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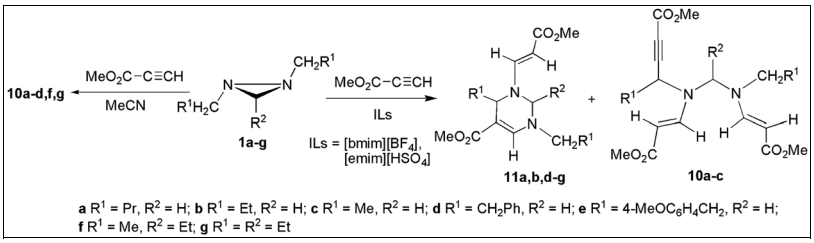

An interaction of 1,2-dialkyldiaziridine and 1,2,3-trialkyldiaziridine with methyl propiolate was studied both in organic solvent (MeCN, CH_2Cl_2, C_6H_6) and in ionic liquids. Earlier unknown linear structures, in which three molecules of methyl propiolate were suited to one diaziridine molecule (adducts 1 : 3), were obtained in MeCN. The diaziridine ring expansion products 1,2,3,4-tetrahydropyrimidine derivatives (adducts 1 : 2) and, along with them in some cases, the same linear structures were obtained in ionic liquids. A mechanism of reactions found was offered. The regioselectivity of reactions was supposed to determine by the structure of substituents in initial diaziridines. This conclusion was supported by quantum chemical calculations.

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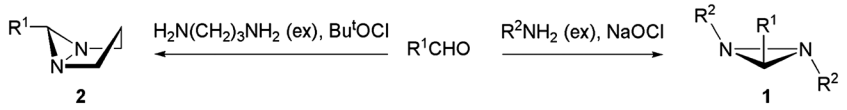
INTRODUCTION

One of the research areas of our laboratory is the development of new approaches to the synthesis of different nitrogen-containing heterocyclic systems on the basis of ring expansion reactions of readily available 1,2-dialkyldiaziridine derivatives **1** and 1,5-diazabicyclo[3.1.0]hexanes **2** [one-step synthesis from carbonyl compounds and primary aliphatic amines for compounds **1** or 1,3-diaminopropane for compounds **2** (Scheme 1) [1,2] under the action of electrophilic reagents, in particular dipolarophiles (ketenes, aroyliso- and aroylisothiocyanates, CS_2, activated nitriles and olefins)] [3–14].

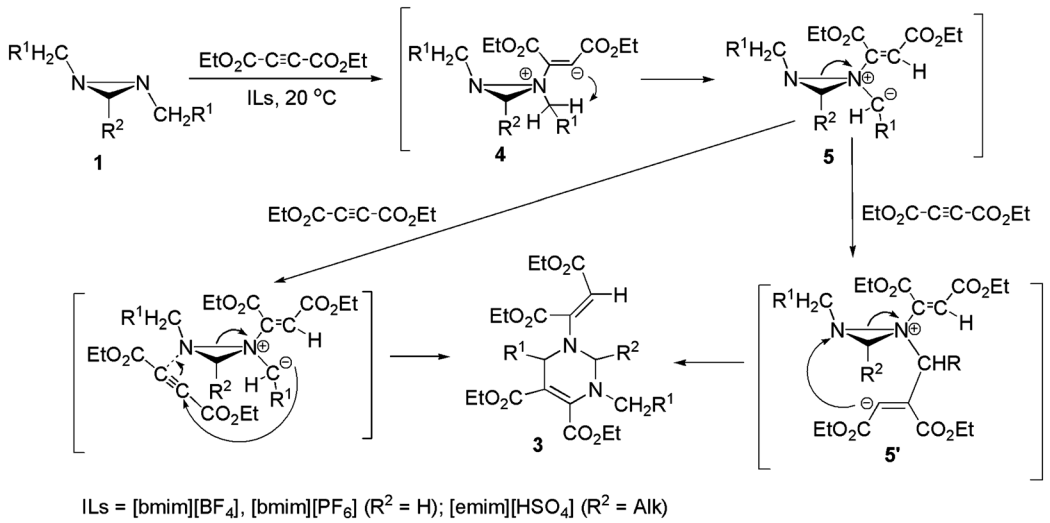
It was found that new heterocyclic systems in conventional organic solvents could be achieved in reactions of compounds **1** and **2** only with highly reactive reagents—arylketenes [3–6] and aroylisocyanates [7]. A reaction between diaziridines **1** and **2** and the other foresaid reagents was successfully performed though only with ionic liquids (ILs) as a reaction medium [8–12]. Recently, we [15] have found a new ring expansion reaction of 1,2-dialkyldiaziridine and 1,2,3-trialkyldiaziridines **1** under the action of diethyl acetylenedicarboxylate in ILs at 20°C resulting in diethyl 1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate **3**. ILs, 1-buthyl-3-methylimidazolium tetrafluoroborate or hexafluorophosphate ([bmim][BF_4]), [bmim][PF_6]), and 1-ethyl-3-methylimidazolium hydrogensulfate ([emim][HSO_4]), were applied as reaction medium. It was assumed that the first reaction step should be the formation of dipolar intermediate **4**. Then the formed anion eliminates the proton from the α-CH_2 fragment of the substituent bonded to the same nitrogen atom generating new dipolar intermediate **5**. The anion in this intermediate enters the reaction with the second molecule of diethyl acetylenedicarboxylate with simultaneous break of N-N bond yielding final compound **3** as a result of formal [4+2]-cycloaddition. These processes are most likely concerted. However, it is impossible to exclude the formation of dipolar intermediates **5′**, anion of which attack the second nitrogen atom of the diaziridine ring followed by the N-N bond break. Both pathways are consistent with the Baldwin rules (6-endo-tet) for such reaction types, which are accompanied by a simultaneous opening of another ring (Scheme 2).

Of note is that the same reaction of 1,2-disubstituted and 1,2,3-trisubstituted diaziridines **1** with dimethyl acetylenedicarboxylate in common organic solvent (benzene) gave only linear products **6** and **7** and the diaziridine ring is opening on N-N bond [16]. The research on this reaction mechanism was assisted by labeled atoms (D). Stemming from the structures of the prepared compounds, the authors [16] assumed that the first reaction step also included the formation of dipolar intermediates **8a**,**b**; however, their stabilization was achieved by the formation of linear compounds **6** and **7** (Scheme 3). Evidently, a possibility to achieve

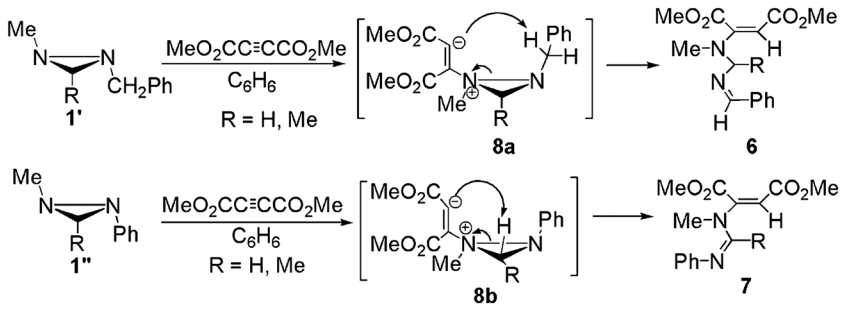
Scheme 1



Scheme 2



Scheme 3



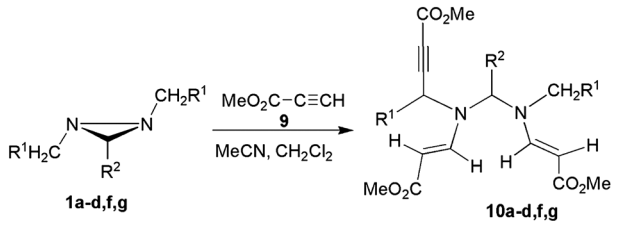
tetrahydropyrimidine derivatives (see Scheme 2) is determined by the influence of ionic liquids capable of stabilizing either charged intermediates or ions [13,14] to proceed with other transformations.

RESULTS AND DISCUSSION

In this article, the research on the ring expansion reactions of 1,2-dialkyldiaziridines (**1a**–**e**) and 1,2,3-trialkyldiaziridines (**1f**,**g**) with activated acetylenes was furthered by a scrutiny of a terminal acetylene representative—methyl propiolate **9**. The reactions were carried out both in organic solvents (MeCN, CH_2Cl_2, C_6H_6) and in ILs at 20°C. It was found that an interaction of diaziridines **1a**–**g** with methyl propiolate **9** in MeCN and CH_2Cl_2 during 1 week (TLC-control) resulted in earlier unknown linear structures **10a**–**d**,**f**,**g**. These new structures were adducts **1a**–**d**,**f**,**g** : **9** = 1 : 3 (Scheme 4). Complex mixture of products was obtained with diaziridine **1e**. In benzene, an interaction of diaziridines **1a**–**g** with compound **9** did not occur.

