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Synthesis on the Basis of 2,2^1-Diproparghyl Ether of Azobenzene, Structure, Properties and their Application

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ABSTRACT:The proposed article relates to the organic chemical synthesis of the derivative of 2,2^1-dipropargyl ether of azobenzene, the study of its chemical properties, the production of copper, silver, mercury acetylenides; iodine, bromine derivatives, use as an industrial plant growth stimulator.

KEY WORDS: azobenzene, diazomethane, hexamethylenediisocyanate, γ,γ^1-diiodine-2,21-dipropargyldiester, γ,γ^1-disilver 2,2^1-dipropargyldiester, bis- [(2,2^1-dipropynyloxy) azobenzene] – mercury, γ,γ^1-dibromo-2,2^1-dipropargyldiester,2,2^1-hydroxymethyl- (4,4^1-dipyrazolyl) azobenzene, bis - {N, N^1-hexamethylene-2,2^1-[hydroxymethyl- (4,4^1-dipirazolyl) -1,1^1-urea], cotton, cucumber, the drug "Roslin".

I.INTRODUCTION

In order to expand the assortment of dyes used in almost all sectors of the national economy, primarily in the chemical, agriculture, technology, and pharmacy and medicine, derivatives of azobenzene are used. They are considered an important component for dyeing synthetic, natural fibers, plastics, paper, film, leather materials and many other items.

II. SIGNIFICANCE OF THE SYSTEM

The paper mainly focuses on how the chemistry derivative of 2,2^1-dipropargyl ether of azobenzenecompounds. The study of literature survey is presented in section III, Proposed methodology and discussion is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and Conclusion.

III. LITERATURE SURVEY

The presence of nitrogen atoms in the molecules of azo compounds, triple $(-C \equiv CH)$ bonds, increases physioligical, pharmacological, biological activity, while reducing toxicity, and also exhibits antifungal, antimicrobial, antiulcer, and many others. properties [1-6].

Derivatives of dipropargyl ethers are known to possess various types of superbiological activity. So, for example, diacetylene containing esters, azo compounds containing aromatic and five-membered heterocycles possess herbicidal, fungicidal growth-promoting, antitumor properties that lower cholesterol and blood sugar and many others. activity [7-13].

The literature [14-15] describes the synthesis of various acetylene compounds with a terminal triple bond. However, we did not find information on the syntheses of azobenzenediacetylene compounds in the o, o^{1}positions and their

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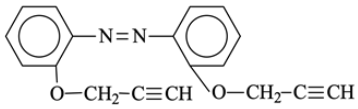
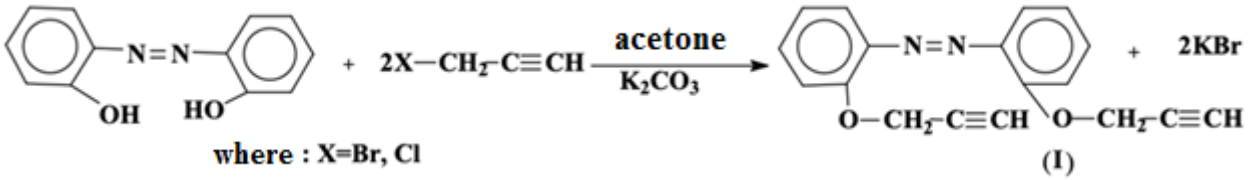
derivatives of the type  , these little-known compounds essentially represent a new kind of compounds whose properties have not been studied.

IV. PROPOSED METHODOLOGY AND DISCUSSION

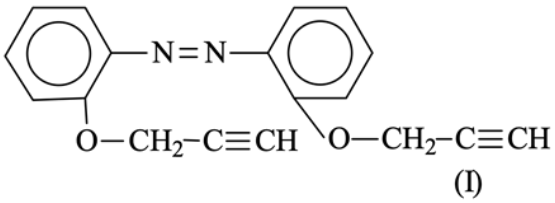
In this regard, we obtained derivatives of 2,2[1] (or 0,0[1]-) dipropargyl ether of azobenzene, by reaction with propargyl bromide in the presence of an organic solvent of acetone, potash and 2,2[1]-dihydroxyazobenzene according to the scheme:



The obtained derivatives of 2,2[1]-dipropargyl ether of azobenzene are crystalline colored substances that are readily soluble in many organic solvents and insoluble in water.

The physicochemical parameters of the derivative of 2,2[1]-dipropargyl ether of azobenzene (I) are given in Table 1.

Table 1. Physicochemical parameters of 2,2[1]-dipropargyl ether of azobenzene (I)

Structural formula	Yield, %	MT, °C	R_f	Bruttoformula	Elemental analysis, %		$M_м$
					Calculated N	Found N	
 (I)	88,6	135-136	0,72	$C_{18}H_{14}N_2O_2$	9,65	9,53	290

The 2,2[1]-dipropargyl azobenzene ester was purified using preparative thin-layer chromatographyon an Al_2O_3 column in a benzene: hexane = 2: 4 system.

