Global Journal of Science Frontier Research: B Chemistry
Volume 20 Issue 2 Version 1.0 Year 2020
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Synthesis and Research of New Compounds of Guanidine on the Basis of α-Chlorether and Chlorazone

By S. R. Hajiyeva, G. I. Bayramov, F. E. Huseynov, T. I. Aliyeva, H. L. Rafiyeva, Z. T. Valiyeva, A. A. Samadova & N. M. Jafarova

Baku State University

Abstract- The reactions of chlorazone with α-chloroethyl esters of n-$C_8H_{17}OH$, n-$C_{10}H_{21}OH$, n-$C_{12}H_{25}OH$, CH_3-CH=CCl-CH_2OH alcohols for the first time were carried out, and chlorazone esters containing two $ROCH_2$ groups of these esters were obtained. The reactions of N_1-alkoxymethyl-N_3-alkoxy-methylguanidine compounds with these chlorazone esters were carried out and 4 new guanidine derivatives (conventionally designated as I-IV) were synthesized, not known in the literature. Studies have been conducted to establish corrosion inhibitory efficiency for each of the newly synthesized compounds of guanidine I-IV in a very strong aggressive environment created in the laboratory. It was established that the inhibitory effectiveness of these compounds in concentrations of 1.0; 2.0; 2.5 mg/l is 99.97-100%. A comparative study of the effective inhibitory properties of the new synthesized guanidine compounds for corrosion protection of steel "St.3" was carried out. Studies have shown that each of the new I-IV compounds of guanidine in terms of environmental safety, economic and environmental efficiency is 5-10 times higher than the inhibitors currently used to protect from corrosion steel processing equipment operating in aggressive environments.

Keywords: guanidine, α- chloroesters, alcohol, chlorazone, synthesis, research, ecological, inhibitor, corrosion, aggressive environment, oil and gas, petrochemical industry, steel, technological equipment.

GJSFR-B Classification: FOR Code: 250399

Strictly as per the compliance and regulations of:

Synthesis and Research of New Compounds of Guanidine on the Basis of α-Chlorether and Chlorazone

S. R. Hajiyeva [α], G. I. Bayramov [σ], F. E. Huseynov [ρ], T. I. Aliyeva [Ω], H. L. Rafiyeva [¥], Z. T. Valiyeva [§], A. A. Samadova [χ] & N. M. Jafarova [ν]

Abstract- The reactions of chlorazone with α-chloroethyl esters of n-$C_8H_{17}OH$, n-$C_{10}H_{21}OH$, n-$C_{12}H_{25}OH$, CH_3-CH=CCl-CH_2OH alcohols for the first time were carried out, and chlorazone esters containing two $ROCH_2$ groups of these esters were obtained. The reactions of N_1-alkoxymethyl-N_3-alkoxy-methylguanidine compounds with these chlorazone esters were carried out and 4 new guanidine derivatives (conventionally designated as I-IV) were synthesized, not known in the literature. Studies have been conducted to establish corrosion inhibitory efficiency for each of the newly synthesized compounds of guanidine I-IV in a very strong aggressive environment created in the laboratory. It was established that the inhibitory effectiveness of these compounds in concentrations of 1.0; 2.0; 2.5 mg/l is 99.97-100%. A comparative study of the effective inhibitory properties of the new synthesized guanidine compounds for corrosion protection of steel "St.3" was carried out. Studies have shown that each of the new I-IV compounds of guanidine in terms of environmental safety, economic and environmental efficiency is 5-10 times higher than the inhibitors currently used to protect from corrosion steel processing equipment operating in aggressive environments.

Keywords: guanidine, α- chloroesters, alcohol, chlorazone, synthesis, research, ecological, inhibitor, corrosion, aggressive environment, oil and gas, petrochemical industry, steel, technological equipment.

I. Introduction

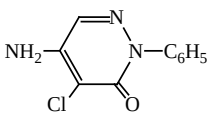
Based on the technical data and the results of our previous studies, it was established that organic compounds containing nitrogen atoms, - CH_2 -, $ROCH_2$ groups and other functional groups, many double bonds possess highly effective inhibitory properties[1].

Therefore, the synthesis and study of this type of compound is considered as one of the most relevant topics in organic chemistry, petrochemistry and ecological chemistry.

