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SYNTHESIS AND PROPERTIES OF THE DIPROPARGYL DIETER DERIVATIVE 2-BROMINE-2-NITRO-PROPANDIOL-1,3 (BRONOPOL)

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ABSTRACT

The article is devoted to a comprehensive study of 2-bromo-2-nitropropanediol - 1,3 (bronopol) in order to expand the derivatives of bronopol as food products, preservatives, in all sectors of the national economy. The derivatives of dipropargyl diester 2 - bromo -, 2 - nitro propanediol - 1,3, γ,γ' -dicopper (2-bromo-,2-nitro-dipropargyl diester) propanediol-1,3 (II), γ,γ' -bis- (silver 2-bromo-, 2-nitro-dipropargyl ether) - propanediol-1,3 (III), mercury-bis- (propargyl ether) - 2 - bromo-, 2nitro-propanediol - 1, 3 (IV), $(\gamma, \gamma'$ -dibromo-dipropargyl diester) - 2-bromo-, 2-nitropropanediol-1,3 (VIII) were synthesized.. We also considered the preparation of γ , γ' -diiodo-dipropargyl diester - 2-bromo-, 2-nitropropanediol-1,3 (V), bis (4,4'-pyrazolyloxymethylene) - 2 - bromo -, 2 - nitro - propanediol - 1.3 (IX). The chemical properties of the 2-bromo-, 2-nitro-, dipropargyl diester of 1,3-propanediol-1,3 were studied, they learned that its $-C \equiv C - H$ group readily undergoes a substitution reaction with Cu_2Cl_2 , $AgNO_3$, $Hg(OCOCH_3)_2$ to produce acetylenides, and the obtained acetylenide can interact with iodine to produce new $R - (OCH_2 - C \equiv C - I)_2$ compounds. The article also describes the synthesis of 2-bromo, 2-nitro-1,3-propanediol bis (4,4'pyrazolyl-hydroxymethylene) and their interactions with hexamethylenediisocyanate, which has an exceptionally super-high reactivity, to produce tetrourea derivatives at temperature 50-55 °C.

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Introduction. The traditional method of synthesizing bronopol, mainly consists in first adding and then brominating. Non-polar toxic and flammable solvents such as ethyl acetate, carbon tetrachloride or dichloroethane must be used in the bromination reaction. The main salt formation of the nitro alcohol intermediate is not stable in the reaction, which is extremely disadvantageous for industrial production: therefore, it is necessary to improve its synthesis path by first brominating nitromethane with the formation of a stable intermediate bromonitromethane and then adding formaldehyde to the reaction to form bronopol.

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The currently intensively developing chemistry of acetylene derivatives of 1,3-propanediol (bronopol), pyrazoles, and urea compounds has attracted the attention of many researchers, both in Uzbekistan and abroad [1-10].

This is due, on the one hand, with the rich possibilities of various chemical transformations that acetylene esters, 2-bromo, 2-nitro-propanediol-1,3, as well as derivatives of pyrazole, urea groups in the molecules of one organic compound represent, and with on the other hand, with different properties valuable for the practical use of the most organic compounds with the above-linked groups.

2-Bromo-2-nitro-propanediol-1,3 or bronopol has a wide spectrum of antibacterial activity [11-12]. Bronopol is even used as a laboratory preservative for milk and as a biocide. Bronopol - found application in water treatment. At this end of use, large volumes of industrial water can be stored and recycled through large evaporative cooling towers, while smaller cooling towers can be used in hotels and public areas of the anti-water building used in air conditioning systems. Therefore, the selected bronopol biocide is effective for large dilutions with an inexpensive, non-volatile, non-aggressive and preferably non-foaming effect, and is also used in pool cleaning. In addition, bronopol is used as a biocide and preservative in technological fluids, paper mills, personal care products, metalworking fluids, fuel storage tanks oils, as well as in water-based paints, inks and adhesives [13-17].

Therefore, in order to expand the derivatives of bronopol as food products, preservatives, in almost all sectors, primarily in the food industries, cosmetics, chemical, pharmacy, medicine, and agriculture, derivatives of bronopol can be used. They are considered an important component to make food safe, leather, cosmetic, medicinal, pharmaceutical and many other sectors of the economy. Compared to other preservatives, bronopol has its advantages.