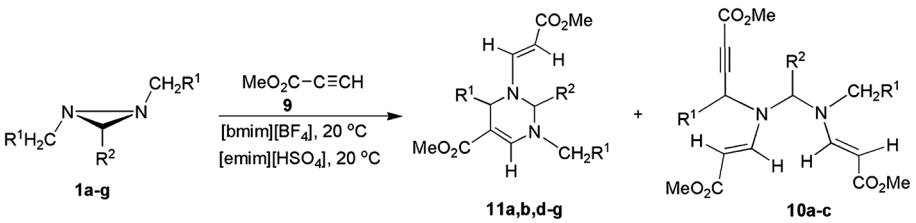
The interaction of compounds **1a**–**g** and **9** in ILs gave a different result. 1,2,3,4-Tetrahydropyrimidine derivatives **11** were obtained in these solvents; however, compounds **10a**–**c** were also yielded in three cases. The reaction regiodirection depended on the structure of initial diaziridines. Cyclic structures **11a**,**b** were prepared from 1,2-dibutyldiaziridine and 1,2-dipropyldiaziridine **1a**,**b**;

Scheme 4



a R^1 = Pr, R^2 = H; **b** R^1 = Et, R^2 = H; **c** R^1 = Me, R^2 = H; **d** R^1 = CH_2Ph, R^2 = H; **f** R^1 = Me, R^2 = Et; **g** R^1 = R^2 = Et

Scheme 5



a R^1 = Pr, R^2 = H; **b** R^1 = Et, R^2 = H; **c** R^1 = Me, R^2 = H; **d** R^1 = CH_2Ph, R^2 = H; **e** R^1 = 4-$MeOC_6H_4CH_2$, R^2 = H; **f** R^1 = Me, R^2 = Et; **g** R^1 = R^2 = Et

however, linear structures **10a**,**b** were simultaneously formed in the reaction of these diaziridines. Only linear product **10c** was isolated from the reaction of 1,2-diethyldiaziridine **1c** and acetylene **9**. Only cyclic products **11d**–**g** were obtained from 1,2-di(2-phenylethyl) diaziridine **1d**, 1,2-di[2-(4-metoxyphenyl)ethyl]diaziridine **1e**, and 1,2,3-trialkyldiaziridines **1f**,**g** (Scheme 5).

ILs, [bmim][BF_4] or [bmim][PF_6], appeared most appropriate for preparing compounds **11a**,**b**,**d**,**e** and **10a**–**c** and [emim][HSO_4]—for compounds **11f**,**g**. In all cases, ionic liquids were regenerated and reused in the same reactions not less than three times. In contrast to the reaction of same diaziridines with diethyl acetylenedicarboxylate, the reaction rate for diaziridines **1a**–**g** with methyl propiolate **9** was low. These reactions ran for 36–72 h at 20°C, and yields of the isolated products were also lower (see Table 1). To optimize the methods for the preparation of compounds **11**, we studied the influence of the reagents ratio (**1b**:**9** = 1 : 1, 1 : 2, 1 : 3) on the reaction outcome taking 1,2-dipropyldiaziridine **1b** as an example. The reactions were performed in IL [bmim][BF_4]. It was found that the ratio **11b** : **10b** increased with a higher amount of methyl

Table 1

Reaction conditions and yields of products obtained.

	MeCN[a] (CH_2Cl_2)[a]			[bmim][BF_4]		
1	Product	Time (day)	Yield (%)	Product	Time (h)	Yield (%)
a	**10a**	7	45 (21)	**10a**	36	36
				11a		41
b	**10b**	7	30 (25)	**10b**	36	33
				11b		32 (61[a])
c	**10c**	7	27 (19)	**10c**	36	25
d	**10d**	7	11[b] (6.5)	**11d**	72	57
e	**10e**	7	–	**11e**	72	42
f	**10f**	7	46 (41)	**11f**[c]	72	28
g	**10g**	7	32 (29)	**11g**[c]	100	13

[a]Ratio of **1b** : **9** = 1 : 3.
[b]Initial **1d** was also isolated.
[c]IL [emim][HSO_4].

propiolate **9**. The reaction conditions (reaction medium, time of reaction) and yields of obtained compounds **10** and **11** are presented in Table 1.

The structures of compounds **10a–c** and **11a**,**b**,**d–g** were established by the aggregated elemental analysis data and spectral characteristics (mass spectra, IR, NMR ^{1}H, ^{13}C, ^{15}N 2D spectra with use of COSY, {^{1}H-^{1}H}gNOESY, {^{1}H-^{13}C}HMBC, {^{1}H-^{13}C}HSQC, and {^{1}H-^{15}N}HMBC methods). Data on the ascertained structures of **10** and **11** are given for particular compounds **10a** and **11a** (see Figs. 1 and 2 and Tables 2 and 3).

The ^{13}C APT spectrum of **10a** fixed five CH_3 groups, six CH_2 groups, five CH groups, and five quaternary carbon atoms, three of which were in the region of carboxylic carbon resonance and two—in the region of acetylene carbon resonance. The ^{1}H spectrum was assigned with the COSY, NOESY, and HSQC 2D spectra. The spectra analysis showed that the molecule contained three carbmethoxy, one *N*-butyl, one 1-substituted *N*-butyl group, one CH_2 group, which had no interactions with other protons, and four sp^2-CH groups. {^{1}H-^{13}C}HMBC 2D spectral correlations allowed the confirmation of the structure of the fragments and interconnections between them as well as of the positions of quaternary carbon atoms. The ^{1}H-^{15}N HMBC spectrum detected two sp^3-N atoms with chemical shifts of −274.7 and −274.0 ppm (with an external reference CH_3NO_2, δ = 0.0 ppm; Table 2). Thus, in **10a**, three molecules of methyl propiolate were added to one molecule of initial diaziridine—one to each nitrogen atoms with the formation of corresponding *trans*-alkenes and one to the α-CH_2 carbon atom of *N*-butyl group with the triple bond preservation. The most important NOE interactions in **10a** were revealed in the NOESY experiment (Fig. 1 and Table 2).

The ^{13}C APT spectrum of **11a** fixed four CH_3 groups, six CH_2 groups, four CH groups, and three quaternary carbon atoms, two of which were in the region of carboxylic carbon resonance. The ^{1}H spectrum was assigned with the COSY, NOESY, and HSQC 2D spectra. The spectra showed that the molecule contained two carbmethoxy, one *N*-butyl, one 1-substituted *N*-butyl group, one CH_2 group, which had no interactions with other protons, and three sp^2-CH groups. {^{1}H-^{13}C}HMBC 2D spectral correlations allowed the confirmation of the structure of the fragments and interconnections between them as well as of the positions of quaternary carbon atoms. The {^{1}H-^{15}N} HMBC spectrum revealed two sp^3 *N* atoms with chemical shifts of −279.3 and −279.6 ppm (with an external reference CH_3NO_2, δ = 0.0 ppm; Table 3). The NMR data for **11a** were correlated with that for **3** [15]. The most important NOE interactions in **11a** were revealed in the NOESY experiment (Fig. 2 and Table 3). Molecular ions were found in the mass spectra of all compounds **10** and **11**.

To explain such unexpected formation of two different structures **11** and **10** in the same conditions at the interaction of diaziridines **1a–g** with methyl propiolate **9** in ILs, we

Table 2

NMR-spectra data for compound **10a**.

Number of atoms in molecule (Fig. 1)	Chemical shifts (ppm) and constants of spin–spin interaction *J* (Hz)		Nontrivial correlations in {^{1}H-^{1}H}gNOESY	Correlations in {^{1}H-^{13}C}HMBC and {^{1}H-^{15}N}HMBC
	^{1}H	^{13}C (**^{15}N**)		
1	–	(**−274.7**)	–	H-2,6,7,8,13
2	4.54 dd (^2J = 18.1)	68.94	H-4,5,6,7,8,9,10	H-4,5,6,9
3	–	(**−274.0**)	–	H-2,4,5,9,10
4	7.41, d (^3J = 13.6)	149.96	H-2,9	H-2,5,9
5	4.72,d (^3J = 13.6)	87.21	H-9	–
5-COOMe	3.68, s	50.93	–	H-4,5,Me
		168.86		
6	4.14, t (^3J = 7.4)	50.54	H-2,7,8,13	H-2,7,13,14
7	7.42, d (^3J = 13.3)	148.07	H-2,6,13	H-2,6,8
8	4.89, d (^3J = 13.3)	89.94	H-2,6	–
8-COOMe	3.66, s	50.66	–	
		169.44		
9	3.04, t (^3J = 8.0)	46.82	H-4,5,10,11	H-7,8,Me
10	1.55, m	27.96		H-9,11,12
11	1.30, m	20.18		
12	0.93, t (^3J = 6.5)	13.63		
13	1.74, m	34.77	H-6,8,14,15	
14	1.44 m, 1.36 m	19.42		
15	0.95, t (^3J = 6.5)	13.29		
16	–	83.30	–	H-6,13
17	–	77.53	–	H-6
17-COOMe	3.77, s	52.82	–	H-6
		153.13		