In this direction, initially with the use of n-$C_8H_{17}OH$, n-$C_{10}H_{21}OH$, n-$C_{12}H_{25}OH$ alcohols, considered to be a cheap raw material and CH_3-CH=CCl-CH_2OH alcohol from the production of synthetic rubber CH_3-CH=CCl-CH_2Cl (1,2-dixlorbuten-2), as well as CH_2O (paraform), α-chloro esters of these alcohols were synthesized.

We give a brief overview of the raw materials (chemical compounds) used for the synthesis of new guanidine compounds.

1. n-$C_8H_{17}OH$(normaloctylalcohol)octanol-1, belongs to the class of high molecular weight alcohols, has a floral-citrus aroma (orange, etc.), is poorly soluble in water, well soluble in ethanol, is in a liquid state of aggregation, molecular weight 130.23 g / mol;ρ_4^{20} = 0.824 g / cm^3, t_{boil} = 195°C, rat dose "LD_{50}"> 5 g / kg, MPC = 10 mg / m^3.
2. n - $C_{10}H_{21}OH$ (normal decyl alcohol) decanol-1, belongs to the class of fatty alcohols, molecular weight 156.27; colorless liquid, it has the aroma of roses, ρ_4^{20} = 0.8297 g / cm^3, n_D^{20} = 1.4372, t_{boil} = 229°C, it is well soluble in ethanol.
3. n-$C_{12}H_{25}OH$ (normal dodecyl alcohol) CH_3 $(CH_2)_{10}CH_2OH$ or $C_{12}H_{25}OH$, ρ_4^{20}= 0.8201 g / cm^3, n_D^{20} = 1.4455, molar mass 186.34 g / mol, colorless, low-viscosity liquid with a floral-citrus aroma (lemon, orange, tangerine), t_{boil} = 259 ° C.
4. CompoundCH_3-CH=CCl-CH_2Cl(1,2-dichlorobutene-2)(low molecular weight formaldehyde polymer, mixture of polyoxymethylene glycol), general formula [-CH_2O-] x, HO - [- CH_2O] xH x = 8 colorless or in the form of white crystals substance, mp = 120-170 ° C.
5. CH_3-CH=CCl-CH_2OH (2-chlorobutene-2-ol-1) alcohol, ρ_4^{20}=1,1060;n_D^{20}=1,4712,t_{boil}= 49-50°C / 50 mm Hg, a liquid with a pungent unpleasant odor, is well soluble in water, ethyl alcohol, benzene and toluene.
6. (CH_2O) n (paraform compound) low molecular weight formaldehyde polymer, mixture of polyoxymethylene glycol), general formula [-CH_2O-] x, HO - [- CH_2O] xH x = 8 ÷ 100; colorless or in the form of white crystals substance, mp = 120-170° C.



Author α σ ρ Ω ¥ § χ ν: Baku State University, AZ 1148 Baku, Z.Khalilovst. e-mail: tarana_chem@mail.ru

7. Chlorazone(1-phenyl-4-amino-5chloropyridazone-6) $C_{10}H_8ClN_3O$, mp = 202 ° C, a substance in the form of white crystals, is dissolved in CH_3OH, a low-toxic substance (rat dose "LD_{50}" - 3600 mg / l), standard «СЭВ1052-78».

The raw materials mentioned above were used after determining their d_4^{20}, n_d^{20} constants and boiling points.

α-Chloroctoxymethyl($C_8H_{17}OCH_2Cl$), α-chlordecoxymethyl ($C_{10}H_{21}OCH_2Cl$), α-chlordodecoxymethyl ($C_{12}H_{25}OCH_2Cl$), α-chlor-2-chlor-5-oxohexane-2 (CH_3-CH=CCl-CH_2O CH_2Cl) esters and obtained on the base of this esters $ROCH_2$-NH-C-NH-CH_2OR compounds and (N_1',N_1'-dialkoxymethylchlororazone) esters [2-4] were synthesized according to the methods described in the literature.

The composition and structure of each of the aforementioned α-chloroesters, N_1',N_1'-dialkoxymethyl-chlororazone, and N_1-alkoxymethyl-N_3-alkoxymethylguanide compounds synthesized in several stages were determined by known methods.

The IR-spectra of the compounds obtained by the reaction of guanidine and α-chloroalkoxymethyl esters in step III are shown, for example, in Fig. 1.