To prove the structure of the 2,2[1]-dipropargyl ester of azobenzene, the method of IR and UV spectroscopy was used (Table 2).

Table 2.IR and UV spectrum of the drug (I)

Compound I	IR-spectra, ν, sm^{-1}					UV spectrum, nm		
	—N=N—	—O—CH_2	—C≡C—		—C≡H	—CH_2-C≡C—H		—N=N—
I	1584-1557	1236	2220	772-728	3310	241-323	379	264

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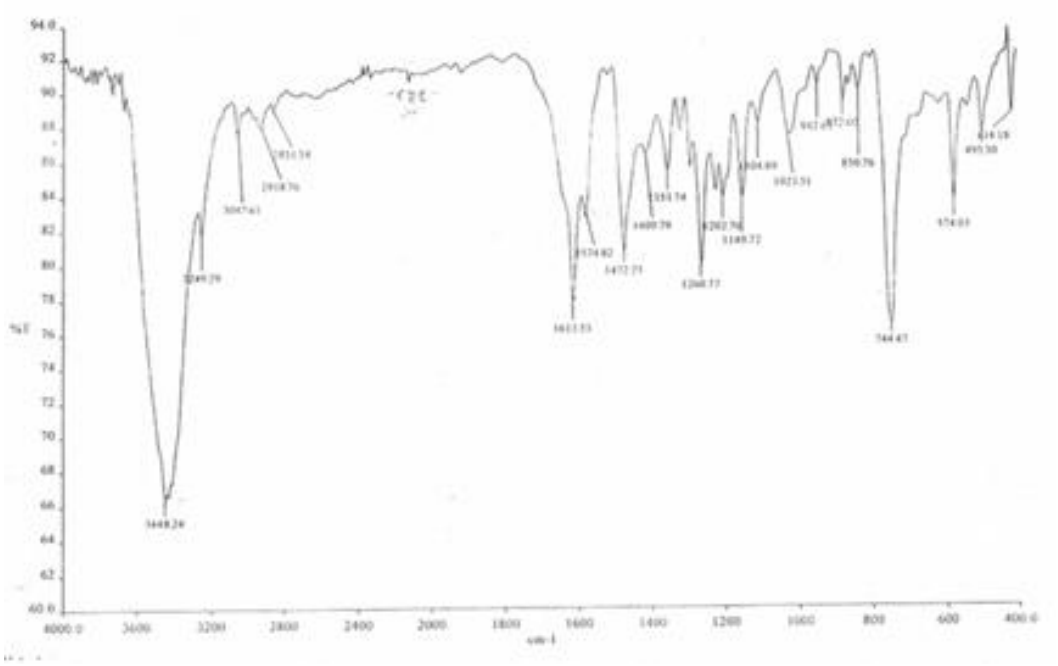

Fig. 1. IR spectrum of 2,2[1] - dipropargyl ether of azobenzene (I).

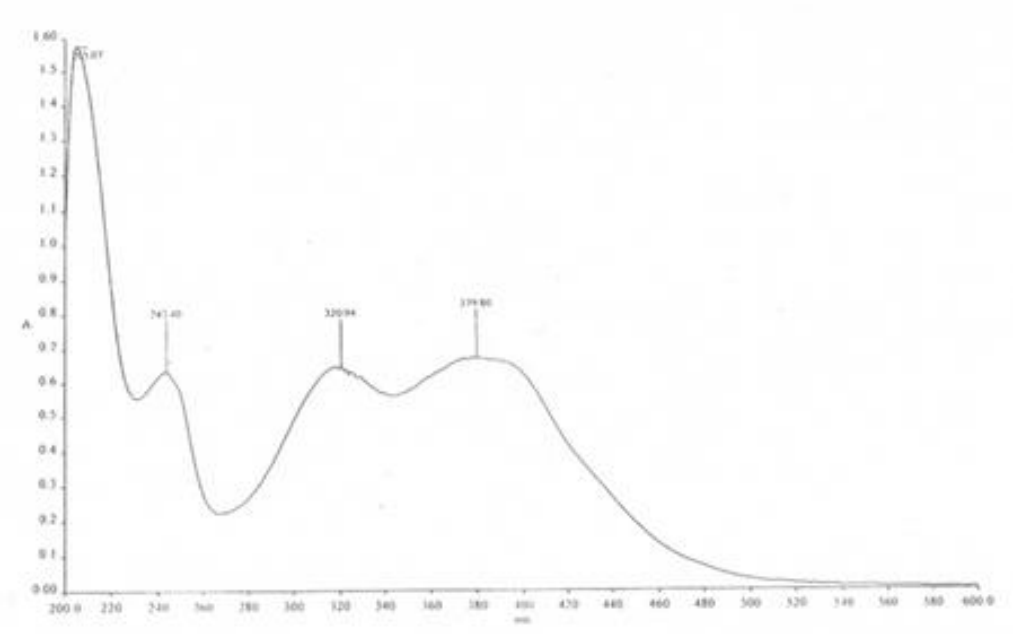

Fig. 2. UV spectrum of 2,2[1] - dipropargyl ether of azobenzene (I).