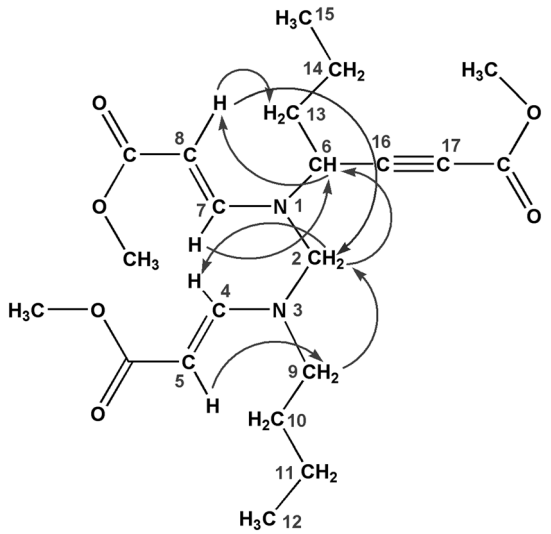


Figure 1. The most important NOE interactions in **10a**.

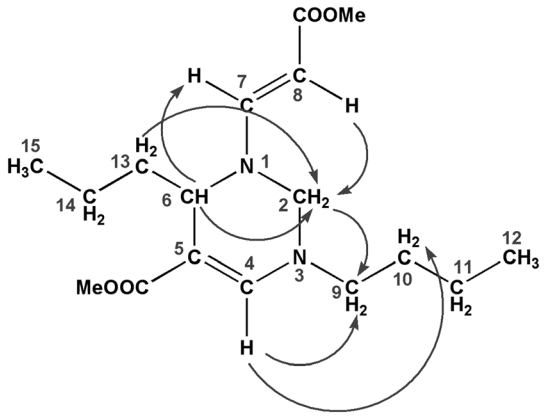


Figure 2. The most important NOE interactions in **11a**.

proposed the following mechanism. Evidently, zwitter-ionic intermediate **12** was formed in the first reaction step independently of the initial diaziridine structure. The negative charge on the olefin carbon atom of this intermediate can theoretically split the proton off from the α-CH_2 group of the substituents bonded to either of the two nitrogen atoms of the diaziridine ring. If it splits the proton off from the α-CH_2 fragment of the substituent bonded to the same nitrogen atom, 1,2,3,4-tetrahydropyrimidines **11** are generated similarly to tetrahydropyrimidine derivatives **3** formation through intermediates **12′**, **12"**, **12"′** (compare Schemes 2 and 6).

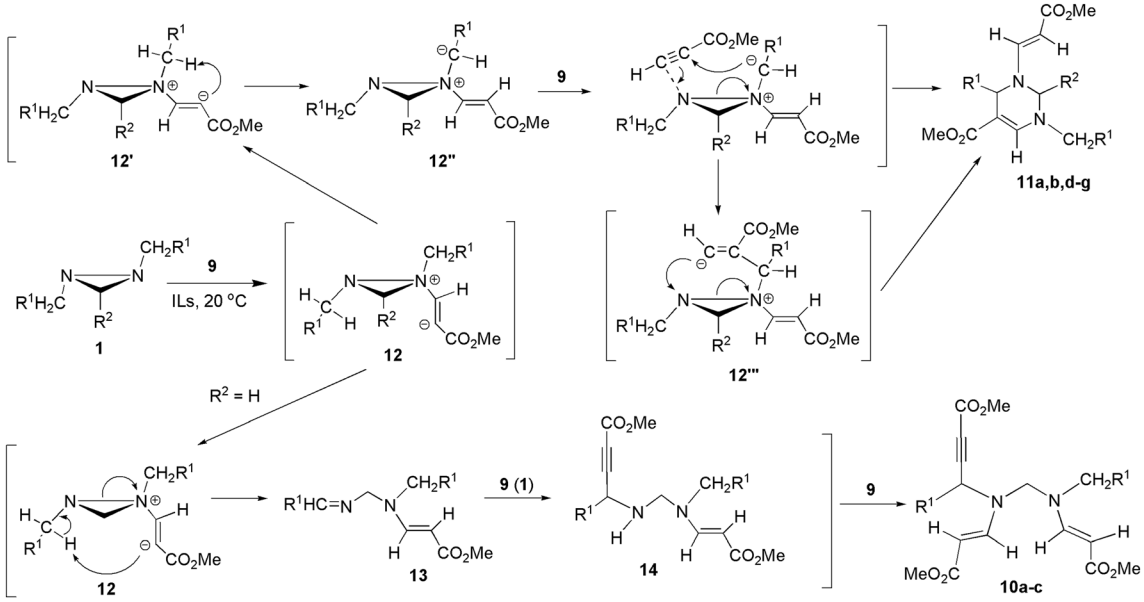
If it splits the proton off from the α-CH_2-fragment of the substituent bonded to the second nitrogen atom, the second intermediate (**13**) is formed after a break of the N-N bond of the diaziridine ring. Then, the second molecule of methyl propiolate **9** is added to the C═N bond generating the third intermediate (**14**) containing the NH group. The ionization of the terminal ≡CH bond of methyl propiolate **9** is necessary to transform imine **13** to intermediate **14**. Evidently initial diaziridines play here a part of bases. The basicity of diaziridines is equal to that of aniline. The intermediate **14** is bonded to the third molecule of methyl propiolate **9** by the Michael reaction route giving linear compounds **10**. If the substituents volume is rather large (e.g., 2-phenylethyl, **1d** or 2-(4-methoxyphenyl)ethyl, **1e**), or initial diaziridines contain a substituent at the cyclic carbon atom (**1f**,**g**), only cyclic products **11** are produced.

Table 3

NMR-spectra data for compound **11a**.

Number of atoms in molecule (Fig. 2)	Chemical shifts (ppm) and constants of spin–spin interaction *J* (Hz)		Nontrivial correlations in {^{1}H-^{1}H}gNOESY	Correlations in {^{1}H-^{13}C}HMBC, {^{1}H-^{15}N}HMBC
	^{1}H	^{13}C (**^{15}N**)		
1	–	(**–279.3**)	–	H-2b,6,7,8,13
2	4.41(a), d (^2J = 12.4)	58.61	H-2b,6,13	H-4,7,9
	4.20(b), d (^2J = 12.4)		H-2a,7,8,9,	
3	–	(**–279.6**)	–	H-2a,2b,4,9,10
4	7.28, s.	143.77	H-9,10	H-2b,9
5	–	98.14	–	H-6,13
5-COOMe	3.66, s	50.61	–	H-4,6
		166.78		
6	4.13, d (^3J = 9.5)	55.62	H-2a,7,8,13	H-2b,4,7,13,14
7	7.42, d (^3J = 13.6)	151.70	H-2b,6	H-2a,2b,6
8	4.81, d (^3J = 13.6)	87.90	H-2b,6	H-2a
8-COOMe	3.64, s	50.64	–	H-8,Me
		169.70		
9	3.14, t. (^3J = 7.4)	53.44	H-2,10,11	H-2b,4,10,11
10	1.56, m	30.74		
11	1.31, m	19.71		
12	0.94, m	13.56		
13	1.76, m; 1.41, m	37.77	H-2a,6	
14	1.37 m	18.91		
15	0.91 m	13.75		

Scheme 6



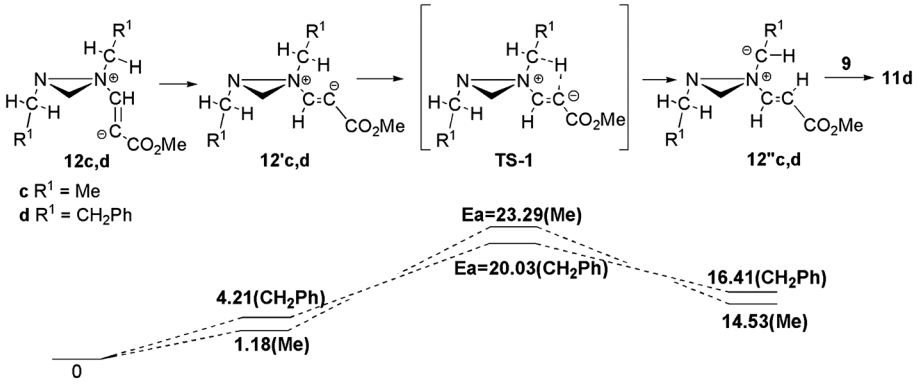
If the substituent's volume is not very large (Pr, Bu, **1a**,**b**), both kinds of the products are generated. In the instance of 1,2-diethyldiaziridine **1c**, with the least steric hindrance, only linear product **10c** is formed (Scheme 6).