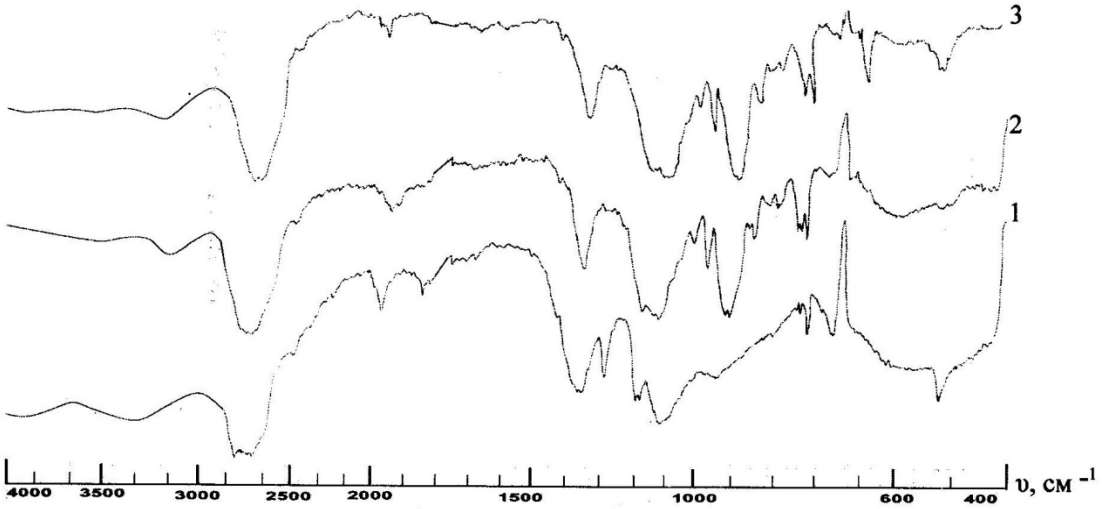


Fig. 1: 1- IR-spectra of the compound of raw materials of guanidine, 2 - compound of N_1-octoxymethyl-N_3-octoxymethylguanidine, 3 - compound of N_1- (2-chlor-5-oxohexene-2) -N_3- (2chlor-5-oxohexene-2) guanidine