The chemical properties of 2,2[1]-dipropargyl azobenzene (I) ester were studied.

It was established that the group-C≡C-Hreadily reacts with Cu_2Cl_2, $AgNO_3$, $Hg(OCOCH_3)_2$ to obtain the acetylenides of the preparation (I) according to the following scheme:

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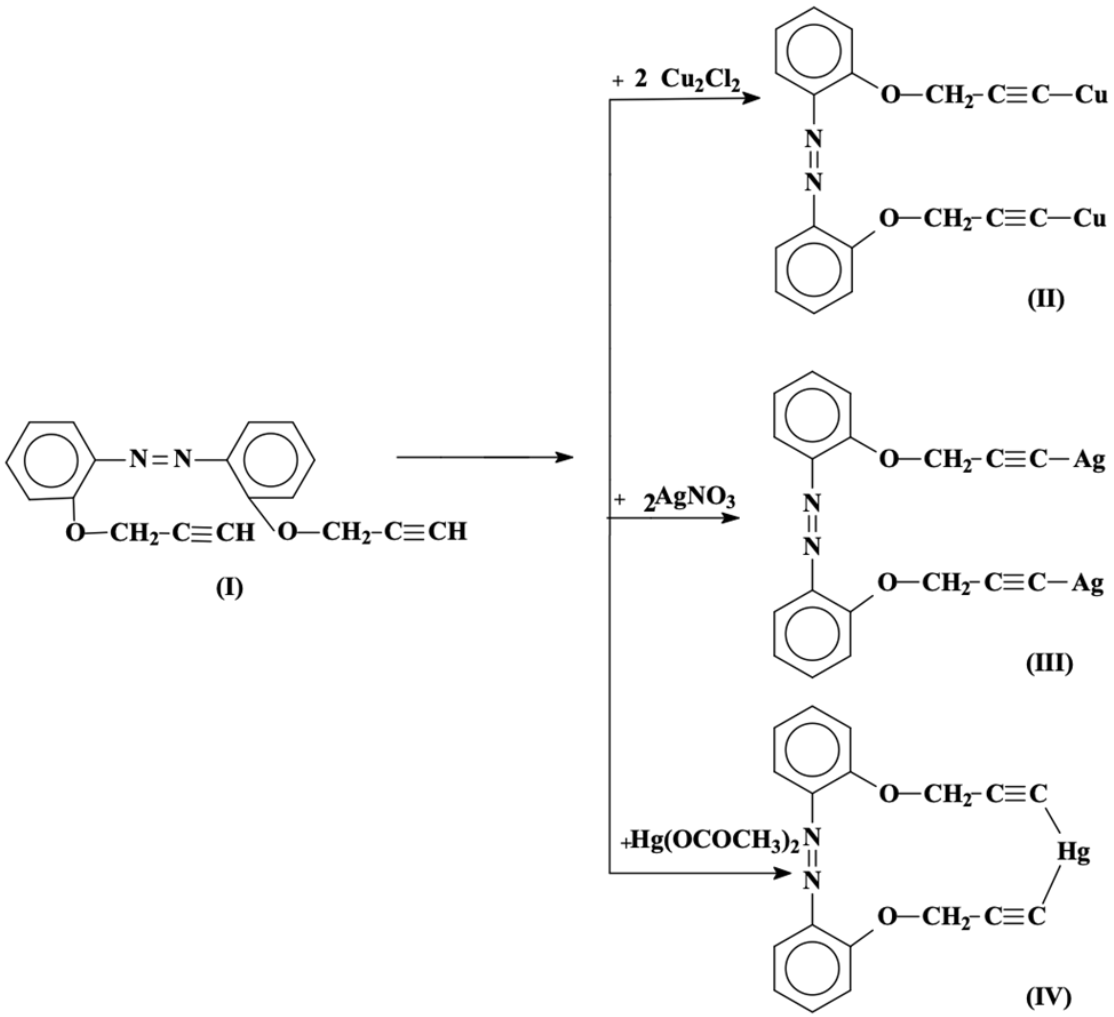
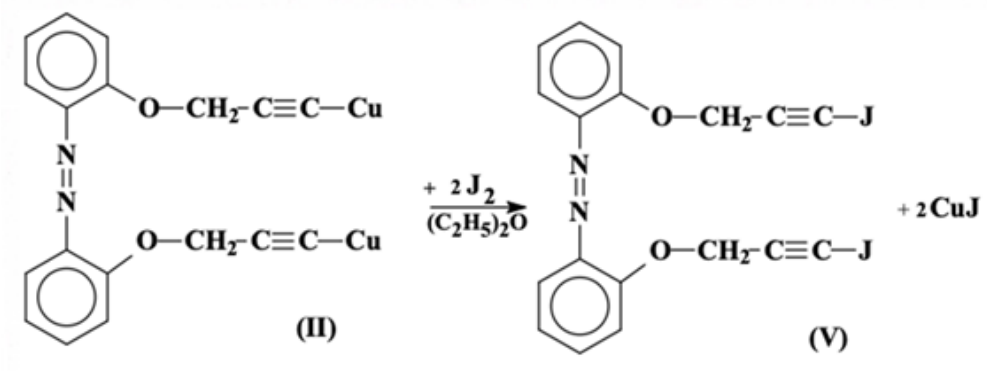