To confirm this hypothesis, quantum chemical calculations were performed for interaction of 1,2-diethyldiaziridine **1c** and 1,2-bis(2-phenylethyl)diaziridine **1d** with methyl propiolate **9** within the framework of density functional theory (DFT) with hybrid potential B3LYP and standard split-valence basis set 6-31G(d) using the Gaussian 98 program package [17]. The position of stationary points was determined by analysis of Hessian matrix according to absence of imaginary frequencies. The nature of transition states was confirmed by calculations of the intrinsic reaction coordinate. The activation barriers of reactions were calculated using the Hartree–Fock (HF) method in the STO-3G basis set, because it was impossible to localize the transition states using the density functional theory.

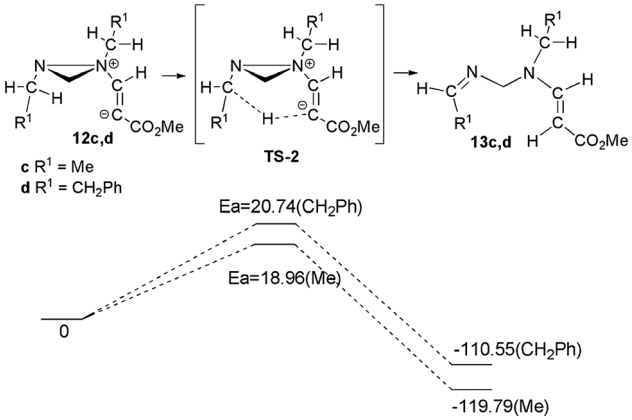
At the first stage, to estimate the reactivity of methyl propiolate **9**, compounds **1c**,**d** and intermediates **12**, we calculated the local Fukui indices and global electrophilicity indices (ω) [18]. It was found that the maximum value of the Fukui index corresponds to unsubstituted carbon atom in methyl propiolate and to nitrogen atoms in diaziridines **1c**,**d**, indicating that the preferred reaction is attachment of nitrogen atoms of compounds **1c**,**d** to unsubstituted carbon atom of methyl propiolate. As follows from analysis of global electrophilicity indices, compound **1c** (ω = 0.18 eV) must enter the reaction with methyl propiolate (ω = 1.52 eV) more readily than compound **1d** (ω = 0.74 eV), since it is of more marked nucleophilic nature (low electrophilicity index).

The global electrophilicity index of intermediate **12c** increases after attachment of methyl propiolate (ω = 0.43 eV), whereas this value remains unchanged for intermediate **12d** (ω = 0.74 eV). Analysis of Fukui indices for

Scheme 7



Scheme 8



intermediates **12c** and **12d** did not reveal any specific features of proton migration from α-CH_2–substituents depending on R^1. Therefore, the reactivity of intermediates **12** was estimated via localization of transition states.

Calculation of the total energy of intermediates **12** and **12′** (see Schemes 7 and 8) showed higher stability of isomer **12**, where the double bond formed after attachment of methyl propiolate **9** to diaziridines **1c** and **1d** is directed at the α-CH_2–fragment of the substituent at the second carbon atom. For the formation of structure **12′** it is necessary that this double bond be closer to the α-CH_2–fragment of the substituent at the first carbon atom, which is possible through rotation about the single bond C-N. The calculations indicate (Scheme 7) that the energy required for this process in the case of R^1 = Me is 1.18 kcal/mol (in HF STO-3G calculations) and 0.03 kcal/mol (in B3LYP 6-31G(d) calculations). For R^1 = CH_2Ph, the corresponding values are 4.21 kcal/mol (HF STO-3G) and 3.10 kcal/mol (B3LYP 6-31G(d)).

Calculations of transition states (TS) for processes of proton migration from the α-CH_2-fragments of substituents bound to both nitrogen atoms in the basis set HF STO-3G showed that at R^1 = Me the activation energy of TS-2 is lower (18.96 kcal/mol) for the attack of intermediate **12c** on the α-CH_2–fragment of the substituent connected to the second nitrogen atom (with formation of intermediate **13c**) than the activation energy of TS-1 (23.29 kcal/mol) required for the attack on the α-CH_2–fragment of the substituent connected to the first nitrogen atom (with formation of intermediate **12''c**). The opposite picture is observed for R^1 = CH_2Ph: the activation energy is lower (20.03 kcal/mol) for the route where the α-CH_2–fragment of the substituent at the first nitrogen atom is attacked (formation of intermediate **12''d**), whereas the activation energy for the second attack center (formation of intermediate **13d**) is 20.74 kcal/mol (Schemes 7 and 8).

Thus, the calculated data obtained by the example of compounds **1c**,**d** confirmed the experimental results on regioselectivity of interaction between diaziridines **1** and methyl propiolate **9** in ionic liquids. The different behavior of these diaziridines in the reaction with methyl propiolate in an organic solvent and in ionic fluids is apparently due to the fact that ionic liquids stabilize intermediates **12′**, enabling them to enter the reaction leading to cyclic compounds **11**.

Therefore, two directions of the diaziridine ring transformation were found in the investigation of the interaction of 1,2-dialkyldiaziridine derivatives **1a–f** with methyl propiolate **9** in ionic liquids: the ring expansion with the formation of 1,2,3,4-tetrahydropyrimidine derivatives **11** (adduct 1 : 2) and in some cases linear structures **10**, in which three methyl propiolate molecules are bonded to one diaziridine molecule (adduct 1 : 3). The regioselectivity of reactions in ionic liquids depends on the structure of substituents in initial diaziridines **1**. This conclusion was supported by quantum chemical calculation. The same reaction in trivial organic solvents leads only to linear compounds **10**, that is, a possibility to generate 1,2,3,4-tetrahydropyrimidine derivatives **11** is only determined by the ILs' influence. Compounds **10** and **11** have not been described in literature and a feasibility of their one-step preparation from available initial compounds supports a high potential of diaziridines as accessible building blocks for the synthesis of various heterocyclic and polyfunctional compounds.

EXPERIMENTAL

Elemental analysis was performed by the CHN Analyzer Perkin-Elmer 2400. The IR spectra (v, cm^{-1}) were measured using a SPECORD-M82 spectrometer. High-resolutionmass spectra (HR MS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The NMR spectra of all compounds were recorded using a Bruker AM-300 spectrometer at 300 MHz for ^{1}H and 75.47 MHz for ^{13}C Spectra as well as Bruker AV-600 instrument with the frequencies 600.13, 150.90, and 60.81 MHz for ^{1}H, ^{13}C, and ^{15}N, correspondingly in $CDCl_3$. The chemical shifts of the signals of $CDCl_3$ residual proton (7.27 ppm) and carbon (77.0 ppm) were used as the internal standard. The ^{15}N spectra were measured with CH_3NO_2 (δ_{15N} = 0.0 ppm) as the external standard. All 2D-spectra were recorded using standard Bruker methods with Z-gradient. The spectra were measured at 30°C. Analytical thin-layer chromatography (TLC) was conducted on silica gel plates (Silufol UV-254). New compounds were purified by column chromatography on Silicagel, 0.060–0.200 mm, 60 A (ACROS). Synthesis of initial diaziridines **1a–c** is described in the work given in the Ref. 19, **1e**,**f** in the work given in Ref. 20, and **1d** in the work given in Ref. 4. Compound **1e** was prepared by analogy with work [21].

General procedure for an interaction of 1,2-dialkyldiaziridines and 1,2,3-trialkyldiaziridines 1a–g with methyl propiolate 9 in organic solvents (MeCN, CH_2Cl_2, C_6H_6). To a stirred mixture of initial diaziridines **1a–g** (1.0 mmol) and 1.5 mL of corresponding solvent at temperature 0–5°C, methyl propiolate **9** (0.252 g, 3.0 mmol) was added

drop-wise for about 1 min, the temperature was raised to 20°C, and reaction mixture was stirred 1 week to disappearance of initial diaziridine (TLC-control). After that, a solvent was evaporated in vacuum; the formed mixture of products was separated by the method of column chromatography on Silicagel (eluent—hexane : ethyl acetate).