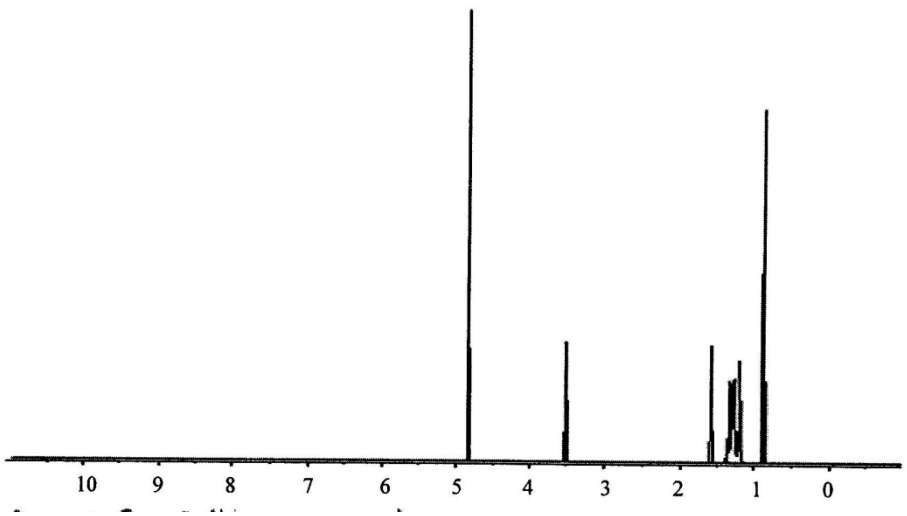


Fig. 2: NMR H spectrum of the compound N_1-octoxymethyl-N_3octoxymethylguanidine

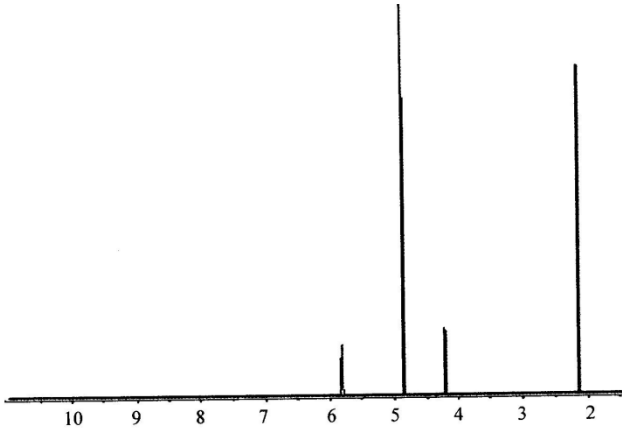
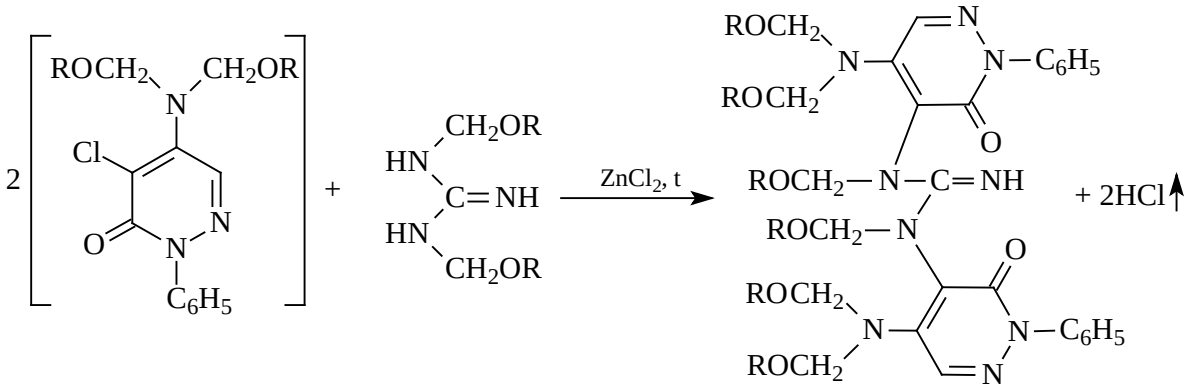


Fig. 3: NMR H spectrum of the compound N_1- (2-chlor-5-oxohexene-2) -N_3- (2 chlor-5-oxohexene-2) guanidine

At the fourth stage, the reactionwith N_1-alkoxymethyl-N_3-alkoxymethylguanidone organic compounds and new derivatives of guanidine were synthesized (compounds I – IV). The synthesis was carried out by a known method in the literature [3]

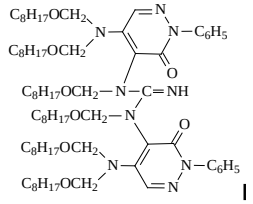
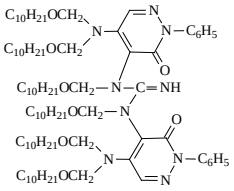
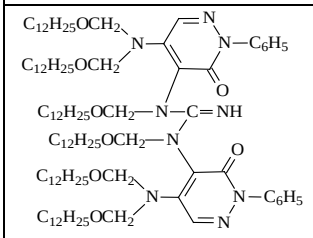
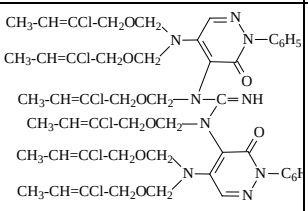


where; R= $–C_8H_{17}$ (I); $–C_{10}H_{21}$ (II); $–C_{12}H_{25}$ (III); $–CH_2–CH=CCl–CH_3$ (IV).

The structure of new synthesized organic compounds I–IV was determined by registering their IR-, mass- and NMR spectra. Information on this is presented in the experimental section.

Percentage yield, physico-chemical constants and elemental analysis of new guanidine derivatives (compounds I - IV) are shown in Table 1.

