

AN OBTAINMENT OF SINGLE-ATOMIC UNCERTAIN ALCOHOLS ON THE BASE OF ACETHYLENE AND PHENYL ACETHYLENE AND HEIR BROMINATION

Kultayev Kuzibay Kazakbayevich,

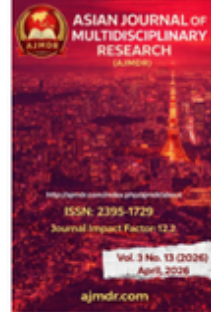
National Pedagogical University of Uzbekistan named after Nizami, faculty of Natural Sciences, department of Chemistry, asso-ciate professor,

E-mail: Kultayev60@.bk.ru

Abstract. Acetylene alcohols and phenyl acetylene allow synthesizing the necessary substances for the chemical industry - synthetic polymers, pharmacological preparations, agricultural pesticides, defoliants, plant stimulants. We investigated the synthesis of tertiary alcohols on the base of acetylene and phenyl acetylene, the conditions for their high productivity, the structure of secondary and tertiary alcohols were determined, and confirmed by physical parameters. The refractive index of light, density, boiling point and productivity were defined. Alcohol molecules are polarized due to a shift in the density of the electron cloud towards the hydroxyl groups in secondary and tertiary alcohols. Their influence to halogen occurs through electrophilic addition. There are trans- and cis-spatial forms of halogen derivatives, which are began with the formation of the π -complex. Halogen formations are colorless liquids, and bromine formations turn into a black liquid over time. The structure of halogen compounds is confirmed by IR and PMR spectra. The constants of halogen compounds were determined, such as light refraction, density and boiling temperature. The influence of the nature of the solvent to the output of product was established.

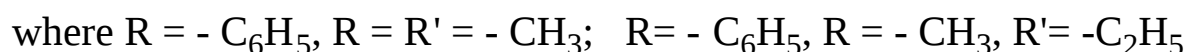
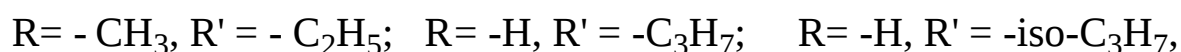
Keywords: dimethylethylcarbinol, phenyldimethylethynylcarbinol, hexin-1-ol-3, dimethylketone, positive induction effect, infrared spectrum, paramagnetic resonance, valence wave vibrations, deformation wave function, spatial isomer, condensation reaction.

INTRODUCTION. Acetylene homologs and aromatic hydrocarbons in chemical industry in production are used as organic colorants, synthetic detergents, plastics and insecticides in agriculture, as well as solvents [1]. The presence of a carbon atom which contains a triple bond in the benzene ring, allows to obtain valuable semi productions as a result of chemical changes in organic synthesis [2].

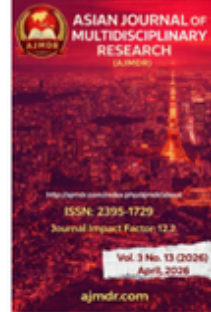


Aromatic hydrocarbons have great prospects in this area. Acetylene alcohols and their halogen derivatives are very important substances on chemical and physiological properties. Pesticides, medicines, bactericides, stimulants and inhibitors were received among these substances [3, 4, 5]. The synthesis of such substances, which contain various substituents in their molecules, in this position, the research of various functional derivatives of acetylene, has theoretical and practical significance. It creates the facility to synthesize a new group of unsaturated multifunctional organic compounds. However, there is no literature on the formation and physiological activity of such substances, which contain an aromatic ring and halogen in the molecule [6]. In the phenyl acetylene molecule, the electron clouds are unevenly distributed, they shift from the phenyl radical to the triple bond. This is due to the hybridization of the carbon atom. In the series of sp^2 , sp – hybridization increases the electronegativity of the carbon atom. Carbon in the phenyl radical has a state of sp^2 - hybridization, and there is sp in the ethynyl radical. Monosubstituted derivatives of acetylene due to the positive induction effect of the electron-donor radicals (+ I), the electron cloud of triple bond shifts towards carbon, the final carbon atom, which is a non-containing radical and this carbon atom is negatively charged. This condition facilitates the exchange reaction and electrophilic addition.

