SYNTHESIS AND PROPERTIES OF VINYL ETHERS OF 3,4-DI(HYDROXYMETHYL)-1,2,5-OXADIAZOLE

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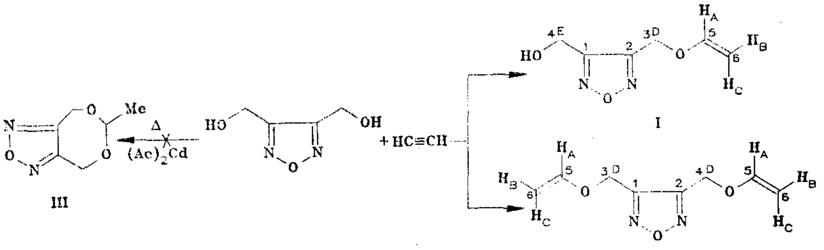
The direct vinylation of 3,4-di(hydroxymethyl)-1,2,5-oxadiazole by acetylene was accomplished for the first time; its mono- and divinyl ethers were synthesized in the presence of cadmium acetate. The physicochemical and spectral properties and conformational structure of the synthesized compounds were studied. It was shown that the s-trans-trans-conformation is the most profitable for the divinyl ether of 3,4-di(hydroxymethyl)-1,2,5-oxadiazole.

The unflagging interest in vinyl ethers is due to the uniqueness of their structure (the presence of a heteroatom conjugated with the π-system of the double bond; and the variety of the chemical conversions in which they can participate [1]. At the same time, the information on α,β-unsaturated ethers of heterocyclic hydroxycompounds is extremely limited. Vinyl ethers of 3,4-di(hydroxymethyl)-1,2,5-oxadiazole are still unknown. Only 3-chloromethyl-4-vinyloxymethyl-1,2,5-oxadiazole has been described [2]. In an attempt to obtain the divinyl ether of 1,2,5-oxadiazole by acid catalytic elimination of butanol from 3,4-di[1-(butoxy)ethoxymethyl]-1,2,5-oxadizole, the corresponding 1,3-dioxepan was obtained with a 50% yield [3].

We accomplished a direct vinylation of 3,4-di(hydroxymethyl)-1,2,5-oxadiazole by acetylene for the first time and studied the main physicochemical and spectral properties of its mono- (I) and divinyl (II) ethers:



The reaction was conducted in dioxane at a temperature of 150-185°C in the presence of 10-15% (of the weight of the oxadiazole) cadmium acetate dihydrate. The monovinyl ether of 3,4-di(hydroxymethyl)-1,2,5-oxadiazole was obtained with a 30% yield by vinylation of the corresponding diol in the presence of 10% $(Ac)_2Cd$ and the temperature 150°C. At a higher temperature (175-180°C) the main vinylation product is the divinyl ether II (yield 40%). Simultaneous increases in the temperature of the reaction and amount of the catalyst (175-185°C, 3 h, 15% $(Ac)_2Cd$) lead to a decrease in the yield both of the mono- (3%) and of the divinyl ether (25%).

It should be mentioned that together with the ethers I and II sought, in all the experiments substantial amount of resin are formed, which is evidently explained by a stepwise polymerization of the vinyl ethers I and II formed with the initial oxadizole and spontaneous oligomerization of the monoether I, which occur under the reaction conditions and lead to linear polyacetals [1, p. 29]. At the same time, we were unable to identify the cyclic acetal III, which might be formed under these conditions by intramolecular cyclization of the vinyl monoether I, among the reaction products [3].

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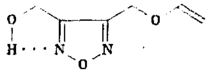
In contrast to aliphatic glycols [1, p. 8], 3,4-di(hydroxymethyl)-1,2,5-oxadiazole is not vinylated in the presence of alkali metal hydroxides (160°C, 3 h, 10% KOH). We were also unable to obtain the desired vinyl ethers using the catalytic system anhydrous cadmium acetate—triethylamine [150°C, 3 h, $(Ac)_2Cd$—Et_3N], which has been extremely useful in the vinylation of fluorinated alcohols [4]. In both cases the original oxadizole was recovered, together with a small quantity of a resinous substance (possibly a destruction product of 1,2,5-oxadiazole in alkali medium).