Table 1: Percentage yield, physico-chemical constants and elemental analysis of synthesized new I - IV compounds of guanidine based on α-chloroesters and chlorazone

Chemical formula and Conditional Compound Number	Yield, %	T_{boil}, °C (mm Hg)	d_4^{20}	n_D^{20}	MR_D found / calculated	Gross formula, mol. weight	Elemental analysis, % Calculated / Found			
							C	H	N	Cl
 I	98,75	320-321 (3)	1,1580	1,6115	384,29 / 384,17	$C_{75}H_{127}N_9O_8$ 1281	70,25 / 69,87	9,91 / 9,67	9,84 / 9,58	-
 II	98,65	335-336 (3)	1,1601	1,6225	410,16 / 439,93	$C_{87}H_{151}N_9O_8$ 1449	72,05 / 71,92	10,42 / 10,21	8,69 / 6,54	–
 III	98,47	350-351 (3)	1,1661	1,6315	494,92 / 494,70	$C_{99}H_{175}N_9O_8$ 1617	73,47 / 73,16	14,73 / 14,51	7,79 / 7,54	–
 IV	96,24	365-366 (3)	1,4108	1,6615	298,84 / 298,63	$C_{51}H_{61}N_9O_8C_6$ 1140	53,68 / 53,42	5,32 / 5,04	11,05 / 10,8	18,68 / 18,2

II. Experimental Part

a) Synthesis of N_1-(octoxymethyl-N', N'-dioctoxymethyl) -N_3- (octoxymethyl-N', N'-dioctoxymethyl) guanidine ((compound I).

In a synthesis flask, 2 g of $ZnCl_2$, (0.01 g-mol) of N_1-octoxymethyl-N_3'-octoxymethylguanidine are placed and 100 ml of ethyl alcohol is added, stirring heated to 70°C. Then (0.02 g-mol) of N_1',N_1'-dioctoxymethyl chlorononе ester is gradually added to the mixture. Stirring is continued for 6 hours at the alcohol condensation temperature. After that, at room temperature, 100 ml of 10% NaOH solution is added to the reaction flask, stirred for 0.5 h, 200 ml of distilled water are added. The organic layer is extracted with diethyl ether, and after the distillation of the ether, it is dried over $CaCl_2$. The residue is distilled in a vacuum unit with the release of synthesis of N_1-(octoxymethyl-N_1',N_1'-dioctoxymethylazone) -N_3-(octoxymethyl- N_1',N_1'-dioctoxymethylazone) guanidine (I), which is a yellow, viscous liquid with a strong specific odor.

Similarly were synthesized N_1-(decoxymethyl-N_1',N_1'-dideoxymethylazone) -N_3- (decoxymethyl-N_1', N_1'-dideoxymethylazone) guanidine (compound II), N1-(dodeoxymethyl-N_1',N_1'-dimethode)–N_3-(dodeoxymethyl-N_1',N_1'-didodecoxymethylazone) guanidine (compound III) and N_1-[(2-chlor-5-oxohexene-2)-N_1',N_1'-di(2-chlor-5-oxohexene-2)azone]-N_3-[(2-chlor-5-oxohexene-2-) N_1', N_1'-di (2-chlor-5-oxohexene-2) azone] guanidine (compound IV).

The compositions and structures of the synthesized compounds I- IV were established on the basis of the data of elemental analysis, IR-, mass-, and NMR spectra.

In the mass spectra of compounds I-IV, it was determined that their molecular masses correspond to molecular ions 1449 m/e, 1617 m/e and 1140 m/e.

In IR-spectrum of comp. IV, the ether group C-O-C 1050, 1080 cm^{-1} appears as an intense band; bond C-N 1310-1350 cm^{-1}; CH_2 group 2950 cm^{-1}; CH_3 group 1380, 1400, 1460, 2990, 3030 cm^{-1}; NH group 2910, 3113, 3340, 3360, 3400, 3450 cm^{-1}; belonging to the

group of azone C = C bond 1680 cm^{-1}; in the benzene ring C = C bond 1440-1465,1500-1510, 1590-1600 cm^{-1};C_6H_5 group 700-780 cm^{-1},C – Cl bond 680 cm^{-1}.

In the NMR spectra of compounds I- IV singlets at 3.94–4.40 ppm.and 4.75-5.55 ppm correspond to the protons of the methylene groups of the fragments > N–CH_2 – and > N–CH_2 – O.

The NMR spectra of the I- IV compounds contain signals of the methylene groups of the ring (wide intense multiplet in the region of 1.41-1.82 ppm), the methyl group (a triplet of 0.8-1.21 ppm), the group - CH_2O - (doublet 2.05 ppm). In the range of 6-8 ppm two doublets correspond to signals of two non-equivalent m-protons of the benzene ring of the I- IV compounds and not changing their position when strongly diluted indicates a strong C = N-hydrogen bond also (2H, -C-N-CH_2O-); groups 3,45-3,47d.; 1,20-1,40 d., 1,50-1,56 d., which confirms the structure of the synthesized I- IV compounds.