Methyl 4-{({butyl[(1E)-3-methoxy-3-oxoprop-1-enyl]amino}methyl)[(1E)-3-methoxy-3-oxoprop-1-enyl]amino}hept-2-ynoate (10[a]). Compound **10a** was obtained as yellow nondistilled oil in yield 45%. Eluent–hexane : ethyl acetate = 3 : 1. R_f= 0.24 (eluent–hexane : ethyl acetate = 2 : 1). IR: 764, 792, 1076, 1128, 1164, 1192, 1252, 1380, 1436, 1456, 1612, 1692, 1736, 2872, 2932, 2956 cm^{-1}; ^{1}H-NMR, δ, ppm: 0.93 (t, 3H, C*H*$_3$(CH$_2$)$_3$N, ^3J = 6.5 Hz); 0.95 (t, 3H, C*H*$_3$(CH$_2$)$_2$CHN, ^3J = 6.5 Hz); 1.30 (m, 2H, CH$_3$C*H*$_2$(CH$_2$)$_2$N); 1.44 and 1.36 (both m, 2H, CH$_3$C*H*$_2$CH$_2$CHN); 1.55(m, 2H, CH$_3$CH$_2$C*H*$_2$CH$_2$N); 1.74 (m, 2H, CH$_3$CH$_2$C*H*$_2$CHN); 3.04 (t, 2H, CH$_3$(CH$_2$)$_2$C*H*$_2$N, ^3J = 8.0 Hz); 3.66 and 3.68 (both s, 6H, C*H*$_3$O); 3.77 (s, 3H, C≡CCO$_2$C*H*$_3$); 4.14 (t, 1H, CH-C≡; ^3J = 7.4 Hz); 4.54 (dd, 2H, NC*H*$_2$N, ^2J = 18.1 Hz); 4.72 (d, 1H, C*H*=CHNC$_4$H$_9$; ^3J = 13.6 Hz); 4.89 (d, 1H, C*H*=CHNCH, ^3J = 13.3 Hz); 7.41 (d, 1H, CH=C*H*NC$_4$H$_9$; ^3J = 13.6 Hz); 7.42 (d, 1H, CH=C*H*NCH, ^3J = 13.3 Hz); ^{13}C-NMR, δ, ppm: 13.29 (*C*H$_3$(CH$_2$)$_2$CHN); 13.63 (*C*H$_3$(CH$_2$)$_3$N); 19.42 (CH$_3$*C*H$_2$CH$_2$CHN); 20.18 (CH$_3$*C*H$_2$(CH$_2$)$_2$N); 27.96 (CH$_3$CH$_2$*C*H$_2$CH$_2$N); 34.77 (CH$_3$CH$_2$*C*H$_2$CHN); 46.82 (CH$_3$(CH$_2$)$_2$*C*H$_2$N); 50.66, 50.93 and 52.82 (O*C*H$_3$); 68.94 (NCH$_2$N); 77.53 (C≡*C*CO$_2$CH$_3$); 83.30 (*C*≡CCO$_2$CH$_3$); 87.21 (*C*H=CHNC$_4$H$_9$); 89.94 (*C*H=CHNCH); 148.07 (CH=*C*HNCH); 149.96 (CH=*C*HNC$_4$H$_9$); 153.13 (C≡C*C*OOCH$_3$); 168.86 and 169.44 (C=C*C*OOCH$_3$); ^{15}N-NMR, δ ppm: −274.0, −274.7; ESI-MS: (M+Na) 431.16. Anal. Calc. for $C_{21}H_{32}N_2O_6$ (408.49): C, 61.75; H, 7.90; N, 6.86. Found:C, 61.63; H, 8.19; N, 6.63.

Methyl 4-([(1E)-3-methoxy-3-oxoprop-1-enyl]{[[(1E)-3-methoxy-3-oxoprop-1-enyl](propyl)amino]methyl}amino)hex-2-ynoate (10b). Compound **10b** was obtained as yellow nondistilled oil in yield 30%. Eluent – hexane : ethyl acetate = 3 : 1. R_f = 0.35 (eluent - hexane:ethyl acetate = 2 : 1). IR: 624, 664, 668, 752, 796, 856, 916, 940, 948, 976, 1056, 1096, 1200, 1260, 1308, 1340, 1388, 1404, 1432, 1436, 1464, 1472, 1496, 1508, 1540, 1560, 1576, 1600, 1624, 1668, 1680, 1700, 1716, 1728, 1732, 1740, 2236, 2332, 2876, 3088 cm^{-1}; ^{1}H-NMR, δ, ppm: 0.89 (t, 3H, *CH*$_3$CH$_2$CH$_2$N, ^3J = 7.3 Hz), 0.99 (t, 3H, *CH*$_3$CH$_2$CHN, ^3J = 7.3 Hz), 1.58 (qv, 2H, CH$_3$*CH*$_2$CH$_2$N, ^3J = 7.3 Hz), 1.82 (m, 2H, CH$_3$*CH*$_2$CHN), 3.01 (t, 2H, CH$_3$CH$_2$*CH*$_2$N, ^3J = 8.1 Hz), 3.66 and 3.67 (both s, 6H, =CHCO$_2$*CH*$_3$), 3.77 (s, 3H, C≡CCO$_2$C*H*$_3$), 4.05 (t, CH-C≡; ^3J = 7.3 Hz), 4.55 (br s, 2H, N*CH*$_2$N), 4.72 (d, 1H, C*H*=CHNC$_3$H$_7$; ^3J = 13.2 Hz), 4.88 (d, 1H, C*H*=CHNCH, ^3J = 13.2 Hz), 7.42 (d, 2H, CH=C*H*N, ^3J = 13.2 Hz); ^{13}C-NMR, δ, ppm: 10.93 (*C*H$_3$CH$_2$CH$_2$N), 11.68 (*C*H$_3$CH$_2$CHN), 19.46 (CH$_3$*C*H$_2$CH$_2$N), 28.45 (CH$_3$*C*H$_2$CHN), 50.68, 51.12 and 52.74 (*C*H$_3$O), 51.68 (CH$_3$CH$_2$*C*HN), 67.26 (N*C*H$_2$N), 77.84 (C≡*C*COOCH$_3$), 83.62 (*C*≡CCOOCH3), 88.22 (*C*H=CHNC$_3$H$_7$), 89.97 (*C*H=CHNCH), 149.67 (*C*H=CCOOCH$_3$), 152.94 (NCH=CH), 154.76 (C≡C*C*OOCH$_3$), 168.27 and 168.92 (C=C*C*OOCH$_3$); ESI-MS: (M+Na) 403.18. Anal. Calc. for $C_{19}H_{28}N_2O_6$ (380.44): C, 59.99; H, 7.42; N, 7.36. Found: C, 61.28; H, 7.22; N, 7.51.

Methyl 4-[({ethyl[(1E)-3-methoxy-3-oxoprop-1-enyl]amino}methyl)(3-methoxy-3-oxoprop-1-enyl)amino]pent-2-ynoate (10c). Compound **10c** was obtained as yellow nondistilled oil in yield 27%. Eluent – hexane : ethyl acetate = 1 : 1.5. R_f= 0.32 (eluent – hexane : ethyl acetate = 1 : 1). IR: 668, 752, 796, 980, 1036, 1072, 1088, 1160, 1192, 1260, 1340, 1432, 1540, 1608, 1696, 1716, 2240, 2340, 2948, 2980 cm^{-1}; ^{1}H-NMR, δ, ppm: 1.13 (t, 3H, *CH*$_3$CH$_2$N, ^3J = 6.6 Hz), 1.50 (d, 3H, *CH*$_3$CHN, ^3J = 6.8 Hz), 3.11 (qv, 2H, CH$_3$*CH*$_2$N, ^3J = 6.6 Hz), 3.66 and 3.67 (both s, 6H, *CH*$_3$CO$_2$CH=CH), 3.77 (s, 3H, C≡CCO$_2$*CH*$_3$), 4.35 (qv, 1H, CH$_3$*CH*N, ^3J = 6.8 Hz), 4.56 (dd, 2H, N*CH*$_2$N, ^2J = 14.7 Hz), 4.74 (d, 1H, C*H*=CHNC$_2$H$_5$; ^3J = 13.2 Hz), 4.91 (d, 1H, C*H*=CHNCH, ^3J = 13.2 Hz), 7.41 (d, 2H, N*CH*=; ^3J = 13.2 Hz); ^{13}C-NMR, δ, ppm: 10.99 (*C*H$_3$CH$_2$N), 18.82(*C*H$_3$CHN), 41.45 (CH$_3$*C*H$_2$N), 45.58 (CH$_3$*C*HN), 50.76, 51.02 and 52.95 (*C*H$_3$O), 68.56 (N*C*H$_2$N), 77.52 (C≡*C*CO$_2$CH$_3$), 83.89 (*C*≡CCO$_2$CH$_3$), 87.37 (*C*H= CHNC$_2$H$_5$), 90.10 (*C*H=CHNCH), 147.88 (CH=*C*HNCH); 149.52 (CH=*C*HNC$_2$H$_5$), 153.21 (C≡C*C*OOCH$_3$); 168.96 and 169.52 (C=C*C*OOCH$_3$); ESI-MS: (M+H) 352.39. Anal. Calc. for $C_{17}H_{24}N_2O_6$ (352.39): C, 57.94; H, 6.86; N, 7.95. Found: C, 57.71; H, 7.01; N, 8.16.

