

Research of the Processes of Synthesis of Acetylene Diols and Study of their Anti-Corrosive Properties

Zokirov Sodikjon

Associate Professor of the Department of Chemical Technology, Namangan Engineering Technological Institute, Republic of Uzbekistan, Namangan

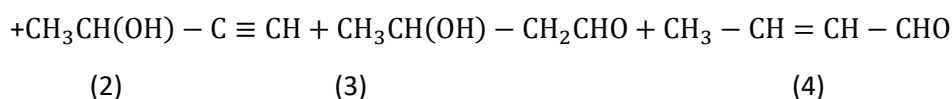
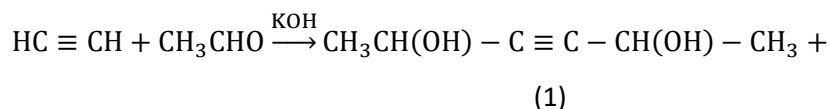
Abstract

In the process of the synthesis of acetylenic diols by the Favorsky reaction based on acetylene and carbonyl compounds, a side reaction also occurs - aldol-crotonic condensation, in which hydroxyaldehyde and crotonic aldehydes are formed. Therefore, acetylenic alcohols and carbonyl compounds were used in the synthesis of acetylenic diols. As a result, secondary-secondary and secondary-tertiary acetylenic diols were obtained in high yields. The anticorrosive properties of the obtained acetylene compounds have been studied.

Keywords: Acetylene alcohols, acetylenic diols, Favorsky reaction, butyraldehyde, dimethyl ketone, methyl ethyl ketone, decyne-5-diol 4,7, corrosion inhibitor

Introduction

Acetylene diols and their derivatives are widely used in various areas of the national economy in the form of herbicides, fungicides, defoliant, drugs, metal corrosion inhibitors and others [1,2,3,9]. In this regard, in this work, we studied the possibility of obtaining acetylenic diols (AD) by the Favorsky reaction from acetylene and the corresponding carbonyl compounds in diethyl ether (DEE) in the presence of a potassium hydroxide catalyst at a reaction time of up to 6 hours and a temperature of 10 ° C. According to GLC and thin layer chromatography data, in this case, four types of compounds are formed, that is, the process proceeds according to the following scheme:

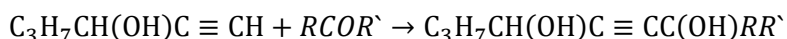


According to the chromatogram, the percentage of synthesized substances (1), (2), (3) and (4) is, respectively, 30: 20: 40: 10

Thus, in the direct preparation of acetylene diols based on acetylene with carbonyl compounds, the process is accompanied by the formation of a number of by-products. It should be emphasized that this reaction proceeds rather easily, but the separation of the obtained compounds is associated with great difficulties. In addition, in the synthesis of acetylenic diols based on acetic and propionic aldehyde, the reaction proceeds towards the formation of hydroxyaldehydes. In this regard, acetylene diols were synthesized on the basis of acetylenic alcohols in high yields.

To obtain AD, butyric aldehyde, dimethyl ketone, methyl ethyl ketone, and the previously synthesized hexin-1-ol-3 were taken as starting reagents. It is known that the Favorsky method is the most convenient for obtaining blood pressure from an automated system.

The formation of secondary-secondary and secondary-tertiary blood pressure during the course of these reactions, regardless of the method of their implementation, can be represented by the following general scheme:



Where 1) $R' = -C_3H_7$, $R = -H$; 2) $R = R' = -CH_3$; 3) $R' = -C_2H_5$, $R = CH_3$

It turned out to be the most fruitful in carrying out the synthesis of AD, as in the case of obtaining AS, in DEE medium in the presence of an excess amount of KOH.

The kinetic features were studied using the example of the synthesis of decyn-5-diol-4,7, based on hexin-1-ol-3 with butyraldehyde, which was carried out in the temperature range $-5 + 20$ ° C for 3 hours in the presence of a KOH catalyst.