THE MAIN PART. The reactions of monosubstituted acetylene derivatives with carbonyl compounds were studied in 1900 by Russian academician A.E. Favorsky. The interaction of aldehydes and ketones with acetylene, including phenylacetylene, occurs in a suspension of potassium hydroxide in completely dry diethyl ether. This reaction is common for the synthesis of secondary and tertiary acetylene alcohols:



On Favorsky, reaction synthesizes aliphatic, alicyclic, aromatic and heterocyclic acetylene and diacetylene alcohols and glycols, hydroxy acids and amino alcohols. Isoprene, obtained on the basis of acetylene alcohols is the starting material for the production of synthetic rubber in production.



The main purpose of this work is to obtain tertiary and secondary acetylene alcohols, studying their physicochemical properties and synthesize on the base of their halohydrins.

The experiments were carried out in a 2000 ml three-necked volumetric flask, equipped with a mechanical stirrer, reflux condenser, thermometer and dropping funnel. 200 g of a mass of a ground suspension of potassium hydroxide in 1000 ml of absolute diethyl ether were prepared, the flask was cooled at - 5° -10 °C and the purified acetylene was passed under stirring. Gaseous acetylene was obtained in an autoclave by the reaction of hydrolysis of calcium carbide and dried from moisture, passing it through concentrated sulfuric acid. The reaction continues for 10 hours, and during this period, 100 ml of acetone are added drop by drop from a dropping funnel. To decompose the yellow potassium complex salt of dimethylethynylcarbinol into alcohol, 100 ml of water are added drop by drop from a dropping funnel. The ether portion is separated, and the aqueous portion is extracted several times with diethyl ether. The ether portion, containing dimethylethynylcarbinol is dried from water with dry calcium chloride, and the formed acetylene alcohol is separated by distillation.

Synthesis of phenyldimethylethynylcarbinol [7.8]

The synthesis of acetylene alcohol was carried out in a three-necked flask with a volume of 300 ml, by equipped with a thermometer, stirrer and reflux condenser. To do this, we prepared a suspension of 20 g of potassium hydroxide and 250 ml of dried diethyl ether in a flask. It cools the flask outside with ice, insist at 50 ° C, and with vigorous stirring of the mixtures, begins to drip the mixture of 5.8 g (0.1 mol) of dimethyl ketone and 5.6 g (0.055 mol) of phenylacetylene at 8-10 ° C during 8-10 h. The reaction mixture is cooled with ice and hydrolyzed with 100 ml of water. The ether portion is separated, the aqueous portion is extracted several times with ether. The ether portion is dried with potash. The ether is distilled and the resulting alcohol is distilled into a Kleisen flask with a reflux condenser by 25 cm high.

The condensation reaction of acetylene with aldehydes and ketones proceeds under the conditions of Favorsky reaction with a high output of 60 -70%. The output of tertiary alcohols in counting to phenylacetylene is 65-75%. The achievement of high outputs of acetylene alcohol depends on the activation of the reaction environ, which is 74.3% as a result of adding ethanol or normal butanol to the reaction mixture (1.0% with respect to the amount of potassium hydroxide). Here, alcohols



act as carriers of potassium ions. The reaction proceeds with the formation of a complex “solvent - acetylene-potassium hydroxide”. The nature of the solvent plays a major role in the formation of this complex.

The structure of the received substances was confirmed by infrared spectroscopy (IR). In the IR-spectrum of n-propylethynylcarbinol, valence vibrations of the methyl and methylene groups are observed at $3000-2800\text{ cm}^{-1}$, and valence vibrations of the C-O groups absorb at $1200-1000\text{ cm}^{-1}$, and $\text{C}\equiv\text{C}$ groups give absorption at $2200-2100\text{ cm}^{-1}$, the absorption line of valence vibrations of the $\equiv\text{C}-\text{H}$ groups correspond to the acetylene group of 3315 cm^{-1} . A wide line in the range of $3450-3000\text{ cm}^{-1}$ represents the vibration of valence vibrations of the OH - groups. In addition, the absorption line, characteristic of deformation vibrations of the methylene group is presented in the region of about 1400 cm^{-1} . It should be noted that the absorption line of $3450-3000\text{ cm}^{-1}$ of the spectrum shows the characteristic lines belonging to the hydroxyl group (OH-).