Figures 4.5 show the NMR spectra of I- IV compounds

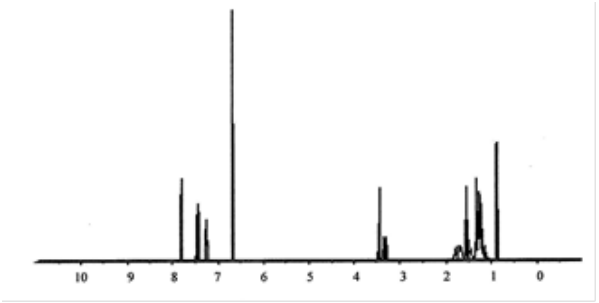


Fig 4: NMR spectrum H of comp. I

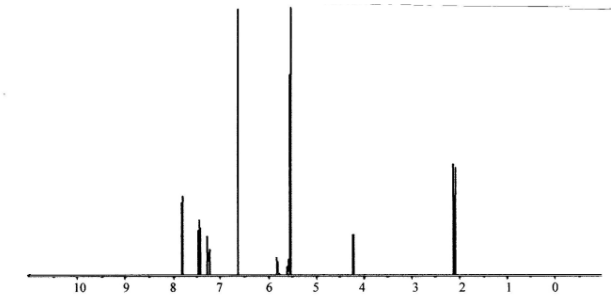


Fig 5: NMR spectrum H of comp. IV

III. Discussion of the Results

To determine the inhibitory effectiveness of the synthesized new derivatives of guanidine (new compounds I - IV), studies were conducted in the literature [2-4]. In order to determine the inhibitory effectiveness of the new compounds I - IV, very corrosive media were created under laboratory conditions[3% NaCl +oil (1:10) + H_2S 500 mq/l; 0,3N HCl + petrol (1:7)+ H_2S 1000 mq/l].

Indicators of the inhibitory effectiveness of these compounds in the determination period are shown in table 2.

Table 2: The results of the study of the inhibitory efficiency of the synthesized new guanidine derivatives (new compounds I – IV)

Conventional number of the compound	Inhibitor concentration, mg / l	3% NaCl+oil (10:1) H_2S 500 mg/l		0.3 N HCl + gasoline (1:7) H_2S 1000 mg/l	
		Corrosion rate, g/cm^2·hour	Effectiveness of the inhibitor,%	Corrosion rate, g/cm^2·hour	Effectiveness of the inhibitor,%
Without inhibitor	–	2.56	–	3.65	–
V	1,0 2,0 2,5	0.0006 0.0003 0.0001	99.97 99.98 100	0.0061 0.0042 0.0001	99.83 99.89 100
VI	1,0 2,0 2,5	0.0003 0.0002 -	99.98 99.99 100	0.0042 0.0015 –	99.89 99.95 100
VII	1,0 2,0 2,5	0.0003 –	99.98 100	0.002 0.0008 –	99.94 99.98 100
VIII	1,0 2,0 2,5	–	100	0.0008 - –	99.98 100
A [4]	200		98.5		98

As can be seen from table 2, each of the synthesized new derivatives I - IV at a concentration of 1; 2; 2.5 mg/l possesses 100% inhibitory activity and exceeds in its qualities the compound known in the literature [4], which obtained the author's certificate and was conditionally called by us compound A, even at its high concentration. And also in the literature [13] was named IFKHAN-92, a high-temperature (up to 140 ^{0}C) corrosion inhibitor for steel in H_2SO_4 solutions, providing an efficiency of Z = 99%, with a content of less than 1% of the mass.

According to [7], the effectiveness of inhibitors of the "AMDOP-IR-7" type increases with increasing concentration of hydrogen sulfide and deoxygenation of the medium. In some cases, the function Z = f ($C_{hydrogen\ sulfide}$) passes through a maximum. This again was confirmed by studies conducted by us.

In order to elucidate the mechanism of the protective action and predict the effectiveness of inhibitors in many of the research studies developed, it was proved that molecules with only one functional group exhibit weak inhibitory properties, if in them there are two such groups, the inhibitory effect is sharply enhanced [2-4; 5-11].