The data obtained showed that with an increase in the temperature and duration of the reaction, the yield of AD increases. Under these conditions, changes in process speed are also directly proportional to temperature. However, the reaction rate at the same temperature decreases uniformly with increasing time, which is most likely due to a decrease in the concentration of the starting reagents and the dilution of the reaction medium, the resulting AD.

Also, during the synthesis of secondary-secondary acetylene diols at a temperature of $+ 10$ ° C and during the synthesis of secondary-tertiary acetylene diols at a temperature of $+ 20$ ° C, the reaction yield reaches a maximum and then decreases.

This is due to the fact that aldehydes are more susceptible to aldol condensation in a strongly alkaline medium than to the formation of diols with acetylene alcohol after $+ 10$ ° C. In ketones, such condensation begins after $+ 20$ ° C.

From the dependence of the reaction rate on the reciprocal temperature in Arrhenius coordinates according to the well-known method [1,3], the E values of the formation of decyn-5-diol-4,7 were calculated both during the synthesis of hexin-1-ol-3 and during its production by the interaction of the AS with n-butyric aldehydes, as well as the formation of 3-methylnonine-4-diol-3,6. In this case, the found values of E are, respectively, 3.01 kJ / mol (12.50 kcal / mol), 3.14 kJ / mol (13.13 kcal / mol), and 4.00 kJ / mol (16.72 kcal / mol). These E values are common in most nucleophilic reactions.

Based on the literature data [2,3,8], the possibility of replacing DEE with THF under the conditions of the formation of blood pressure was also studied. At the same time, the best yield of the target product was achieved with the ratio of AC and KOH 1: 4-5 in the temperature range of 20-25 °C. In the case of a further increase in temperature, here, too, self-condensation of the initial carbonyl compounds mainly occurs. It should be emphasized that a similar phenomenon with the use of THF, the Favorsky reaction was observed in [3].

Thus, as a result of the performed experiments, it was found that with a successful choice of optimal conditions, hexin-1-ol-3 exhibits a sufficiently high reactivity to interact with carbonyl compounds with the formation of the corresponding AD.

Table 1 and 2 show the synthesized AD, their yields under optimal reaction conditions, as well as some physicochemical constants; for comparison, such data are also presented for hexin-1-ol-3.

The inhibiting activity of the synthesized diols in relation to hydrogen sulfide corrosion of steel was studied in the laboratory "Anti-corrosion protection" at JSC "Oil and Gas" Uzbekistan.

The tests were carried out in a gas condensate: water environment in a ratio of 1: 1 on samples in the "D" steel category in the form of 4x2x0.1 cm³ plates. In this case, the concentration of the inhibitor is 0.25-1.0 g / l. The inhibitory activity of the preparations was revealed by weighing the used steel plates before and after the experiment.

The test results for the study of the protective properties of the corrosion inhibitor of the synthesized diols are shown in Table 3.

Tests carried out during heating in the presence of hydrogen sulfide (concentration 2 g / l) at a temperature of 60 ° C, inhibitor concentration 1 g / l, in gas condensate: water 1: 1, showed that its degree of protection in the liquid phase reaches 90-93% in the gas phase 78 %.

Experimental Part

IR spectra of the synthesized compounds were recorded on a UR-20 device in a thin layer in solution, and solid in the form of tablets with potassium bromide or sodium chloride. PMR - 1H spectra were taken on a Varian XL - 400 instrument, GLC were taken on an LKhM - 80 - MD chromatograph with a flame ionization detector. The reaction products were separated by column chromatography on sliogel by elution.