Results and discussion. The presence in the molecules of propanediol -1,3 bromine atoms, nitro-triple ($-C \equiv CH$) bonds, increases antifungal, biocidal, antiseptic, bactericidal, physiological, pharmacological, biological activity while reducing toxicity, and also exhibits antimicrobial, anticholesterol, anti-cancer and many other properties [18-24].

From the literature it is known that derivatives of dipropargyl ethers have various types of superbiological activity. For example, acetylene containing esters, nitro-bromine contained in one carbon, 1,3-propanedihydroxy possess growth-promoting, antimicrobial, antiseptic preservatives for dairy products, in the manufacture of cheese, which reduce bad cholesterol and blood sugar, as well as many other activities [25 -30].

In the literature [31-33], the synthesis of various *N*, *S* acetylene compounds with a terminal triple bond is given. However, information on the synthesis of glycerol diacetylene compounds in the 1,3-positions, and in the 2-position containing bromo and nitro groups and their derivatives of the type:

$$CH_2 - O - CH_2 - C \equiv CH$$

$$Br - C - NO_2$$

$$CH_2 - O - CH_2 - C \equiv CH$$

we have not found, these little-known compounds essentially represent a new kind of compounds whose properties have not been studied. In this regard, we obtained derivatives of the 1,3-dipropargyl diester of 2-bromo- 2-nitro-1,3-propanediol interacting with propargyl bromide in the presence of an organic solvent of 2-bromo-2-nitro- propanediol-1,3 according to the scheme:

$$CH_{2}OH \qquad CH_{2} - O - CH_{2} - C \equiv CH$$

$$Br - C - NO_{2} + 2XCH_{2} - C \equiv CH \longrightarrow Br - C - NO_{2} + 2HX$$

$$CH_{2}OH \qquad (I).$$

Where: X = Br, Cl, I.

The obtained derivatives of 2-bromo-2-nitro-dipropargyl diester propanediol-1,3 are highly soluble substances in many organic solvents and sparingly soluble in water.

The physico-chemical parameters of the derivative of 2-bromo-2-nitro-dipropargyl 1,3-propanediol (I) are shown in Table 1.

Table.1. Thysico-chemical	paran	ile ters	01 2	eromo 2 mao a					
	`.	${\mathbb C}$			Ele	mental a	analys	is, %	$M_{\scriptscriptstyle \mathcal{M}}$
Structural formula	t, %	melt.	$ m R_{ m f}$	Gross	Calcu	ılated	F		
Structural formata	Exit,	T. m		formula	N	Br	N	Br	
$CH_2 - O - CH_2 - C \equiv CH$									
Br - C - NO ₂	94,4	66-86	0,71	$C_9H_{10}NBrO_4$	5,07	28,95	4,97	28,79	275,9
$CH_2 - O - CH_2 - C \equiv CH$									

Table.1. Physico-chemical parameters of 2-bromo-2-nitro-dipropargyl diester-1,3-propanediol.

Purification of the 2-bromo-2-nitro-dipropargyl diester of 1,3-propanediol was carried out using preparative thin-layer chromatography on Al_2O_3 in the toluene system: hexane = 2:5. To prove the structure of 2-bromo-2-nitro-dipropargyl diester of propanediol-1,3, the method of IR- and UV-spectroscopy was used (Table 2).

Table.2. IR- and UV- spectra of compounds (I).

	•		IR-sp	ectra,	ν, cm ⁻¹	l	UV-spectra, nm
№ compound.	Structural formula	$- \jmath \equiv \jmath -$	<i>H</i> 2 ≡	$-0 - CH_2 -$	$C-NO_2$	C-Br	$-CH_2 - C \equiv CH$
Ι	$CH_2 - O - CH_2 - C \equiv CH$ \mid $Br - C - NO_2$ \mid $CH_2 - O - CH_2 - C \equiv CH$	21	3312	1236	1556-1377	664	241-323

The chemical properties of 2-bromo-2-nitro-dipropargyl diester of propanediol-1,3 (I) were studied. It was found that the $-C \equiv C - H$ group easily undergoes a substitution reaction with Cu_2Cl_2 , $AgNO_3$, $Hg(OCOCH_3)_2$ to produce acetylenide compounds (I) according to the following scheme:

Of interest was the interaction of copper diacetylinide 2-bromo-2-nitro-dipropargyl diester propanediol-1,3 with iodine, in order to obtain new $R - (OCH_2 - C \equiv C - I)_2$ little known compounds.