We also undertook an attempt to synthesize vinyl ethers of 3,4-di(hydroxymethyl)-1,2,5-oxadiazole by revinylation of the latter with butylvinyl ether and vinyl acetate in the presence of mercury salts and mineral acids. However, the divinyl ether II is formed with a yield of ~5% only when vinylbutyl ether is used (in the presence of mercury acetate). Revinylation of the oxadiazole with vinyl acetate under analogous conditions leads to the formation of the corresponding 1,3-dioxepan III, which, in our opinion, is just what should have been expected, since the acetic acid liberated in the course of this reaction should speed up the cyclization of the monovinyl ether I.

The synthesized mono- and divinyl ethers of 3,4-di(hydroxymethyl)-1,2,5-oxadiazole are colorless mobile liquids with a weak ether odor.

In the IR spectrum of the ether II, absorption bands of the stretching vibrations of the C=C bond (1642 and 1621), the planar deformational vibrations of C—H (1320), the stretching vibrations of the C—O group (1197), the out-of-plane deformational vibrations of C—H in the CH_2=, CH= groups (965 and 827 cm^{-1}), which characterize the presence of CH_2=CHO groups in the investigated compound, are observed [1]. It is difficult to identify the adsorption bands of the C=N stretching vibrations. In the initial 3,4-di(hydroxymethyl)-1,2,5-oxadiazole, it appears at 1596 cm^{-1} and has low intensity. Therefore, in the spectra of vinyl ethers it most likely is overlapped by a very intense absorption band of the stretching vibrations of the C=C bond. The absorption bands characterizing the vibrations of 1,2,5-oxadiazole [5] have low intensity and are frequently overlapped by the absorption bands of the vinyloxy group.

In an investigation of the IR spectrum of the ether I in CCl_4 solution, two absorption bands are detected in the region of the stretching vibrations of the OH groups (3627 and 3593 cm^{-1}), the intensity ratio of which remains constant when the concentration is varied from 0.01 to 0.001 M (thickness of the absorbing layer 1-5 cm). The high-frequency band belongs to the free OH group, the low-frequency band (preserved in the spectrum of the ether I even at a concentration of 0.001 M) to the intramolecular hydrogen bond. The ratio of the extinctions of these bands is evidence of predominance of a nonassociated form of the OH group. The absence of a second maximum of the bound hydroxyl (present in the spectra of dilute solutions of hydroxyalkylvinyl ethers in CCl_4 [6]) indicates the presence of only one type of hydrogen bond in this compound. In this case the interaction of the OH group with the nitrogen atom in the five-membered ring is the most probable:



In contrast to aliphatic hydroxyl-containing vinyl ethers [6], the monoether I does not contain conformations with intramolecular hydrogen bonds at the vinyloxy group, which is not unexpected, since the formation of this structure, in the first place, requires closing of unprofitable 7- and 8-membered rings, and in the second place, the basicity of the vinyloxy group is weakened in this case by its close proximity to the acceptor heteroaromatic ring.

The relative basicity of the divinyl ether of 3,4-di(hydroxymethyl)-1,2,5-oxadiazole (in units of the shift $\Delta\nu OH$ of phenol as a proton donor) was measured under conditions analogous to [1, p. 237]. In the region of the stretching vibrations of the OH group of phenol, a broad absorption band is detected ($\Delta\nu OH = 148$), possessing a shoulder on the low-frequency side ($\Delta\nu OH \approx 213$ cm^{-1}), which confirms the presence in the investigated compound of at least two electron donor centers, one of which is evidently the oxygen atom of the vinyloxy group ($\Delta\nu OH = 148$ cm^{-1}) or the ring [7], the other represents the nitrogen atoms. Since the basicity of the weakest of the observed donor centers of the vinyl ether II is approximately 30 cm^{-1} higher than the basicity of divinyl ethers of aliphatic glycols ($\Delta\nu OH$ 118-123 cm^{-1}) [7], it can be assumed that it is the oxygen atom in the ring. The absence of a second maximum in the IR spectrum of a dilute solution of the ether I can evidently be considered as indirect evidence for this hypothesis, if we assume that the basicity of the vinyloxy group is lowered, while the formation of an intramolecular associate at the oxygen atom in the ring is sterically impossible on account of the flat structure of the oxadiazole ring.