Based on the requirements presented in the literature [12], multifunctional reagents, inhibitors must meet environmental safety. Based on the above, we have synthesized new organic nitrogen-containing compounds that meet all these requirements. It appears that the presence of double bonds, multifunctional groups —CH_2OR and nitrogen atoms in the composition of new compounds I - IV and an increase in the electron density contribute to the formation of a complex between the inhibitor molecule and the metal on the steel surface, creating a high adsorption and the steel surface becomes passive to corrosion.

Based on the conducted research, it can be considered that the synthesized new guanidine derivatives (new compounds I - IV) can be used as inhibitors in the oil-gas producing, oil refining and petrochemical industries to protect steel technological equipment from corrosion and can guarantee high both economic and environmental efficiency.

As can be seen from the compositions and structures of new guanidine derivatives (new compounds I - IV), these compounds can find their use as additives, biologically active substances, insecticides, flotation reagents, as well as in other directions.

From the above mentioned it follows that the synthesis of compounds of this type and their research in the synthesis of organic chemistry can be assessed as very relevant.

References Références Referencias

1. Rachev H., Stefanova S. Handbook of corrosion//M .: Mir, 1982. P.62.
2. Bayramov G.I. Synthesis and study of new guanidine derivatives based on-chloralkyl and alkenyl-oxymethyl esters and chlororazone. //J. Natural and technical sciences, No. 2, 2009, p. 37-43.
3. Hajiyeva S.R., Bayramov G.I., Aliyeva T.I. et al. Synthesis and study of a new derivative of sulfadimezin based on dioxymethylchlorazon ester as an environmentally effective inhibitor. //Young scientist. International scientific journal. No. 6, 2019, p. 1-5.
4. Shikhmamedbekova A.Z., Mamedyarova I.F., Bayramov G.I., Mamedalieva G.G., et al. N,N'-diphenyl - N' octoxy methyl-guanidine as a steel corrosion inhibitor in a two-phase system. Author's certificate, USSR, No. 1031141, 1983, A C07 C129 / 12; C23 F 11/14.
5. Shel N.V., Tsygankova L.E., Kimya R. The new generation of metal corrosion inhibitors for the oil and petrochemical industry. XVIII Mendeleev Congress on General and Applied Chemistry. M.: Nauka. 2007, p.1608
6. Faritov A.T., Khudyakova L.P. et al., Methodology for selecting corrosion inhibitors for "Orenburgneft" JSC // Problems of collection, preparation and transport of oil and oil products: Coll. scient. works. IPTET - UFA, 2003. p. 167-171
7. Shiryayeva R.N., KudashevaF.Kh., Gumayev N. et al. Inhibition of tar deposits of asphaltenes and paraffins on pipelines with chemical reagents// J. Chemistry and technology of fuels and oils. M.: Ed. Rus.State.Univ.Oil and Gas named after I.M. Gubkin, No. 3, 2009, p.52-53
8. Khudyakova L.P. The system of ensuring the safety of operation of oil and gas equipment and pipelines working in aggressive media.//IPTER- 2008. Ufa. p. 39
9. Investigation of the effect of hydrogen sulfide on corrosion processes in the performance characteristics of structural elements of pipelines and tanks. // Problems of collection, preparation and transportation of oil and petroleum products: Collection of scientific works / IPTER-2005, Issue 65, p. 27-40
10. Khudyakova L.P., Spashenko, A.Yu.,Antipov, Yu.N. Assessment of the degree of danger of stress-corrosion cracks // STJ "Problems of collection, preparation and transportation of oil and oil products" / IPTER. Ufa. 2007. Issue 3 (69). p. 39-41
11. Khudyakova, L.P., Spashenko, A.Yu. et al. Estimated values of the rate of corrosion-mechanical cracking of oil and gas equipment and pipelines. // STJ "Problems, collection, preparation

and transport of oil and oil products" IPTER. Ufa. 2007. Issue 3 (69). p.61-63.
12. Gurvich L.M., Sherstiev N.M. Multifunctional surfactant compositions of technological operations of oil production. M.: VNIIOENG, 1994, p.268
13. Frolova L.V., Agafankin F.V. et al. Inhibiting of hydrogen sulphide corrosion of carbon steels by N-ethanol-butylenamine and its mixtures with a tertiary amine.//J. Corrosion: materials, protection. M.: "Science and Technology" LLC publishing house. 2010, No.1, p.15.