The reaction of compound II-IV with iodine was carried out in an environment of sulfuric ether at room temperature for 0.5-1 hours according to the following scheme:

$$CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot Cu$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot Cu$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot Ag$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot Ag$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

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$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

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$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

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$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

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$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

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$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

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$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C \equiv C \cdot I$$

$$| CH_{2} \cdot O \cdot CH_{2} \cdot C$$

Physico-chemical characteristics (V-VIII) of the compounds are given in table. 3.

Table 3. Physico-chemical characteristics (V-VIII).

1 abic 3.1	llysice		R _f	eteristics (V-VIII).			Elem	ental a	analys	sis %	
№ compound	Exit, %	T. melt. °C		Gross formula			Found				
V	94,7	116-117	0,74	$C_9H_8NI_2BrO_4$	527	2,65	48,09	15,14	2,49	47,87	15,10
VI	96,4	117-118	0,66	$C_9H_8NI_2BrO_4$	527	2,65	48,09	15,14	2,51	47,89	15,8
VII	82,3	116-118	0,72	$C_9H_8NI_2BrO_4$	527	2,65	48,09	15,14	2,47	48,01	15,06
VIII	7,67	39-40	0,61	$C_9H_8NBr_3O_4$	433,7	3,22	-	55,26	3,24	-	55,18

Buildings V-VIII are established by elemental analysis, IR-spectroscopy, and molecular weight (Tables 3 and 4).

	. Певресии от		· /	spectro 11 s	m-1							
	IR-spectra, v, sm ⁻¹											
№ compound	<i>-)</i> ≡ <i>)-</i>	<i>I −)</i> ≡	$\equiv C - Br$	$-0 - CH_2 -$	C-Br	$C-NO_2$	-CH ₂ -					
V	2214	2238	-	1114	660	1554-1376	2871					
VI	2217	2241	-	1113	663	1553-1376	2873					
VII	2213	2236	-	1112	664	1393-1374	2871					
VIII	2204	-	2224	1113	661	1554-1374	2872					

Table 4. IR spectra of compounds (V-VIII).

To clarify the reactivity of the $-C \equiv C$ – group, intermolecular cyclization reactions were carried out, where 1,2-pyrazole derivatives of compounds (I) were obtained. Reactions in organic synthesis proceeding with the participation of a triple bond allow developing simple methods for the preparation of valuable nitrogen-containing five-membered heterocyclic compounds from a biological, pharmacological point of view, such as 1,2-pyrazoles, pyrroles, thiophenes containing various hetero atoms.

Based on the foregoing, previously unknown compounds were synthesized containing various hetero atoms $-C \equiv C$, in connection with the fact on their basis various functional five-membered heterocycles with potentially very high pharmacological and biological activity can be obtained.

The synthesis of the derivative 1,2 - pyrazole (IX) was carried out by the interaction of the drug (I) with diazomethane according to the following reaction scheme:

ero atoms
$$-C \equiv C$$
 —, in connection with the fact on their basis various functional five-member procycles with potentially very high pharmacological and biological activity can be obtained. The synthesis of the derivative 1,2 - pyrazole (IX) was carried out by the interaction of g (I) with diazomethane according to the following reaction scheme:

$$CH_2 - O - CH_2 - C \equiv CH$$

$$CH_2 - O - CH_2 - C \equiv CH$$

$$CH_2 - O - CH_2$$

$$T = 175 \text{ y}$$

$$CH_2 - O - CH_2$$

$$T = 175 \text{ y}$$

4,4'- bis (pyrazolyl-hydroxymethylene) 2-bromo-2-nitro-1,3-propanediol - (IX) the structure of the obtained compound was confirmed by elemental analysis and IR-spectroscopy.

Physico-chemical parameters are given in table. 5.

Table 5. In the IR-spectra, characteristic absorption bands are observed in the region typical of the pyrazole ring in the region of 1612, 1122, 924 cm⁻¹.

		Ç	$ m R_{f}$			Elemental analysis, %		
Structural formula	it, %	melt.		Gross formula	M_m	Calculated	Found	
	Exit,	Т. ш		G1000 10111W1W	V	N	N	
$CH_2 - O - CH_2$ $Br - C - NO_2$ $CH_2 - O - CH_2$ H	91,2	109-110	0,64	$C_{11}H_{12}N_6BrO_4$	371,9	22,58	22,47	

The aromaticity of the cycle is preserved, but the ability to electrophilic substitution at carbon atoms decreases sharply. At the same time, the presence of undivided pairs in heteroatoms increases the probability of an electrophilic attack on nitrogen, contributing to tautomeric transformations and the formation of quaternary salts.