TABLE 1. ^1H and ^{13}C NMR Spectra of Mono (I) and Divinyl (II) Ethers of 3,4-Di(hydroxymethyl)-1,2,5-oxadiazole

Compound	Chemical shifts (δ, ppm, TMS) in $(CD_3)_2CO$												CHFS, J, Hz		
	H_A	H_B	H_C	H_D	H_E	H_{OH}	C (1)	C (2)	C (3)	C (4)	C (5)	C (6)	$J^{cis}_{H_AH_B}$	$J^{trans}_{H_AH_C}$	$J^{gem}_{H_BH_C}$
I	6,45	4,08	4,30	4,98	4,78	4,54	151,62	151,81	59,67	54,19	151,33	89,00	6,51	14,02	−2,5
II	6,58	4,18	4,43	5,12	—	—	151,59	151,59	59,51	59,51	151,29	89,10	6,75	14,23	−2,5

To obtain information on the conformational structure of the divinyl ether II we measured its dipole moment in benzene solution at 25°C. As a comparison of the experimentally found value of μ (3.29 D) with the values of the dipole moments calculated according to a vector additive scheme (on the basis of the fragmentary moments of the flat conformer of methylvinyl ether μ = 1.0 D and 1,2,5-oxadiazole μ = 3.38 D) shows, for the theoretically possible conformations (s-trans-trans μ = 3.30 D, s-cis-cis μ = 2.31 D, s-cis-trans μ = 2.62 D, s-trans-gauche μ = 2.60 D, s-cis-gauche μ = 3.70 D, s-gauche-gauche μ = 3.38 D) the most profitable is the s-trans-trans-conformation (relative to the ring and the oxygen atoms of the vinyloxy groups; moreover, a flat s-trans-structure was ascribed to the fragment $CH_2OCH{=}CH_2$).

It is known that the shielding of the ^{13}C nuclei of the carbon atoms of the vinyl fragment approximately reflects the redistribution both of σ- and of π-electron density [8]. In the ethers I and II the corresponding values of the chemical shifts for the atoms $C_{(5)}$ and $C_{(6)}$ are close (Table 1). Evidently the replacement of one vinyloxy group by a hydroxyl has little effect on the conformation of the molecule, and shielding of the nuclei of the $C_{(5)},_{(6)}$ atoms is determined chiefly by the p,π-conjugation of the unshared electron pair of oxygen with the vinyl radical and by the electronegativity of the heterocyclic fragment, and not by steric interaction of the $-CH_2OCH{=}CH_2$ groups through space, which indirectly confirms the trans-trans-conformation of these compounds. The positions of the signals of the $C_{(5)},_{(6)}$ atoms in the ethers I and II practically coincide with the corresponding values for the carbon atom in the vinyl ether of 1,1,3-trihydrotetrafluoropropanol-1 $CH_2{=}CHOCH_2CF_2CF_2H$ (151.31 and 89.19 ppm), in which the shielding influence of p,π-conjugation of the double bond with the oxygen atom on the nucleus of the terminal carbon is compensated to a substantial degree by the unshielding effect of the electronegative group, $-CH_2CF_2CF_2H$.·

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 instrument in CCl_4 at a concentration of 0.3 M, cuvette thickness 0.006 cm. The basicity, expressed in $\Delta\nu_{OH}$, was determined according to the well-known procedure [9] (phenol concentration 0.02 M, cuvette thickness 0.4 cm). The ^1H and ^{13}C NMR spectra were recorded on a Bruker WP-200 SY spectrometer at a working frequency of 200.13 MHz for ^1H and 50.17 MHz for ^{13}C in a pulsed system, followed by Fourier transformation. The ^{13}C NMR spectra were recorded both with complete and with selective uncoupling from spin–spin interaction with the $^{13}C-\{^1H\}$ protons. The samples were 30% (by volume) solutions in $(CD_3)_2CO$, internal standard 5% TMS, temperature 30°C, accuracy ±0.01 ppm. The purity of the samples, according to the PMR spectra, exceeded 98%.