In the PMR^1H spectrum of n-propylethynylcarbinol, the triplet signal corresponding to the methylene group presents at 0.9–1.0 m.p. (6H).

The signal, corresponding to the protonacetylene groups, appears at 2.25 m.p. with a chemical shift. (1 H), and the signal, corresponding to the proton of the hydroxyl group is 3.20 m.p. (1H), the proton of the groups of C - H interacts with the hydroxyl group with forming 4.25 m.p. in triplet form, and the displacement belonging to the proton of the methylene groups is expressed from 1.5 to 1.7m.p.

The IR spectrum of the synthesized dimethylethynylcarbinol (Fig. 1) and the PMR^1H -spectrum (Fig. 2), the PMR^1H spectrum 1-phenyl-3-methylbutin-1-ol-3 (Fig. 3) completely confirm their chemical structure.

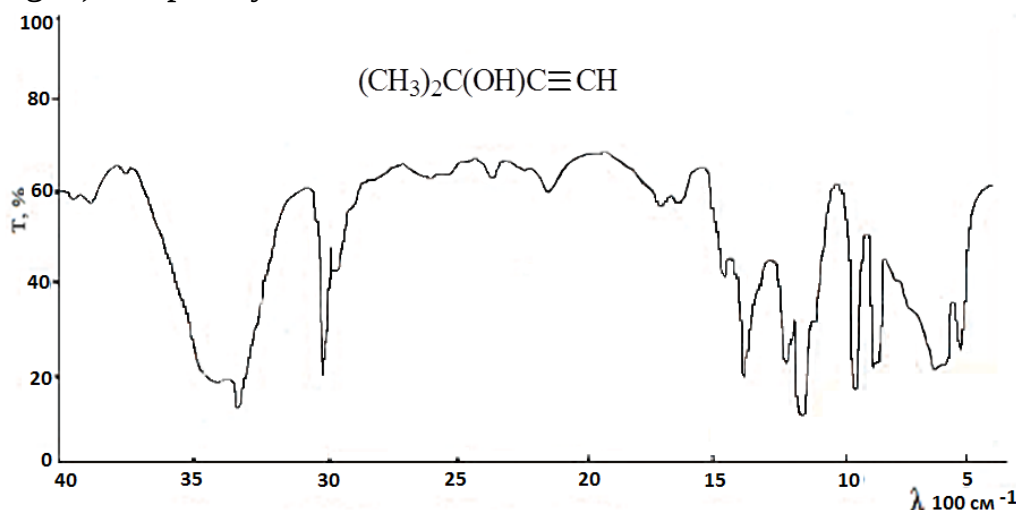


Fig.1. IR-spectrum dimethylethynylcarbinol.