The mutual influence of the lone electron pairs of heteroatoms and the π -electron sextet of the ring is even more important in determining the inclined ability of these heterocycles, 1,2-pyrazoles exhibit weak acidic properties.

Thus, the reflected achievements and modern level of work in the field of chemistry of derivatives of heterocyclic systems convincingly show and prove that in recent years, methods for the synthesis of heterocyclic esters of 1,2-pyrazole or 1,2-pyrazoline have been actively developed. The rings of 1,2-pyrazole (or 1,2-pyrazoline) are extremely stable, and many of its derivatives can be distilled without decomposition and melting. Data of the IR-spectra of compounds (IX) are shown in table 6.

Table 6. IR-spectra of compounds (IX).

	P	1 compounds	().		
			IR-spectra, v, c	m ⁻¹	
№ compound	C – Br	-N - H	$-0-CH_2-$	H	$C-NO_2$
IX	664	3412	1228	1612, 1118, 925	1557-1369

Thus, the introduction of a triple bond led to the appearance of a gamma of a variety of pharmacological, physiological, and biological activities, as well as the ability to inhibit metal corrosion, the formation of complex compounds, the formation of polymers, and much more.

The interaction of compound (IX) with hexamethylene diisocyanate (X).

Diisocyanates are among the compounds having an extremely super-high reactivity. Secondary amines with heterocyclic groups containing *N-H* bonds have the highest reactivity with respect to the isocyanate [14–16].

We were the first to obtain derivatives of the tetraurea of the interaction of hexamethylenediisocyanate with compound (IX) at a temperature of 50-55 °C according to the scheme:

$$CH_{2} - O - CH_{2}$$

$$Br - C - NO_{2}$$

$$CH_{2} - O - CH_{2}$$

$$H$$

$$CH_{2} - O - CH_{2}$$

$$H$$

$$H$$

$$IX$$

$$CH_{2} - O - CH_{2}$$

$$H$$

$$H$$

$$IX$$

$$CH_{2} - O - CH_{2}$$

$$H$$

$$H$$

$$H$$

$$GH_{2} - O - CH_{2}$$

$$H$$

$$H$$

$$GH_{2} - O - CH_{2}$$

$$H$$

$$GH_{2} - O - CH_{2}$$

$$GH_{3} - O - CH_{2}$$

$$GH_{4} - O - C$$

The synthesis was carried out in dimethylformamide at a temperature of the reaction medium of 50-52 ° C for 3.0-3.5 hours. It should be noted that the new environmentally friendly tetraurea derivatives are obtained in the form of a snow-white powdery product (X), with fairly high yields, without waste.

Physico-chemical characteristics of compounds (X) are given in table. 7.

Table 7. Physico-chemical para	amete	rs of t	the dr	ug (X).			
	%	lt. °C	4		М	Elemental a	
Structural formula	Exit,	T.melt.	$ m R_{ m f}$	Gross formula	$M_{\scriptscriptstyle M}$	Calculated	Found
	田	T.				N	N
$CH_2 - O - CH_2$ $Br - C - NO_2$ $CH_2 - O - CH_2$ $CH_2 - O - CH_2$ $CH_2 - O - CH_2$ $CH_2 - N$ $CH_2 - N$ $CH_2 - N$	7,16	147-148	0,59	$C_{38}H_{52}Br_2N_{14}O_{12}$	1055,8	18,56	18,49

Compounds were purified by recrystallization from ethyl alcohol. The identity of compounds (X) was established by TLC on Silitol plates.

The following systems were used as eluents:

System I: $CHCl_3 : CH_3OH : HCOOH = 9 : 1 : 0,3$;

System II: $HCOOH : CH_3COCH_3 : CCl_4 = 0.7 : 6.0 : 0.5$;

Structure {bis - (N, N '- hexamethylene) $[\alpha, \alpha', \alpha, \alpha'$ - tetra-hydroxymethylene - 4.4', 4.4' tetrapyrazolilo - 1.1', 1.1' - tetra urea] - bis - $(\beta$ - bromo -, β - nitro - propane) (X) is confirmed by the data of elemental analysis, as well as IR- and PMR- spectroscopy. In the IR-spectrum of compounds (X), there is a wide absorption band in the region of 1716 cm⁻¹ characteristic of the -C = 0 group, and the

absorption band in the region of 1626 cm⁻¹ corresponds to the absorption of N-C-N- bonds, a strong absorption band in the region of 3307 cm $^{-1}$ is characteristic of N-H groups (Table 8).