Of interest was the interaction of 2,2[1] – diacetylenide of copper dipropargyl ether of azobenzene with iodine in order to obtain new compounds $(-O-CH_2-C\equiv C-I)$of a little known compound.

The reaction of compound II-IV with iodine was carried out in an environment of sulfuric ether at room temperature for 0,5-1,0 hours according to the following scheme:



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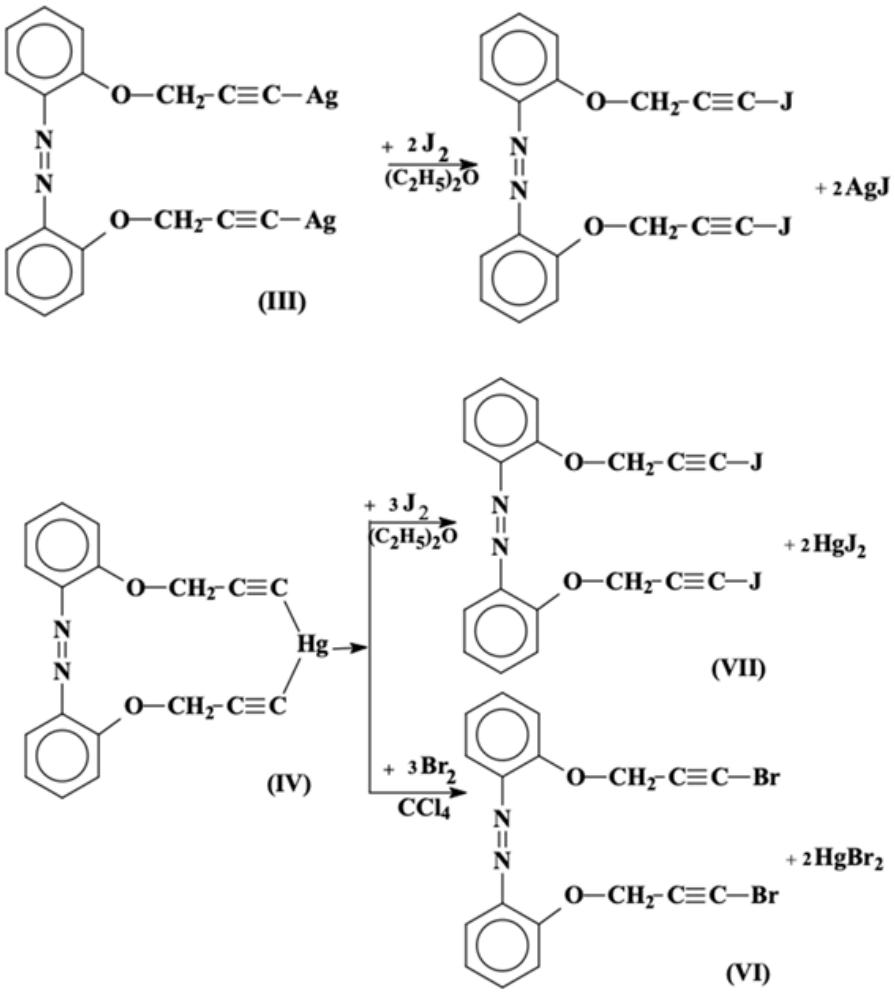

Physico-chemical characteristics (V-VII) of the compounds are shown in table 3.

Table 3. Physicochemical Characteristics of Preparations (V-VII)

Compound №	Yield, %	MT, °C	Rf	Brutto formula	M_M	Elementalanalysis, %					
						Calculated			Found		
						N	J	Br	N	J	Br
V	93,6	197-198	0,73	$C_{18}H_{12}N_2J_2O_2$	542	5,16	46,86	-	5,11	46,71	-
VI	95,3	198	0,71	$C_{18}H_{12}N_2Br_2O_2$	447,8	6,25	-	35,68	6,24	-	35,49
VII	89,6	197-199	0,69	$C_{18}H_{12}N_2J_2O_2$	542	5,16	46,86	-	5,10	46,77	-

The structure of V-VII was established by elemental analysis, IR spectroscopy, and molecular weight (Tables 3 and 4).