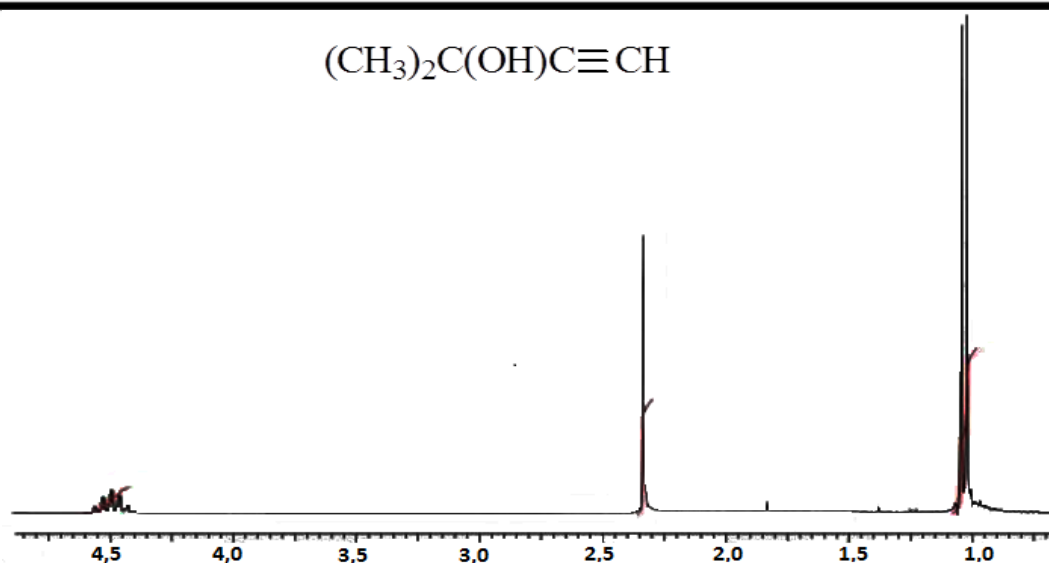


Fig.2. PMR 1H – spectrum dimethylethynylcarbinol

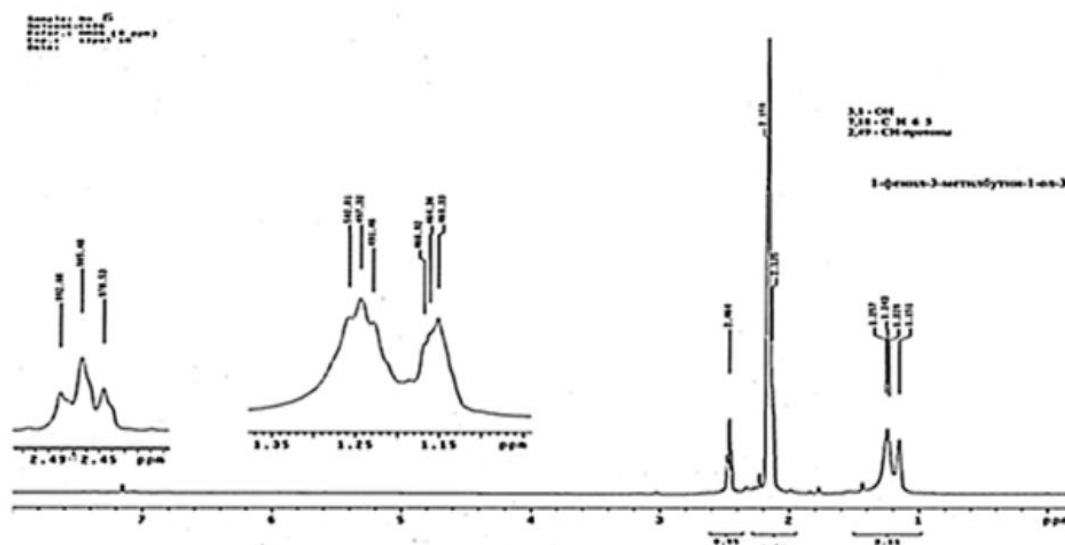


Fig.3. PMR 1H- spectrum 1-phenyl-3-methylbutin-1-ola-3

Physico-chemical characteristics of acetylene compounds

No.	Name of substance	Molecular mass	Temperature melting, °C	Boiling temperature, °C	n_D^{20}	Density, g/ml d_n^{20}	Output, %
1	Phenylacetylene	102,14	-44,8 °C	141,7°C	1,5492	0,9281	75
2	Dimethylethynylcarbinol	84	-	102-104 °C	1,4211	0,8611	68



3	Methylethyl-ethynylcarbinol	98	-	118-122°C	1.4310	0,8692	15 - 97
4	H-propyl-ethynylcarbinol	97	-	87-88/ 10 mm. m.c. (mercury column)	1,4350	0,8710	75,9
5	Isopropylethynylcarbinol	97	-	133-134	1,4352	-	68,1
6	1- phenyl- 3-methylbutin-1-ol -3	160	-	147	1,4560	1,9320	74.1
7	1- phenyl-3-methylpentin-1-ol-3	174	161-162	-	1,4887	1.1658	66,2