Table 8. IR- and PMR-spectra of compounds (X)

			IR-s	pectra, v, cr	/				PMR-sp	oectra, δ	, ppm.
№ compound	H - N -	$-0 - CH_2$	H	N - C - N - O H	$-CH_2$	$(-CH_2-)_6$	$C-NO_2$	C-Br	$1 - 6 - CH_2 - CH_2 -$	$2-5-CH_2-$	$-N-CH_2-$
X	3307	1233	1613, 1124, 925	1626	2870	766-731	1556- 1368	666	2,81	1,28-1,06	3,29

Experimental part.

1. Synthesis of 2-bromo- 2-nitro-dipropargyl diester of 1,3-propanediol: (I) In a flask equipped with a reflux condenser 20.0 g (0.1 mol) of 2-bromo, 2-nitro-propanediol-1,3, 23.8 g/mol of freshly brewed propargyl bromide, 30 g of calcined potassium carbonate and 350 ml of anhydrous acetone as solvent was placed, the reaction mixture was heated in a water bath at 90 ° C for 8 hours and 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. Obtained by the specified method, 2-bromo-, 2-nitro-dipropargyl diester of propanediol-1,3 - colorless with T. melting. = 56 - 57 °C. The yield of product (I) is 82.3% (of theoretical). $R_f = 0.71$;

Found,%: C 37.97; H 3.47; Br 28.79; N, 4.97; Calculated for $C_9H_{10}BrNO_4$, % :, C 39.14; H 3.62; Br 28.96; N, 5.07;

2. Synthesis of γ, γ' -diphene (2-bromo-2-nitro-dipropargyl diester) propanediol-1,3 (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 dilute alcohol solution of 20.0 g of 2-bromo, 2-nitro-dipropargyl diester-propanediol-1,3. The resulting bright yellow precipitate was filtered off and washed with a weak solution of hydroxylamine hydrochloride, water and sulfuric ether. The precipitate is dried in an oven at $50 \,^{\circ}$ C [].

3. Synthesis of γ , γ' -bis- (silver 2-bromo-, 2-nitro-dipropargyl ether) - propanediol-1,3 (III).

To an alcohol solution of 2.0 g (0.01 mol) of 2-bromo-, 2-nitro-dipropargyl diester - propanediol-1,3 was added an alcoholic solution (calculated) of silver nitrate. Quickly precipitated slightly colored precipitate was filtered, washed with alcohol and water. The product was dried at 64 - 70 °C in an oven. Yield (III) quantitative:

Found,%: Ag 43.91; Calculated for $C_9H_8Ag_2NBrO_4$, %: Ag 44.06;

4. Synthesis of mercury-bis- (propargyl ether) - 2 - bromo- 2-nitro-propanediol - 1.3 (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. 2.0~g (0.01~mol) of 2-bromo- 2-nitro-dipropargyl diester-propanediol -1.3 in 50~ml of methanol was added to the solution with continuous stirring over 30~minutes. A crystalline precipitate of the mercury derivative gradually precipitated. The precipitate was filtered off, washed with 50~ml of methanol and repeatedly with water. After drying, a light grayish powder with T. melting. = $194~-195~^{\circ}$ C (decomp.). The yield of product (IV) is 88.6% (of theoretical).

Found,%: Hg 42.13; Calculated for $C_9H_8HgNBrO_4$,%: Hg 42.27;

5. Preparation of γ , γ' -diiod- dipropargyl diester - 2-bromo- 2-nitropropanediol-1,3 (V).

A two-necked flask was equipped with a stirrer and a conventional glass funnel. 40.0 g (0.1 mol) are placed in the flask above the obtained precipitate γ , γ' -diphene – (2-bromo-2-nitro dipropargyl diester) - propanediol – 1,3 and 250 ml of dry diethyl ether. 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. The yield of the product (γ , γ' -diiod --dipropargyl diether) is 2-bromo-, 2-nitropropanediol-1,3 (V) - 94.7% (of theoretical). $R_f = 0.71$;

Found,%: *C* 20.33; *H* 1.44; *Br* 15.03; *N*, 2.44; *I* 47.93; Calculated for *C*₉*H*₈*I*₂*BrNO*₄,%: *C* 20.46; *H* 1.51; *Br* 15.14; *N* 2.65; *I* 48.09;