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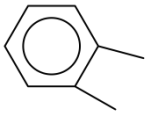
Table 4. IR Spectra of Compounds (V-VII)

Compound №	IR-spectra, ν, sm^{-1}						
	—C≡C—	—N=N—	—O—CH_2		—CH_2—	—C≡C—J	—C≡C—Br
V	2128	1583	1111	771-734	1382	2241	-
VI	2131	1585	1113	770-775	1384	-	2226
VII	2128	1584	1112	770-737	1386	2243	-

V. EXPERIMENTAL RESULTS

The course of the reaction and the individuality of the compounds are monitored by TLC on aluminum oxide of (II) degree of activity with the appearance of spots by iodine vapor. IR spectra recorded on a spectrometer VR-20.

A. Synthesis of 2,2[1]-dipropargyl diester of azobenzene (I)

A flask equipped with a reflux condenser was charged with 19,0 g (0,1 mol) of 2,2[1]-dihydroxyazobenzene, 23,8 g/mol of freshly distilled propargyl bromide, 30 g of calcined potassium carbonate and 350 ml of anhydrous acetone as solvent, the reaction mixture heated in a water bath at a temperature of 90 °C for 8 hours and was left overnight. The mixture was filtered, the product was removed from the filtrate with ether. After evaporation of the solvent, the precipitate was recrystallized from benzene.

The 2,2[1]-dihydroxy azobenzenedipropargyl ether obtained in this way is a brick-colored crystalline substance with a melting point of 135-136 °C. Yield I – 88,6% (of theoretical); Rf = 0,72;

Found, %: C 74,32; H 4,74; N 9,56;

Calculated $C_{18}H_{14}N_2O_2$, %: C 74,48 H 4,82 N 9,65

B. Synthesis of γ, γ[1]-dicuprum-2,2[1]-dipropargyl diester of azobenzene (II)

Copper chloride, taken with a 25-30% excess, is completely dissolved in 25% ammonia with the addition of a small amount of hydroxylamine hydrochloride. The prepared copper chloride solution is added to a diluted alcohol solution of 29,0 g of 2,2[1]-dipropargyl azobenzenediester. The resulting bright yellow precipitate is filtered off and washed with a weak solution of hydroxylamine hydrochloride, water and sulfuric ether. The precipitate is dried in an oven at 50 °C [14].

C. Synthesis of γ,γ[1]-diargentum-2,2[1]-dipropargyl diester of azobenzene (III)

To an alcohol solution of 2,90 g (0,01 mol) of 2,2[1]-dipropargyl azobenzenediester was added an alcohol solution (calculated) of silver nitrate. A colored precipitate precipitates quickly, filtered, washed with alcohol and water. The product was dried at 64-70 °C in an oven. The output is quantitative.

Found, %: Ag 42,71

Calculated $C_{18}H_{12}Ag_2N_2O_2$,%: Ag 42,83

D. Synthesis of bis- [(2,2[1]-dipropynyloxy) azobenzene] -mercury (IV)

In a three-necked flask equipped with a reflux condenser, a stirrer and a dropping funnel, 10 g of mercury acetic acid, 22 g of potassium iodide, 50 ml of water were placed and heated to complete dissolution, after which 18 ml of 10 % sodium hydroxide solution were added. 2,90 g (0,01 mol) of 2,2[1]-dipropargyl azobenzenediester in 50 ml of methanol was added to the solution with continuous stirring over 30 minutes. A crystalline precipitate of the mercury derivative

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gradually precipitated. The precipitate was filtered off, washed with 50 ml of methanol and repeatedly with water. After drying, a light grayish powder with a melting point of 234-235 °C (decomp.) was obtained. The yield of product (IV) is 93% (of theoretical).

Found, %: Hg40,88

Calculated$C_{18}H_{12}Hg_2N_2O_2$, %: Hg41,05

E. Obtaining γ,γ^1-diiodine-2,2^1-dipropargyl diester of azobenzene (V)

A two-necked flask was equipped with a stirrer and a conventional glass funnel. 27,1 g (0,05 g / mol) of the obtained precipitate of α-β, β^1-diacetylenide of copper, 2,2^1-dipropargyl diester of azobenzene and 250 ml of dry ether are placed in the flask. To a suspension of diacetylenide (II) in ether, 25,4 g (0,05 g / mol) of metallic iodine are added in small portions with vigorous stirring. Each subsequent portion is added after bleaching the solution. The precipitate was filtered, the ether was distilled off, the crude product (V) was purified by recrystallization from methanol. Mpγ, γ^1-diiod-2,2^1-dipropargyl diesterofazobenzene (V) 197-198 ^{o}C, yield of the preparation (V) 93,6 % (of theoretical). [15]. Rf = 0,69;