Table 1. Acetylene diols synthesized from hexin-1-ol-3

No	Diols and their structural formulas	Gross formula	yield%	T _{boiling.} °C	η_D^{20}	α_D^{20} , g/cm ³
I	Hexin-1-ol-3	C ₆ H ₁₀ O	45-80	140-142/740	1,4350	0,8710
	$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{C} \\ \\ \text{OH} \\ \equiv \text{CH} \end{array}$					
II	decine-5-diol-4.7	C ₁₀ H ₁₈ O ₂	45-60	195-197-76	1,4710	0,9621
	$\begin{array}{c} \text{C}_3\text{H}_7 - \text{CH} - \text{C} \equiv \text{C} - \text{CH} \\ \qquad \qquad \\ \text{OH} \qquad \qquad \text{OH} \\ - \text{C}_3\text{H}_7 \end{array}$					
III	2-Methyloctine-3-diol-3,5	C ₉ H ₁₆ O ₂	42-75	139-141-38	1,4520	0,9398
	$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{C} \\ \\ \text{OH} \\ \text{CH}_3 \\ \\ \equiv \text{C} - \text{C} \\ \\ \text{OH} \\ - \text{CH}_3 \end{array}$					
IV	3-methylnonine-4-diol-3.6	C ₁₀ H ₁₈ O ₂	43-73	158-160-38	1,4625	0,9472

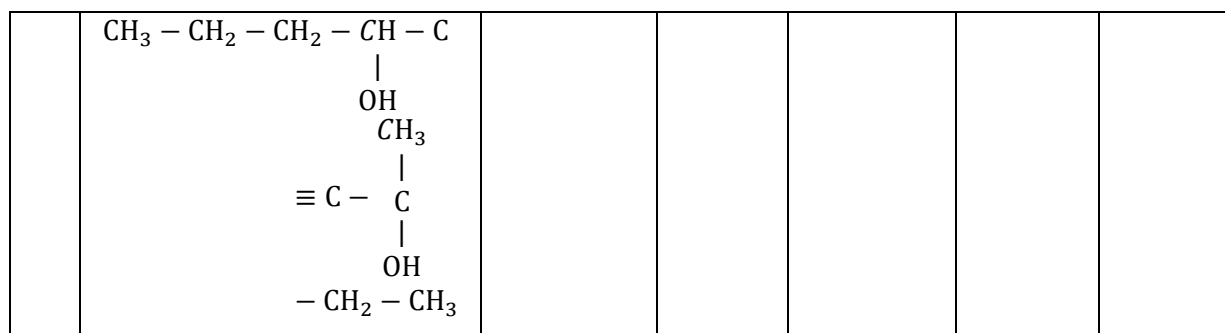


Table 2 Data on the yields, melting points, and elemental composition of the synthesized compounds

Compounds	yield%	T _{boiling} . °C	d ₄ ²⁰	n _D ²⁰	Elemental composition (%)				
					Calculated		Gross formula	Found	
					C	H		C	H
II	45-60	195-197/76	0,9621	1,4310	70,58	10,57	C ₁₀ H ₁₈ O ₂	70,50	10,60
III	42-75	139-141/38	0,9398	1,4520	72,00	10,66	C ₉ H ₁₆ O ₂	72,05	10,44
IV	43-73	158-160/38	0,9472	1,4625	70,60	10,50	C ₁₀ H ₁₈ O ₂	70,55	10,53

Table 3 Results of testing the inhibiting properties of synthesized acetylenic diols

№	Compounds	Inhibitor concentration, g / l.	Corrosion rate, g / cm ³ .h		Degree of protection, %		Note
			Duration of the experiment, hour				
			24	72	24	72	
1	II	0	0,07	0,37	-	-	Samples in inhibited media retain a shiny surface, no ulcers, no pitting
		0,25	0,089	0,0222	92,6	94,4	
		0,50	0,076	0,0222	93,4	94,9	
		0,75	0,079	0,0185	93,8	95,5	
		1,00	0,070	0,0148	94,4	96,8	
2	III	0	0,07	0,37	-	-	
		0,25	0,084	0,0220	92,0	93,9	
		0,50	0,075	0,0219	92,8	93,5	
		0,75	0,070	0,0180	93,2	95,0	
		1,00	0,068	0,0141	94,0	96,2	
3	IV	0	0,07	0,37	-	-	
		0,25	0,084	0,0212	91,5	93,2	

		0,50	0,071	0,0205	91,8	94,1
		0,75	0,068	0,020	92,6	94,5
		1,00	0,061	0,018	93,5	65,2

In the IR spectra of AD, in particular that for decyne-5-diol-4,7, stretching vibrations of methyl and methylene groups in the region of 3000-2800 cm^{-1} and -C-O- at 1150 1000 cm^{-1} are clearly manifested. However, in the spectrum, the expected bands corresponding to the deformation vibration of the $\text{C}\equiv\text{C}$ bond in the range of 2130-2080 cm^{-1} are absent, which is due to the symmetric arrangement of functional groups in AD molecules. At the same time, there are wide, smoother maxima in the region of 3600-3120 cm^{-1} , characteristic of hydroxyl groups included in intramolecular hydrogen bonds, in addition, the spectrum contains bands related to methine groups at 1450 cm^{-1} and methylene groups at 1390 cm^{-1} .