An analysis of published materials shows that the optimal conditions for the formation of acetylene alcohols in the reaction of condensation of acetylene and its derivatives with carbonyl compounds are poorly studied. Besides, information on the synthesis of acetylene alcohols and their derivatives, chemical properties, physical and chemical constants and properties, as well as the use of products derived from them were insufficient now. Tertiary acetylene alcohols have polar bonds of O - H and O - C and unallocated electron pairs. The chemical properties of acetylene alcohols are due to hydroxyl (OH-) and ethynyl groups ($-C\equiv C-$). Simple chemical properties in such compounds are manifested in the presence of a hydroxyl groups, where the ethynyl group is considered neutral and it does not matter. However, under the influence of strong electrophilic reagents, the ethynyl group can react in the same way as the hydroxyl group [9, 10]. Acetylene alcohols do not have a pronounced acidity, they are less acidic than the limit. This is due to the donor property of methyl groups (effect + I), that the electron density accumulates in the oxygen atom. Anion of tertiary acetylene alcohol has strong basic properties.

Acetylene alcohol bromination reaction.

The bromination reaction of dimethylethynylcarbinol was carried out in a non-polar solvent, which in tetrachloride carbon in the presence of a light emitting lamp for 5-6 hours with stirring with a magnetic stirrer at room temperature. As a result

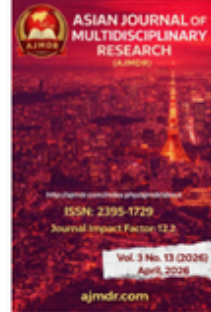


of gas chromatographic analysis, it was found that the product consists of mixtures of cis and trans-dibromohydrins. The output of dibromo derivatives depends on the nature of the solvent, polar (50% acetic acid can also be used) or a nonpolar molecule of solvent, concentration of solvent and temperature. At high temperatures (above 25 °C), trans-dibromo derivatives are formed, and at low temperatures (-50 °C) cis-dibromoisomers are formed.

Physico-chemical characteristics of the reaction products

No.	Name by systematic nomenclature	Output, %	Boiling temperature, °C	n_D^{20}	D_n^{20}
1	Trans-1,2- dibromo-3-methylbutene-1-ol-3	74,2	76 -77/ 7 mm. m.c.	1,5469	1,8551
2	Trans-1,2-dibromo-3-methylpentene -1-ol-3	70,1	94-95/10 mm. m.c.	1,5392	1,7472
3	Trans-1,2-di-bromhexene-1-ol-3	53-54	120-122/7 mm. m.c.	1,5320	-
4	Cis-1,2-dibromo-3-methylbutene-1-ol-3	63,4	79 -80/6 mm. m.c.	1,5416	1,8451
5	Cis-1,2-dibromo-3-methylpentene -1-ol-3	72,5	68 - 69 /9 mm. m.c.	1,5388	1,7372
6	Cis-1,2-di-bromhexene-1-ol-3	43- 44	129 -130 /7 mm. m.c.	1,5172	-
7	Trans -1,2 - di bromo-1-phenyl-3- methylbutene-1-ol -3	52	79-80/8 mm. m.c.	1,5564	1,5564
8	Cis -1,2- dibrom-1-phenyl-3-methylbutene-1-ol -3	8	70-71/7 mm. m.c.	1,5514	1,7345

The structure of the received substances was confirmed by infrared (IR) and PMR methods. The valence vibrations of the methyl and methylene groups in the synthesized molecules of trans-1,2-dibromo-3-methylbutene-1-ol-3 are in the range of 3000 - 2800 cm^{-1} , the valence vibrations of the C-O groups make up 1200-900 cm^{-1} , the line of absorption groups of - C = C for the trans-isomer is 1680-1640 cm^{-1} , for the cis-isomer at 1665-1635 cm^{-1} , = C-H valence vibration of the C-H bonds



appears at $3095-3010\text{ cm}^{-1}$, and deformation vibrations of which are manifested at $1420-1290\text{ cm}^{-1}$. The valence vibrations of the C-Br groups are visible on the characteristic absorption line at $1080-1000\text{ cm}^{-1}$ and $700-500\text{ cm}^{-1}$. It should be noted that the absorption line of $3450-3000\text{ cm}^{-1}$ of the spectrum shows the characteristic lines, belonging to the free hydroxyl group (OH-). For a monosubstituted benzene ring, an absorption corresponds in the region of $1175-1125\text{ cm}^{-1}$ and strain absorption in the region of $770-730\text{ cm}^{-1}$.