Found, %: C 39,74; H 2,16; N 5,10; J 46,71;

Calculated$C_{18}H_{12}J_2N_2O_2$,%: C 39,85 H 2,21 N 5,16 J 46,86

F. Synthesisofγ,γ^1-dibromo-2,2^1-dipropargyl azobenzene diester

According to the method described above, 0,58 g of bromine in 5 ml of CCl_4 was added dropwise to 4,88 g of bis-[(2,2^1-dipropynyloxy) azobenzene] - mercury (IV) in 40 ml of carbon tetrachloride over 20 minutes. After completion of the reaction, the reaction mixture was filtered, the solvent was distilled off, and the residue was recrystallized from CCl_4. γ,γ^1-dibromo-2,2^1-dipropargyl diester of azobenzene is a grayish powder with a melting point of 67-68 °C. Yield – 84 % (of theoretical):

Found, %: Br 35,44

Calculated$C_{18}H_{12}Br_2N_2O_2$,%: Br 35,68

VI. CONCLUSION AND FUTURE WORK

Growth-stimulating activity of drugs I and V

To identify the growth-promoting activity of compounds of 2,2^1-dipropargyl ether of azobenzene (I), γ,γ^1- diiodine-2,2^1-dipropargyl ether of azobenzene (V), tests were carried out in the laboratory of the Institute of Plant Chemistry of the Academy of Sciences of the Republic of Uzbekistan under laboratory conditions, vegetable seeds, crops and cotton served as biotests.

The experiments used cucumbers of the Uzbekistan-740 variety, tomatoes of the Temp variety and medium-fiber cotton of the S-6524 variety. The preparations were dissolved in DMF and the pre-sowing seed lock method was used for 17-19 hours. The concentrations used were 0,1; 0,01; 0,001; 0,0001; 0,00001%.
The repetition of experiments is 4-fold. The counts were carried out by measuring the length of the stem and root of 10-day-old seedlings of cotton.

It was noted that all preparations tend to stimulate the growth of the root system of young seedlings, both vegetable crops and cotton.

Primary screening was carried out according to the methodology of Yu.V. Rakitin. This method allows you to quickly determine the degree of physiological activity of new chemical compounds, which is detected by stimulation or inhibition of germination of plant seeds, as well as by changing the length of the roots and the length of the stem part. The preparations were tested by the method of seed locking in solutions of various concentrations, followed by germination in Petri dishes.

Control seeds were soaked in distilled water.

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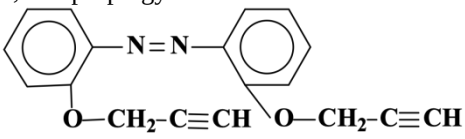
Each series of experiments is accompanied by control. In control variants, only a pure solvent is added to the nutrient medium.

The result of the experiments is recorded after 3,5,7 and 10 days after inoculation (tab. 5-7).

Table 5.The effect of the preparation (I) on the germination of seeds and the growth of seedlings of cotton cultivar «S-6524"

Experiences A drug	Concentration, %	Germination, %	Cotton	
			Root growth,%	Stem growth, %
Control - water	without	80,0	100,0	100,0
2,2[1]-dipropargyl ether of azobenzene 	0,1	82,6	112,7	106,8
	0,01	85,1	115,3	108,7
	0,001	87,3	123,4	115,5
	0,0001	84,2	116,7	108,6
	0,00001	80,0	121,4	113,4
«Rostlin» (famous)	0,75-1,0	80,0	103,1	102,4

Comparative tests also show that the test drug (I), i.e. the derivative of 2,2[1]-dipropargyl ether of azobenzene showed a higher growth-promoting activity at a concentration of 7,5 to 75,000 times lower than the Roslin drug currently used in many agricultural sectors of Uzbekistan.

The preparation (I) on cotton culture showed biological activity at a concentration of 0,00001% (75,000 times diluted) stimulated root growth of 121,4%, and the stem growth of 113,4 % was higher than the control and the well-known drug Roslin (concentration 0, 75-1,0).

The drug (I) on tomatoes, similar to previous cultures, showed a very high biological activity of 117,8% at a concentration of 0,00001% (even 75,000 times diluted). The drug (I) on the culture of cucumber also showed biological activity, at a concentration of 0,00001% (i.e., 75,000 times diluted).

It contributed to root growth by 126,3%, slightly lower than stem growth by 115,4%, but above the control and the well-known drug Roslin (concentration 0,75-1,0%).

Thus, the low-toxic (LD_{50}= 4730 ppm/cd) preparation (I) showed high biostimulating properties on the seeds of tomato, cucumbers and cotton at 0,00001% concentration.