Methyl 4-([(1E)-3-methoxy-3-oxoprop-1-enyl]{[[(1E)-3-methoxy-3-oxoprop-1-enyl](2-phenylethyl)amino]methyl}amino)-5-phenylpent-2-ynoate (10d). Compound **10d** was obtained as yellow nondistilled oil in yield 11%. Eluent – hexane : ethyl acetate= 3 : 1. R_f = 0.53 (eluent – hexane : ethyl acetate = 2 : 1). ^{1}H-NMR, δ, ppm: 2.79 (m, 2H, PhC*H*$_2$CH$_2$N); 3.11 (m, 2H, PhC*H*$_2$CH); 3.09 and 3.33 (both t, 2H, PhCH$_2$C*H*$_2$N, ^3J = 7.0 Hz); 3.72 and 3.73 (both s, 6H, C*H*$_3$O); 3.77 (s, 3H, C≡CCO$_2$C*H*$_3$); 3.75 and 3.80 (both d, 2H, NCH$_2$N, ^2J = 14 Hz); 4.21 (t, *CH*-C≡; ^3J = 7.0 Hz), 4.77 (d, 1H, CH$_2$NCH=C*H*; ^3J = 13.0 Hz); 4.87 (d, 1H,CHNCH=*CH*CO$_2$Me, ^3J = 14.0 Hz); 7.12–7.31 (m, 10H, 2Ph); 7.46 (d, 1H, CH=C*H*NCH, ^3J = 14.0 Hz); 7.56 (d, 1H, CH=C*H*NCH$_2$, ^3J = 13.0 Hz); ^{13}C-NMR, δ, ppm: 29.78 (PhC*H*$_2$CH$_2$N); 32.0 (PhC*H*$_2$CH); 36.16 (NCH$_2$CH$_2$Ph); 50.90, 51,11, 51.18 (MeO); 53.03 (*C*H-C≡); 67.28 (N*C*H$_2$N);78.05 (C≡*C*CO$_2$Me); 82.76 (C≡*C*CH); 87.61 (*C*H=CHNCH$_2$); 90.72 (*C*H=CHNCH); 125.44, 126.84, 128.72, 128.85, 129.04, 135.50, 138.0 (Ph), 147.28 (CH=*C*HNCH); 149.42 (CH=*C*HNCH$_2$); 168.83, 168.84, 169.24 (*C*OOCH$_3$); Anal. Calc. for $C_{29}H_{32}N_2O_6$ (504.57): C, 70.21; H, 6.18; N, 5.77. Found: C, 69.03; H, 6.39; N, 5.55.

Methyl 4-[(1-{ethyl[(1E)-3-methoxy-3-oxoprop-1-enyl]amino}propyl)(3-methoxy-3-oxoprop-1-enyl)amino]pent-2-ynoate (10f). Compound **10f** was obtained as yellow nondistilled oil in yield 46%. Eluent – hexane : ethyl acetate = 4 : 1. R_f= 0.4 (eluent – hexane : ethyl acetate = 1 : 1); ^{1}H-NMR, δ, ppm: 0.97 (t, 3H, C*H*$_3$CH$_2$CH, ^3J = 7.0 Hz), 1.13 (t, 3H, C*H*$_3$CH$_2$N, ^3J = 7.1 Hz), 1.52 (d, 3H, C*H*$_3$CH, ^3J = 7.1 Hz), 1.96 and 1.89 (both m, 2H, CH$_3$C*H*$_2$CH), 3.11 and 3.03 (both m, 2H, CH$_3$C*H*$_2$N), 3.67 and 3.69 (both s, 6H, C*H*$_3$OCOCH=CH), 3.74 (s, 3H, C*H*$_3$OCOC≡C), 4.28 (qv, 1H, CH$_3$C*H*, ^3J = 7.1 Hz), 4.47 (t, 1H, N-C*H*-N, ^3J = 7.3 Hz), 4.75 (d, 1H, C*H*=CHNC$_2$H$_5$, ^3J = 13.2 Hz), 4.96 (d,1H, C*H*=CHNCHCH$_3$, ^3J = 13.6 Hz), 7.48 (d, 1H, CH=C*H*NC$_2$H$_5$, ^3J = 13.2 Hz), 7.54 (d, 1H, CH=C*H*NCHCH$_3$, ^3J = 13.6 Hz); ^{13}C-NMR, δ, ppm: 10.29 (*C*H$_3$CH$_2$CH), 11.40 (*C*H$_3$CH$_2$N), 19.03 (*C*H$_3$CH), 24.76 (CH$_3$*C*H$_2$CH), 40.84 (CH$_3$*C*H$_2$N), 43.02 (CH$_3$*C*H), 50.65 and 50.90 (*C*H$_3$OCOCH=CH), 52.77 (*C*H$_3$OCOCtbond]C), 76.02 (CH$_3$OCO*C*≡C), 79.48 (N-*C*H-N), 84.23 (CH$_3$OCOC≡*C*), 86.72 and 89.56 (CH$_3$OCO*C*H=CH), 145.31 and 146.79 (CH$_3$OCOCH=*C*H), 153.25 (CH$_3$O*C*OC≡C), 169.11 and 169.74 (CH$_3$O*C*OCH=CH); ESI-MS: (M+H) 381.29. Anal. Calc. for $C_{19}H_{28}N_2O_6$ (380.44): C, 59.99; H, 7.42; N, 7.36. Found:C, 60.11; H, 7.29; N, 7.50.

Methyl 4-((3-methoxy-3-oxoprop-1-enyl){1-[[(1E)-3-methoxy-3-oxoprop-1-enyl](propyl)amino]propyl}amino)hex-2-ynoate (10g). Compound **10g** was obtained as yellow nondistilled oil in yield 32%. Eluent – hexane : ethyl acetate = 4:1. R_f= 0.46 (eluent – hexane : ethyl acetate = 3 : 1); IR: 607, 666, 757, 794, 901, 945, 975, 1081, 1174, 1188, 1208, 1260, 1381, 1435, 1458, 1607, 1687, 2877, 2966, 3339 cm^{-1}; ^{1}H-NMR, δ, ppm: 0.91 (m, 9H, CH_3CH_2), 1.30–2.05 (m, 6H, CH_3CH_2), 3.08 (m, 2H, $CH_3CH_2CH_2N$), 3.70 (br s, 9H, CO_2CH_3), 3.75 (m, 1H, CH_3CH_2CHN), 4.32 (m, 1H, NCHN), 4.75 (d, 1H, CH=CHNC$_3$H$_7$, ^3J = 12.3 Hz), 4.89(d, 1H, CH=CHNCH, ^3J = 14.4 Hz), 7.30 (d, 1H,CH=CHNCH, ^3J = 14.4 Hz), 7.49 (d, 1H, CH=CHNC$_3$H$_7$, ^3J = 12.3 Hz); ^{13}C-NMR, δ, ppm: 9.62 ($CH_3CH_2CHNC_3H_7$), 10.98 ($CH_3CH_2CH_2N$), 11.14 (CH_3CH_2CHN), 21.43 ($CH_3CH_2CHNC_3H_7$), 26.32 ($CH_3CH_2CH_2N$), 26.81 (CH_3CH_2CHN), 50.18, 51.78 and52.52 (CO_2CH_3), 53.53 ($CH_3CH_2CH_2N$), 55.22 (CH_3CH_2CHN), 69.28 (NCHN), 86.06 (CH=CHNC$_3$H$_7$), 89.97 (CH=CHNCH), 95.23 (C≡CCO$_2$CH$_3$), 98.15 (C≡CCO$_2$CH$_3$), 145.83 and 147.18 (NCH=CHCO$_2$CH$_3$), 166.02 (C≡CCO$_2$CH$_3$), 169.01 and 169.16 (C=CCO$_2$CH$_3$); ESI-MS: (M+H) 409.34. Anal. Calc. for $C_{21}H_{32}N_2O_6$ (408.49): C, 61.75; H, 7.90; N, 6.86. Found:C, 61.49; H, 7,68; N, 6.93.

General procedure for an interaction of 1,2-dialkyldiaziridines and 1,2,3-trialkyldiaziridines 1a–g with methyl propiolate 9 in ionic liquids. To a stirred mixture of 1.0 mmol of initial diaziridine **1** and 0.5 g ionic liquid ([bmim][BF_4] or [bmim][PF_6] for 1,2-dialkyldiaziridines **1a**–**e** or [emim][HSO_4] for 1,2,3-trialkyldiaziridines **1f**,**g**) at temperature 0–5°C, methyl propiolate **9** (0.168 g, 2.0 mmol) was added drop-wise for about 1 min, the temperature was raised to 20°C, and reaction mixture was stirred 36 h for diaziridines **1a**–**c** (72 h for diaziridines **1d**–**f** and 100 h for diaziridine **1g**) to disappearance of initial diaziridine (TLC-control). After that, the products obtained were extracted from ionic liquid with a mixture of solvents (CH_2Cl_2 : Et_2O = 1 : 6 six to seven times by 7 mL), then the solvents were evaporated. Compounds **10** and **11** were isolated by the method of column chromatography on Silicagel (eluent—hexane : ethyl acetate in different ratio). Ionic liquid was reused in the same reaction three times.