In the PMR spectrum, synthesized by trans-1,2-dibromo-3-methylbuten-1-ol-3, the triplet signal, corresponding to the methyl group presents at 0.9–1.0 m.p. (6H). = C – H signal for the proton in the C – H group has with a chemical shift to the trans state at 6.86 m.p. (1H) and to the cis-state at 6.75 m.p. (1H). In the signal, corresponding to the proton (1 H) hydroxyl group with a chemical shift of 3.20 m.p. (1H) is expressed in distances of 7.4-7.8m.p., and there are signals, specific for protons in the phenylring (5H).

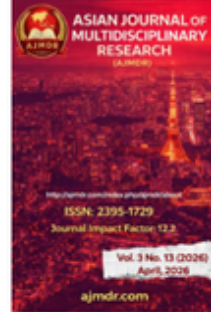
Conclusion. The condensation reactions of aldehydes and ketones with acetylene and phenyl acetylene occurred in high output by using a solvent of dry diethyl ether, the temperature of the system was maintained in the range of $-5 - (-10)^\circ\text{C}$, and the duration of the reaction was 10-12 hours.

The spatial form of halogen derivatives of tertiary ethylene alcohols are in the cis- and trans configurations. When it was used chloroform or carbon tetrachloride as a solvent, the outputs of trans-dihalohydrins were higher than cis-isomers at 25°C , respectively.

The structural formulas of alcohols, synthesized on base of acetylene and phenylacetylene, as well as halogen derivatives were confirmed on their base by IR and PMR spectra, and their physicochemical constants were also determined.

Recommendations:

1. The reactions of acetylene and phenyl acetylene with the corresponding carbonyl compounds proceed at 25°C under normal conditions with the formation of acetylene alcohols. This occurs under duration of the reaction for 5–6 h and using because of solvent of diethyl ether. Tertiary acetylene alcohols can be received by thermal decomposition of diols.
2. Tertiary acetylene alcohols are aromatic substances, so they can be used as perfumes.



3. Acetylene alcohols have inhibitory properties, reducing corrosion damage to metals. It is necessary to study the inhibitory properties, inherent to their chlorinated and brominated derivatives.

References

1. Melnikov N.N., Baskakov Yu.A. Chemistry of herbicides and plant regulators. – Moscow, 1962.
2. American patent 2584420. Chem. Abstracts, 1952, 46, 9605.
3. Sirlibaev S., Kurbanov A.I., Turgunov E., Kul'taev K.K., Koblov R.K., Khikmatov A. Herbicidal activity in the production of acetylene alcohols. – T.: 1985, No. 11. – Pp.105 -107.
4. Kurbanov A. I., Sirlibaev T. S., Turgunova E., Kul'taev K. K., Kovlova R. K., Tarikov S. A. The biological activity of some acetylene amino alcohols and halogen-containing products. Agrochemistry, 1986, No. 4. – Pp. 86 - 89.
5. Sirlibaev T.S., Kul'taev K.K., Kurbanov A.I. The study of the antimicrobial activity of some acetylene compounds in products obtained primarily. – Tashkent, 1989, 8 with Dep, in UZRISTI, No. 957-Uz 89.
6. Kurbanov A.I. Synthesis based on secondary, tertiary acetylene alcohols and pyridylacetylene, possible applications of the compounds obtained, doctoral dissertation. – Tashkent, 1998.
7. Favorsky A.E., Skosarevsky M.P. South Russian Physical Chemical Society 1900, No. 32. – P.652
8. Ziyadullaev O.E. Synthesis and technology of aromatic acetylene alcohols, IX vinyl esters based on phenylacetylene. PhD thesis. – Tashkent, 2012.
9. Neyland O.Ya. Organic chemistry. – Moscow, Higher School, 1990, 750 p.
10. Askarov I.R., Isaev V.T., Maksumov A.G. Kyrgyz organic chemistry. – Tashkent, 2012. – P. 258.
- [9]. Neyland O.Ya. Organic chemistry. – Moscow, Higher School, 1990, 750 p.
- [10]. Askarov I.R., Isaev V.T., Maksumov A.G. Kyrgyz organic chemistry. – Tashkent, 2012. – P. 258.