Table 6. The effect of the drug (I) on the germination of seeds and the growth of seedlings of tomato varieties «Temp»

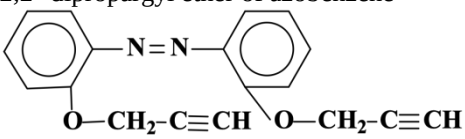
Experiences A drug	Concentration, %	Germination, %	Tomato	
			Root growth,%	Stem growth, %
Control - water	without	50,0	100,0	100,0
2,2[1]-dipropargyl ether of azobenzene 	0,1	50,0	106,0	118,5
	0,01	59,0	115,3	121,7
	0,001	58,1	140,4	125,8
	0,0001	49,7	113,5	107,7
	0,00001	52,3	117,8	106,3
«Rostlin» (famous)	0,75-1,0	52,1	101,7	100,2

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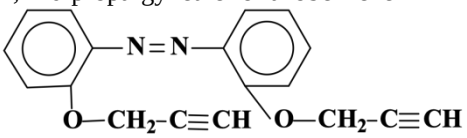
Table 7. The effect of the drug (I) on the germination of seeds and the growth of seedlings of cucumbers cultivar «Uzbekistan-740"

Experiences A drug	Concentration, %	Germination, %	Cucumber	
			Root growth,%	Stem growth, %
Control - water	without	100,0	100,0	100,0
2,2[1]-dipropargyl ether of azobenzene 	0,1	100,0	107,3	109,2
	0,01	100,0	108,6	111,3
	0,001	100,0	116,2	109,6
	0,0001	100,0	120,4	111,7
	0,00001	100,0	126,3	115,4
«Rostlin» (famous)	0,75-1,0	100,0	103,1	101,1

The results of determining the growth-promoting activity of compound γ, γ^1-diiodo-2,2[1]-dipropargyl ether of azobenzene (V) are presented in Tables 8,9,10.

The preparation (V) on cotton culture showed biological activity at a concentration of 0,00001% (75,000 times diluted), stimulated root growth of 108,7%, and stem growth of 116,2% above the control and the well-known drug Roslin (concentration 0,75-1,0).

Table 8. The effect of the preparation (V) on the germination of seeds and the growth of seedlings of cotton cultivar «S-6524"

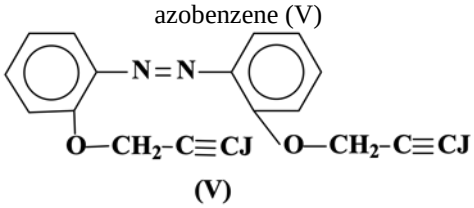
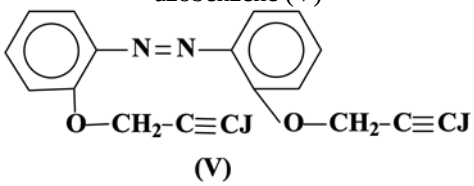
Experiences A drug	Concentration, %	Seed germination after 5 days, %	The growth of seedlings on the 10th day, in %	
			cotton	
			root	stem
Control - water	without	100,0	100,0	100,0
γ,γ^1- diiodine -2,2[1]-dipropargyl ether of azobenzene (V)  (V)	0,1	100,0	103,2	106,2
	0,01	100,0	109,7	113,4
	0,001	100,0	105,4	114,5
	0,0001	100,0	106,3	111,7
	0,00001	100,0	108,7	116,2
«Rostlin» (famous)	0,75-1,0	102,2	101,3	102,1

Table 9. The effect of the drug (V) on the germination of seeds and the growth of seedlings of tomato varieties «Temp"

Experiences A drug	Concentration, %	Seed germination after 5 days, %	The growth of seedlings on the 10th day, in %	
			tomato	
			root	stem
Control - water	without	50,0	100,0	100,0
γ,γ^1- diiodine -2,2[1]-dipropargyl ether of azobenzene (V)  (V)	0,1	53,0	108,7	107,4
	0,01	50,7	115,6	108,6
	0,001	45,0	110,3	131,3
	0,0001	61,3	105,6	114,4
	0,00001	55,0	108,7	105,8
«Rostlin» (famous)	0,75-1,0	51,4	101,3	100,5

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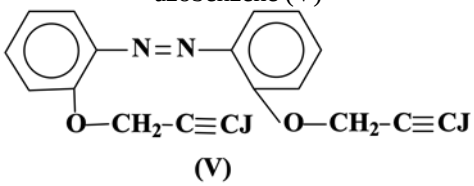
The preparation (V) on tomatoes, similarly to previous cultures, showed very high biological activity, where root growth was observed at 115,6%, and stem growth at 131,3% at a concentration of 0,001% (even 750-fold dilution).

