofuranones (IVa) and (IVb) are formed in an equal ratio. Together with this, the fact that the effect of the character of the alkyl radicals on the tertiary hydroxylated C atom on the direction of the hydration is absent, makes it possible to postulate that the resonance effects of the $CH(OH)CH_3$ group also participate in the distribution of the electron density.

Under the same conditions, the NMR spectra of the hydration products of the primary-tertiary acetylenic γ-glycols ($R' = CH_3$, C_2H_5; $R = CH_3$; $CRR' = C_6H_{10}$) correspond to tetrahydrofuranones with structure b

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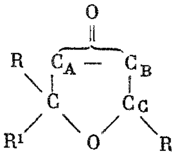
*Deceased.

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Yaroslavl Pedagogic Institute. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1175-1178, May, 1975. Original article submitted July 15, 1974.

TABLE 1. Parameters of NMR Spectra of Substituted Tetrahydrofuranones (IV)-(IX)



Compound	R	R^1	R^2	δ, ppm						J, Hz				Amount isomer,
				$H_{A(B)}$	$H_{B'(A')}$	H_C	CH_3C	R	R^1	$J_{AA'}$	J_{BC}	$J_{B'C}$	J_{H-CH_3}	
(IVa)	CH_3	CH_3	CH_3	2,45	2,26	4,22	1,35	1,35	1,35	17,5	6,5	10,0	5,8	50
(IVb)	CH_3	CH_3	CH_3	2,26	2,26	3,90	1,27	1,40	1,40	—	—	—	6,8	50
(Va)	CH_3	C_2H_5	CH_3	2,30	2,12	4,26	1,35	1,32	1,14; 2,17	18,0	6,5	7,5	6,0	50
(Vb)	CH_3	C_2H_5	CH_3	1,18	2,26	3,84	0,87	1,32	1,14; 2,18	17,5	—	—	6,8	50
				2,14	2,22	3,95	1,14	1,39	1,14; 2,18	17,5	—	—	6,8	
(VIa)	C_5H_{10}		CH_3	2,47	2,12	4,29	1,35		1,42	18,0	6,3	10,5	6,0	50
(VIb)	C_5H_{10}		CH_3	2,18	2,26	3,87	1,19		1,42	18,0	—	—	6,8	50
(VII)	CH_3	CH_3	H	2,26	2,26	3,90	—	1,34	1,34	—	—	—	—	100
(VIII)	CH_3	C_2H_5	H	2,26	2,20	3,86	—	1,61	0,92; 1,64	17,6	—	—	—	100
(IX)	C_5H_{10}		H	2,17	2,17	3,82	—		1,55	—	—	—	—	100

(the CO group is in the 3 position), which is in agreement with the literature data [7, 8]. In [5] these compounds were erroneously assumed to be type *a* tetrahydrofuranones.

EXPERIMENTAL METHOD

The NMR spectra were recorded on a Tesla BS487B spectrometer at a frequency of 80 MHz and ~ 20°C. The solvent was CCl_4, the internal standard was HMDS, and the δ scale was used.

Hydration of 2-Methyl-3-hexyne-2,5-diol (I). To a mixture of 0.5 g of HgO, 0.5 ml of conc. H_2SO_4, and 2 ml of H_2O was added in drops a solution of 4.3 g of the glycol in 50 ml of ether, and the mixture was stirred for 3 h at ~20°C. The ether layer was separated, neutralized with soda solution, and dried over $MgSO_4$. The residue from the removal of the ether was vacuum-distilled. We obtained 3 g (72%) of product with bp 49-50°C (17 mm), n_D^{20} 1.4416, which, based on the NMR data, was a mixture of 2,5,5-trimethyl-4-tetrahydrofuranone (IVa) and 2,5,5-trimethyl-3-tetrahydrofuranone (IVb) in a 50 : 50 ratio. Found: C 65.36; H 9.18%. $C_7H_{12}O_2$. Calculated: C 65.62; H 9.37%. The IR spectrum has an absorption band with ν 1760 cm^{-1} (CO group), while the frequencies of the OH group and multiple bonds are absent.

CONCLUSIONS

Based on the NMR spectral data, secondary-tertiary acetylenic γ-glycols add water under the influence of mercuric sulfate to give the 2-methyl-5,5-dialkyl-4- and 2-methyl-5,5-dialkyl-3-tetrahydrofuranones in a 1 : 1 ratio.

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