In the PMR spectrum of trans-decyne-5-diol-4, there are proton signals for the methyl group with δ 0.78-0.98 ppm. (6H), methylene group δ 1.2-1.7 ppm. (8H), hydroxyl proton with δ 4.2-4.4 ppm. (2H) and methine proton with δ 4.58-4.69 ppm. (2H). Moreover, the latter in the cis isomer of this substance is observed with a chemical shift in the range δ 4.22-4.32 ppm.

Synthesis of 2-Methyloctine-3-Diol-2,5

In a three-necked flask equipped with a stirrer, dropping funnel and thermometer, were placed 9.8 g (0.1 mol) of hexin-1-ol-3 and 16.8 g (0.3 mol) of powdered dry KOH in 240 ml of absolute diethyl ether. Then the flask was vigorously stirred for 30-35 minutes. 5.8 g (0.1 mol) of dimethyl ketone in 40 ml of absolute diethyl ether was added dropwise to the resulting suspension over 3 hours, and then the reaction mixture was left overnight. The next day, the mixture was diluted with 50 ml of distilled water while cooling, and then the ether layer was separated, and the aqueous layer was extracted three times with ether. The combined ether extracts were successively washed with 20 ml of water, 20 ml of 10% acetic acid, and then again with water and dried over calcined potassium carbonate. After distilling off the solvent, the remaining condensate was fractionated. The resulting blood pressure in the amount of 9-10 g (56-64% of theoretical) was isolated by distillation at 139-141 ° C and 38 mm. Hg ($n_D^{20}=1,4520$, $n_4^{20} = 0,49398$ g / cm).

Conclusion

As a result of the experiments, 3 acetylenic diols were obtained. Of these, two, secondary-tertiary acetylenic diols are new, not described in the literature. All synthesized compounds exhibit anti-corrosion properties in relation to metals.

REFERENCES

- Chemistry of acetylene. Managing editor M.F.Shostakovskiy. M.: Publishing house Nauka, 1968 -528p.
- Kotlyarevskiy I.L., Schwarzberg M.S., Fisher L.B. Reactions of acetylene compounds. - Novosibirsk.: Nauka, 1967.-354p.
- E. Turgunov, S. Zokirov, S.S. Zokirov. Acetylene alcohols // Monograph. UDC: 821-512-133-9. BBK: 84 (5Rus) 7. E-4. ISBN: 978-9943-5068-8-6 219 sheet.
- Patent No. 25971 SFRY. Method of obtaining alkyndiols // Koppe Herbert, Reile Karl. // SFRY -RZhKh -1969 -11H312П
- Patent No. 2712560. USA. Getting alkynes. // Mekinly Clud, Fahnoe Fredezich, Fuller Donald. // (USA) -RZhKh.-1956. - 62718P
- Patent No. 23636167. Processing of acetylene glycols. / Rbert J /, Mc Mahon, Helbert C. // (USA) -RLC. -1972. -20N27P 10749

Libman NM, Kuznetsov SG Amino alcohols of the Acetylene series. 1. Obtaining 1,1 disubstituted -4-dialkylaminobutins-1. // Journal of organic chemistry. -1960. –T.30 p.1197

Rose J.D., Gale R.A. Acetylene reactions. Part V. Reactions of phenylacetylene with secondary amines. J. Chem. Soc., PerkinL. 1949. No. 1. P.792

A.S. 1624945. "Corrosion inhibitor in hydrogen sulfide-containing environments" / Kurbanov A.I., Sirlibaev T.S. Zokirov S., Popova R.A., Denisov A.N. October 1, 1990.