Table 10. The effect of the drug (V) on the germination of seeds and the growth of seedlings of cucumbers varieties «Uzbekistan-740"

Experiences A drug	Concentration, %	Seed germination after 5 days, %	The growth of seedlings on the 10th day, in %	
			cucumbers	
			root	stem
Control - water	without	100,0	100,0	100,0
γ,γ[1]- diiodine -2,2[1]-dipropargyl ether of azobenzene (V)  (V)	0,1	100,0	106,3	105,6
	0,01	100,0	109,6	107,8
	0,001	100,0	107,7	119,2
	0,0001	100,0	108,8	114,2
	0,00001	100,0	103,4	113,6
«Rostlin» (famous)	0,75-1,0	100,0	101,7	98,7

The preparation (V) on the culture of cucumber also showed biological activity, at a concentration of 0,001% (i.e., 750 times diluted). It contributed to an increase in root growth by 109,6%, and the growth of the stem by 119,3% higher than the control and the well-known drug "Roslin" (concentration 0,75-1,0%).

In conclusion, both tested compounds (I) and preparation (V) synthesized by non-waste technology, even when diluted 75,000 times, are several 1,1-1,3 times superior in stimulating activity to the currently used known drug Roslin.

REFERENCES

[1] Makhsumov A.G., Baltaboev U.A., Maksumov D.N., Makhammad Z. N, N[1]-hexamethylene bis [(2,6-diiod-4-carboxy) phenyl carbamate], which has radiopaque activity / / Patent RUz., № 1800.

[2] Makhsumov A.G., Rakhimova I.V., KholmatovH.Kh., Shukurov A., Tillyaev K., Eganova EP 3-iodine-propin-2-yl- (ortho-bromobenzoate), which has antimicrobial properties // copyright certificate of the USSR, № 646583

[3] Rakhimova I.V., Makhsumov A.G., Shukurov A., Salikhodzhaev Z., Tillyaev K.1-iodine-3- (ortho-iodine-carboxyphenyl) -1-propine, which has an antimicrobial effect and the method for its preparation // copyright certificate of the USSR, № 756789.

[4] Makhsumov A.G., Madikhanov N., Muradkhodzhaev N.K. 4-[3-(2,4,6-triiodophenoxypropin-1)-3(2,4,6-triiodophenoxymethylene) pyrazole], which has radiopaque activity. // copyright certificate of the USSR, № 758722.

[5] Makhsumov A.G., Murojodzhaev N.K., Alimov R., Madikhonov N.γ-iodine-propargyl ether 2,4,6-triiodophenol exhibiting radiopaque properties // copyright certificate of the USSR, № 722068.

[6] Makhsumov A.G., Tadzhibaev U., Ruzybakiev R.M., Ismailov F.N., Khakimov Z.Z., Fazylov A.A. γ-iodine-propargyl ester of sorbic acid with antimicrobial and antifungal effects // copyright certificate of the USSR, № 722073.

[7] Makhsumov A.G., Kabulova M.A., Nasriddinov S.D., Belukha U.K., Sheina R.A., Ismailov F.N. 4-iodopyrazolyl-3-methylene- (o-fluorobenzoate), exhibiting bactericidal and fungistatic activity. // copyright certificate of the USSR, № 805610

[8] Makhsumov A.G., Kabulova M.A., Gigienova E.I., Kwon M.G., Ruzybakiev R.M., MazhidovaM.Kh. γ-iodofluorobenzoic acid, showing bactericidal activity. // copyright certificate of the USSR, № 805603.

[9] Makhsumov A.G., Ibrahimov I. The method of obtaining γ-iodine-propargyl ether. // copyright certificate of the USSR, № 230119.

[10] Makhsumov A.G., Sladkov A.M., Abidov U.A. The method of obtaining dipropargyl ether 4,4[1]-dioxazobenzene.// copyright certificate of the USSR, № 218160.

[11] Makhsumov A.G., Abidov U.A., Safaev A. A method for producing 2,4,6-triiodophenoxy N- (butyn-2) -amines // copyright certificate of the USSR, №. 252206.

[12] Makhsumov A.G., Ibrahimov I., Abidov W.A., Safaev A. Method for the production of γ-iodine-propargyl ether of naphthols. // copyright certificate of the USSR, № 225160.

[13] Makhsumov A.G., Mirzaboev E.A., Safaev A. A method for producing p-iodophenoxy N- (butyn-2) -decahydroquinoline // copyright certificate of the USSR, № 237139.

[14] Makhsumov A.G. "Synthesis and study of propargyl ethers and their derivatives" // Doctoral dissertation, Tashkent, Tashkent State University, 1971. P. 349-351.

[15] Makhsumov A.G. "Synthesis and study of propargyl ethers and their derivatives" // Doctoral dissertation, Tashkent, Tashkent State University, 1971. P. 354..