Methyl 1-butyl-3-[(1E)-3-methoxy-3-oxoprop-1-enyl]-4-propyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (11a) and methyl 4-{({butyl[(1E)-3-methoxy-3-oxoprop-1-enyl]amino}methyl)[(1E)-3-methoxy-3-oxoprop-1-enyl]amino}hept-2-ynoate (10a). Compound **11a** was obtained as yellow nondistilled oil in yield 41%. Eluent – hexane : ethyl acetate = 2 : 1. R_f = 0.53 (eluent – hexane : ethyl acetate = 2 : 1). IR: 668, 760, 1080, 1216, 1436, 1616, 1680, 2876, 2960, 3020 cm^{-1}; ^{1}H-NMR, δ, ppm: 0.91 (m, 3H, $CH_3(CH_2)_2CH$), 0.94 (m, 3H, $CH_3(CH_2)_3N$), 1.31 (m, 2H, $CH_3CH_2(CH_2)_2N$), 1.37 (m, 2H, $CH_3CH_2CH_2CH$), 1.56 (m, 2H, $CH_3CH_2CH_2CH_2N$), 1.41 and 1.76 (both m, 2H, $CH_3CH_2CH_2CH$), 3.14 (t, 2H, NCH_2, ^3J = 7.4 Hz), 3.64 and 3.66 (both s, 6H, $(CO_2CH_3)_2$), 4.13 (d, 1H, $CHCH_2$, ^3J = 9.5 Hz), 4.20 and 4.41 (bothd,2H, NCH_2N, ^2J = 12.4 Hz), 4.81 (d, 1H, HC=CHCO$_2$CH$_3$ ^3J = 13.6 Hz), 7.28 (s, 1H, CH=CCO$_2$CH$_3$), 7.42 (d, 1H, NCH=CH, ^3J = 13.6Hz); ^{13}C-NMR, δ, ppm:13.56($CH_3(CH_2)_3N$), 13.75 ($CH_3(CH_2)_2CH$), 18.91($CH_3CH_2CH_2CH$), 19.71 ($CH_3CH_2(CH_2)_2N$), 30.74 ($CH_3CH_2CH_2CH_2N$), 37.77 ($CH_3CH_2CH_2CH$), 50.61 and 50.64 (CO_2CH_3), 53.44 (NCH_2), 55.62 ($CH_3(CH_2)_2CH$), 58.61 (NCH_2N), 87.90 (HC=CHCO$_2$CH$_3$), 98.14 (CH_3CO_2C=CH), 143.77 (CH_3CO_2C=CHN), 151.70 (CH=CHCO$_2$CH$_3$), 166.78 and 169.70 (C=O); ^{15}N-NMR, δ ppm: –279.3 (NCH=CH), –279.6 (CH_2NCH_2); ESI-MS:(M+H) 325.21. Anal. Calc. for $C_{17}H_{28}N_2O_4$ (324.42): C, 62.94; H, 8.70; N, 8.64. Found:C, 63.28; H, 8.53; N, 8.83.

Compound **10a** was isolated in yield 36%.

Methyl 4-ethyl-3-[(1E)-3-methoxy-3-oxoprop-1-enyl]-1-propyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (11b) and methyl 4-([(1E)-3-methoxy-3-oxoprop-1-enyl]{[[(1E)-3-methoxy-3-oxoprop-1-enyl](propyl)amino]methyl}amino)hex-2-ynoate (10b). Compound **11b** was obtained as yellow nondistilled oil in yield 32%. Eluent – hexane : ethyl acetate = 2 : 1. R_f = 0.48 (eluent – hexane: ethyl acetate = 2 : 1). IR: 496, 571, 619, 700, 746, 764, 795, 817, 885, 934, 949, 956, 994, 1032, 1052, 1075, 1091, 1142, 1169, 1180, 1240, 1310, 1341, 1357, 1423, 1432, 1455, 1495, 1509, 1618, 1670, 1692, 2861, 2946, 2989, 3006, 3027, 3063, 3086, 3149, 3423 cm^{-1}; ^{1}H-NMR, δ, ppm: 0.84 (t, 3H, CH_3CH_2CH, ^3J = 7.4 Hz), 0.85 (t, 3H, $CH_3CH_2CH_2N$, ^3J = 7.4 Hz), 1.37 and 1.83 (both m, 2H, CH_3CH_2CHN), 1.54 (m, 2H, $CH_3CH_2CH_2N$), 3.06 (t, 2H, $CH_3CH_2CH_2N$, ^3J = 7.2 Hz), 3.60 (s, 6H, CO_2CH_3), 4.00 (dd, ^3J = 9.8 Hz and^3J = 2.6 Hz), 4.16 and 4.35 (both d, 2H, NCH_2N, ^2J = 12.1 Hz), 4.76 (d, 1H, =CHCO$_2$CH$_3$ ^3J = 13.3 Hz), 7.24 (s, 1H, CH=CCO$_2$CH$_3$), 7.38 (d, 1H, NCH=CH, ^3J=13.3 Hz); ^{13}C-NMR, δ, ppm: 10.25 (CH_3CH_2CH), 11.00 ($CH_3CH_2CH_2N$), 22.11 ($CH_3CH_2CH_2N$), 28.49 (CH_3CH_2CH), 50.55 and 50.66 (CO_2CH_3), 53.83 ($CH_3CH_2CH_2N$), 57.29 (CH_3CH_2CHN), 58.54 (NCH_2N), 87.84 (NCH=CH), 98.01 (CH=CCO$_2$CH$_3$), 143.90 (CH=CCO$_2$CH$_3$), 151.81 (NCH=CH), 166.83 and 169.75 (C=O); ^{15}N-NMR, δ ppm: –287.0 (NC_3H_7), –287.6 (NCH=CH); ESI-MS: (M+H) 297.18. Anal. Calc. for $C_{15}H_{24}N_2O_4$ (296.37): C, 60.79; H, 8.16; N, 9.45. Found: C, 60.51; H, 8.29; N, 9.93.

Compound **10b** was isolated in yield 33%.

The same reaction in [bmim][PF_6] resulted in compounds **11b** in yield 20% and **10b** in yield 29%.

At molar ratio of **1b** : **9** = 1:1 yield of **11b** was 9% and **10b** was 7%. At molar ratio of **1b** : **9** = 1 : 3, only compound **11b** was isolated in yield 61%.

Methyl 4-[({ethyl[(1E)-3-methoxy-3-oxoprop-1-enyl]amino}methyl)(3-methoxy-3-oxoprop-1-enyl)amino]pent-2-ynoate (10c). Compound **10c** was isolated in yield 25%.

Methyl 4-benzyl-3-[(1E)-3-methoxy-3-oxoprop-1-enyl]-1-(2-phenylethyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (11d). Compound **11d** was obtained as yellow nondistilled oil in yield 57%. R_f = 0.46 (eluent—hexane : ethyl acetate = 2 : 1). IR: 413, 480, 526, 554, 595, 635, 750, 764, 793, 854, 914, 975, 1061, 1084, 1128, 1176, 1227, 1256, 1336, 1347, 1384, 1421, 1435, 1459, 1610, 1694, 2237, 2876, 2952, 3086, 3351 cm^{-1}; ^{1}H-NMR, δ, ppm: 2.75 and 3.15 (both m, 2H, $PhCH_2CHN$), 2.79 (m, 2H, $PhCH_2CH_2N$), 3.36 (m, 2H, $PhCH_2CH_2N$), 3.61 and 3.70 (both s, 6H,CO_2CH_3), 3.96 and 4.08 (both d, 2H, NCH_2N, ^2J=11.9Hz), 4.41 (m, 1H, $PhCH_2CHN$), 4.60 (d, 1H,=CHCO$_2$CH$_3$ ^3J = 13.7 Hz), 7.08–7.32 (m, 12H, 2C$_6$H$_5$, NCH=CH, CH=CCO$_2$CH$_3$); ^{13}C-NMR, δ, ppm: 36.02 ($PhCH_2CH_2N$), 40.34 ($PhCH_2CHN$), 50.60 and 50.78 (CO_2CH_3), 55.16 ($PhCH_2CH_2N$), 56.53 ($PhCH_2CHN$), 59.96 (NCH_2N), 88.03 (NCH=CH), 97.18 (CH=CCO$_2$CH$_3$), 126.58, 126.97, 128.38, 128.62, 128.71, 128.82, 128.87, 128.91, 129.48, 137.63, 137.76 (2C$_6$H$_5$), 144.00 (CH=CCO$_2$CH$_3$), 150.87 (NCH=CH), 166.64 and 169.48 (C=O); ESI-MS: (M+Na) 443.48. Anal. Calc. for $C_{25}H_{28}N_2O_4$ (420.51): C, 71.41; H, 6.71; N, 6.66. Found: C, 71.33; H, 6.90; N,6.42.