The dielectric permeability of the solutions was measured on a Tangens-2M instrument by the method of beats at a frequency of 1.0 MHz; the density of the solutions was determined by the method of hydrostatic weighing with a torsion balance directly in the dielcometer.

Vinylation was conducted in a rotating steel autoclave with a 0.5-liter capacity. The initial pressure of acetylene was 1215.9-1418.6 kPa.

Monovinyl Ether of 3,4-Di(hydroxymethyl)-1,2,5-oxadiazole (I). A mixture of 5 g (38 mmoles) 3,4-di(hydroxymethyl)-1,2,5-oxadiazole, 10 ml of dioxane, and 0.5 g (2 mmoles) cadmium acetate are loaded into an autoclave, and acetylene is delivered. The autoclave is heated with rotation to 150°C and exposed at this temperature for 3 h. When the autoclave has cooled to room temperature, the reaction mixture is unloaded and redistilled under vacuum; yield 1.8 g (30%) of the ether I, bp 90-91° (2 hPa); n_D^{20} 1.4799; d_4^{20} 1.2145. Found: C 46.6; H 5.3; N 17.7%; M 1.56; MR_D 36.48. $C_6H_8N_2O_3$. Calculated: C 46.1; H 5.1; N 17.9%; M 156; MR_D 37.40.

Divinyl Ether of 3,4-Di(hydroxymethyl)-1,2,5-oxadiazole (II). A solution of 5 g (38 mmoles) 3,4-di(hydroxymethyl)-1,2,5-oxadiazole in 10 ml of dioxane and 0.5 g (2 mmoles) cadmium acetate are placed in an autoclave, and acetylene is delivered. The rotating autoclave is heated for 4 h at 180°C. The autoclave is cooled, the reaction mixture unloaded and redistilled under vacuum. Yield 2.9 g (40%) of the ether II, bp 70-72°C (2 hPa); n_D^{20} 1.4700; d_4^{20} 1.1250. Found: C 52.6; H 5.6; N 15.0%; M 186.8; MR_D 45.13. $C_8H_{10}N_2O_3$. Calculated: C 52.7; H 5.51 N 15.4%; M 182; MR_D 46.27.

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INTERACTION OF N,N'-POLYOXYETHYLENEDIPHTHALIMIDES WITH DIETHYLENETRIAMINE AND MASS SPECTRAL BEHAVIOR OF THE MACROCYCLIC DIAMIDES OF PHTHALIC ACID FORMED

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The reaction of diethylenetriamine and diphthalimides containing a polyoxyethylene fragment yielded macrocyclic diamides of phthalic acid, and the fragmentation of these compounds under the action of electron impact was studied. It was established that their decomposition consists of an initial ejection of a C_2H_4N radical, presuming a rearrangement of the molecular ions to the corresponding N-substituted phthalimides, followed by the splitting out of ethylene oxide and water molecules in various orders. These mass spectral principles can be used to establish the number and sequence of monomer units in the macrocycles.

It is known that the reaction of N,N'-polyoxyethylenediphthalimides with polyoxyethylenediamines leads to macrocyclic diamides of phthalic acid [1, 2]. However, the necessity of the conversion of part of the polyoxyethylenediphthalimide to polyoxyethylenediamine [3] and the use of the latter in the synthesis of macrocyclic diamides is a shortcoming of this method.

We found that macrocyclic diamides of phthalic acid IIb-d are formed in the action of readily available diethylenetriamine on the diphthalimides Ib-d in methanol—water medium.

A small amount of 3-azapentane-1,5-diphthalimide (III) is formed as a side product of the reaction, and its presence hinders the isolation of the compound IIa in pure form.

A convenient analytical method for establishing the structure of the products of the reaction described is the method of mass spectrometry.

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