6. Synthesis of γ , γ' -dibromo-(dipropargyl diester) - 2-bromo-2-nitropropanediol-1,3 (VIII).

According to the above procedure, 4.76 g (0.01 g / mol) of mercury - bis - (propargyl ether) - 2 - bromo -2-nitro - propanediol - 1,3 (IV) in 40 ml of carbon tetrachloride was added dropwise 0.58 g of bromine in 5 ml of CCl_4 for 20 minutes. After completion of the reaction, the reaction mixture was filtered, the solvent was distilled off, the residue was recrystallized from CCl_4 . γ , γ' -dibromo-dipropargyl diester - 2-bromo-, 2-nitropropanediol-1,3 - grayish-colored powder with a T melting. = 39 - 40 °C. The product yield of γ , γ' -dibromo-dipropargyl diester - 2-bromo-2-nitropropanediol-1,3 (VIII) - 82.4% (of theoretical). $R_f = 0.70$;

Found,%: Br 55.11; Calculated for $C_9H_8Br_3NO_4$, %: Br 55.28;

7. Preparation of bis- (4,4'-pyrazolyloxymethylene) - 2 - bromo - 2 - nitro - propanediol - 1,3 (IX).

20.0~g~(0.1~mol) of dipropargyl diester - 2 - bromo -2 - nitro - propanediol - 1.3, previously dissolved in 300~ml of diethyl ether, are added to a conical flat-bottomed flask, then 2~g~(0.05~mol) of a freshly prepared solution of diazomethane in 30~ml of diethyl ether are gradually poured in small portions. The reaction mixture is placed in a dark, dark place at a temperature of 17 - 18~c. The mixture is left for 8~to~9~days, and as the yellow color of the diazomethane solution disappears, its new portions

are added until a triple bond with the ammonia solution of copper monochloride is negative, then the solvent is evaporated, the product is purified by TLC on alumina in the benzene system: hexane = 1:3; the target product is a crystalline substance with a melting point of 109-110° C. R_f = 0.64;

Found,%: *C 35.51; H 3.16; Br 21.36; N, 22.59;*

Calculated for $C_{11}H_{12}N_6BrO_4$, %: C 35.49; H 3.22; Br 21.48; N, 22.58;

8. Preparation of bis - (N, N '- hexamethylene) [α , α ', α , α ' - tetra-hydroxymethylene - 4.4', 4.4' - tetrapyrazolilo - 1.1', 1.1' - tetroureas] - bis - (β - bromo - β - nitro-propane) (X).

In a three-necked flask equipped with a reflux condenser, a thermometer, and a stirrer,7.44 g (0.02 mol) of bis - (4.4' - pyrazolyl-hydroxymethylene) - β - bromo- β - nitro - α , α' - propanediol are placed then 25 ml of triethylamine, 40 ml of DMF are added at a temperature of 40 - 47 ° C, while stirring, 1.7 g (0.011 mol) of hexamethylene diisocyanate dissolved in 8 ml of DMF are added dropwise. The reaction mixture is stirred for 3.0 hours at a temperature of the reaction mixture of 49 - 53 ° C. After the time, the contents of the flask are transferred to a glass, water is added. The precipitate was washed with TLC. After drying, a slightly colored powder is obtained with a yield (X) of 91.7% (of theoretical). T.melting = 147 - 148 ° C; R_t = 0.59;

Found,%: C 43.06; H 4.79; N, 18.49; Br 15.02;

Calculated for $C_{38}H_{52}Br_2N_{14}O_{12}$, % : C 43.19; H 4.92; N, 18.56; Br 15.13;

Conclusions. The currently intensively developing chemistry of acetylene derivatives of pyrazolyl urea compounds has attracted the attention of many researchers, both in the Republic of Uzbekistan and around the world [14-16].

This is connected, on the one hand, with the rich possibilities of various chemical transformations that acetylene, urea, and pyrazole groups provide in the molecules of organic compounds, and, on the other hand, with the properties of the most organic compounds with the above-mentioned groups that are valuable for practical use.

There are many examples where the introduction of a triple bond led to the appearance of a gamma of various pharmacological, physiological and biological activities, as well as the ability to inhibit metal corrosion to form complex compounds, form monomers, polymers, and much more.

The further development of acetylene 1,3-propanediol, and their derivatives, is an extremely urgent task of the 21st century.

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