Ionic liquid after extraction of compound **11d** was evaporated in vacuum at 80°C during 3 h and two times reused for the synthesis of compound **11d**, which was isolated in yields 54 and 60%, correspondently.

Methyl 4-(4-methoxybenzyl)-3-[(1E)-3-methoxy-3-oxoprop-1-enyl]-1-[2-(4-methoxyphenyl)ethyl]-1,2,3,6-tetrahydropyrimidine-5-carboxylate (11e). Compound **11e** was obtained as yellow nondistilled oil, 42% yield. Eluent—hexane : ethyl acetate = 1 : 3. R_f = 0,36. IR: 566, 596, 666, 765, 797, 852, 906, 971, 1050, 1061, 1082, 1158, 1213, 1247, 1318, 1365, 1433, 1607, 1692, 2877, 2949, 2972, 3351 cm^{-1};^{1}H-NMR, δ, ppm: 2.71 (m, 2H, Ar$CH_2$$CH_2$N), 2.77 and 3.27 (both m, 2H, ArCH_2CHN), 3.31 (m, 2H, ArCH$_2$$CH_2$N), 3.59, 3.68, 3.73 and 3.76 (all s, 12H, OCH_3), 4.02 (qv, 2H, NCH_2N, ^3J = 12.4 Hz), 4.35 (m, 1H, ArCH$_2$$CH$N), 4.58 (d, 1H, =C$HCO_2CH_3$ ^3J = 13.2 Hz), 6.76–7.10 (m, 9H, 2C_6H_4, NCH=CH), 7.29 (s, 1H, CH=CCO$_2$CH$_3$); ^{13}C-NMR, δ, ppm: 29.55 (ArCH$_2$CH$_2$N), 39.29 (ArCH$_2$CHN), 50.31, 50.46, 50.65 and 50.91 (OCH$_3$), 55.17 (ArCH$_2$$CH_2$N), 56.57 (ArCH$_2$$C$HN), 59.85 (NCH$_2$N), 87.75 (NCH=$C$H), 96.93 (CH=$CCO_2CH_3$), 113.64, 113.92, 114.30, 129.51, 129.73 129.77, 129.85, 130.44, 158.44 and 158.67 (2C$_6$H$_4$), 144.11 (CH=CCO$_2$CH$_3$), 150.92 (NCH=CH), 166.70 and 169.53 (C=O); ESI-MS: (M+Na) 502.87. Anal. Calc. for $C_{25}H_{28}N_2O_4$ (480.23): C, 67.48; H, 6.71; N, 5.83. Found: C, 67.54; H, 6.39; N, 5.92.

Methyl 1,2-diethyl-3-[(1E)-3-methoxy-3-oxoprop-1-enyl]-4-methyl-1,2,3,6-tetrahydropyrimidine-5-carboxylate (11f). Compound **11f** was obtained as yellow nondistilled oil in yield 28%. Eluent – hexane : ethyl acetate = 4:1. R_f = 0.7 (eluent – hexane : ethyl acetate = 1 : 1); ^{1}H-NMR, δ, ppm: 0.95 (t, 3H, CH_3CH$_2$CH, ^3J = 7.4 Hz), 1.24 (t, 3H, CH_3CH$_2$N, ^3J = 7.2 Hz), 1.45 (d, 3H, CH_3CH, ^3J = 6.8 Hz), 1.79 (m, 2H, CH$_3$$CH_2$CH), 3.23 (m, 2H, N$CH_2$), 3.69 and 3.70 (both s, 6H, (CO$_2$$CH_3$)$_2$), 4.26 (m, 1H, N$CH$N), 4.31 (qv, 1H, CH$_3$$CH$, ^3J = 6.8 Hz), 4.76 (d, 1H, HC=CHCO$_2$CH$_3$ ^3J = 13.1 Hz), 7.33 (s, 1H, CH=CCO$_2$CH$_3$), 7.50 (d, 1H, NCH=CH, ^3J = 13.1 Hz); ^{13}C-NMR, δ, ppm: 10.12 (CH$_3$CH$_2$CH), 14.55 (CH$_3$CH$_2$N), 18.91 (CH$_3$CH), 26.33 (CH$_3$$CH_2$CH), 48.66 (CH$_3$$C$H), 50.64 (N$CH_2$), 50.64 and 50.72 (CO$_2$$CH_3$), 54.82 (N$C$HN), 85.57 (HC=$CHCO_2CH_3$), 97.07 (CH$_3CO_2$$C$=CH), 141.54 (CH$_3CO_2$C=$C$H), 149.77 (N$C$H=CHCO$_2CH_3$), 166.90 and 170.13 (C=O); ^{15}N-NMR, δ ppm: −267.4 (NCH=CH), −269.2 (NCH$_2$); ESI-MS: (M+H) 297.21 Anal. Calc. for $C_{15}H_{24}N_2O_4$ (296.37): C, 60.79; H, 8.16; N, 9.45. Found:C, 60.93; H, 8.04; N, 9.68.

Methyl 2,4-diethyl-3-[(1E)-3-methoxy-3-oxoprop-1-enyl]-1-propyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (11g). Compound **11g** was obtained as yellow nondistilled oil in yield 13%. Eluent – hexane : ethyl acetate = 4 : 1. R_f = 0.26. (eluent – hexane : ethyl acetate = IR: 668, 765, 796, 972, 1052, 1080, 1156, 1229, 1260, 1429, 1606, 1687, 2851, 2875, 2926, 2962, 3090 cm^{-1}; ^{1}H-NMR, δ, ppm: 0.89 (t, 3H, CH_3CH$_2$CHN, ^3J = 7.5 Hz), 0.99 (t, 3H, CH_3CH$_2$CHC=, ^3J = 7.4 Hz), 1.04 (t, 3H, CH_3(CH$_2$)$_2$N, ^3J = 7.5 Hz), 1.56 (m, 2H, CH$_3$$CH_2CH_2$N), 1.56 and 1.73 (both m, 2H, CH$_3$$CH_2$CHN[1]), 1.80 and 2.04 (both m, 2H, CH$_3$$CH_2$CHC=), 3.11 (m, 2H, N$CH_2$), 3.66 and 3.68 (both s, 6H, (CO$_2$$CH_3$)$_2$), 4.25 (m, 1H, CH$_3CH_2$$CH$C=), 4.30 (m, 1H, N$CH$N), 4.77 (d, 1H, HC=C$HCO_2CH_3$, ^3J = 13.2 Hz), 7.29 (s, 1H, CH=CCO$_2$CH$_3$), 7.57 (d, 1H, NCH=CH, ^3J = 13.2 Hz); ^{13}C-NMR, δ, ppm: 10.23 (CH$_3$CH$_2$CHN), 10.98 (CH$_3$CH$_2$CHC=), 11.90 (CH$_3$(CH$_2$)$_2$N), 22.62 (CH$_3$$CH_2CH_2$N), 26.31 (CH$_3$$CH_2$CHN), 31.91 (CH$_3$$CH_2$CHC=), 50.64 and 50.69 (CO$_2$$CH_3$), 55.10 (CH$_3CH_2$$C$HC=), 55.23 (N$CH_2$), 69.24 (N$C$HN), 86.05 (HC=$CHCO_2CH_3$), 96.33 (CH$_3CO_2$$C$=CH), 142.18 (CH$_3CO_2$C=$C$H), 152.99 ($C$H=CHCO$_2CH_3$), 167.00 and 170.13 (C=O); ESI-MS: (M+Na) 347.19. Anal. Calc. for $C_{17}H_{28}N_2O_4$ (324.42): C, 62.94; H, 8.70; N, 8.64. Found: C, 62.71; H, 8.95; N, 8.43.

1,2-Bis[2-(4-methoxyphenyl)ethyl]diaziridine (1e). Yield 31%. mp = 55°C (Et$_2$O). ^{1}H-NMR, δ, ppm: 2.43 (s, 2H, CH$_{2ring}$), 2.55 (m, 2H, NCH$_{2a}$), 2.78 (m, 2H, NCH$_{2b}$), 2.85 (m, 4H, CH_2Ar), 3.71 (c, 6H, CH$_3$O), 6.70 and 7.25 (both d. 8H, CH in Ar, ^3J = 7.60 Hz); ^{13}C-NMR, δ, ppm: 34.3 (CH$_2$Ar), 55.1 (NCH$_2$CH$_2$), 56.9 (CH$_{2ring}$), 62.8 (CH$_3$O), 113.3, 129.6, 131.7, 157.9 (Ar).

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