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Study of Cyclyzation of *o*-(1-Alkynyl)- and *o*-(1,3-Butadiynyl)aryltriazenes under the Action of Acids

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Abstract—The investigation of Richter cyclization of *o*-(1-alkynyl)- and *o*-(1,3-butadiynyl)arenediazonium salts generated by acid cleavage of triazenes was carried out by the methods of NMR and ESI MS (Electrospray Ionization Mass Spectrometry). The effect was shown of the substituents at the carbon atom of the triple bond and in the aromatic ring, of the solvent, temperature, and the reagents ratio on the rate of the cyclization and the yield of its products, 4-bromo-3-alkyl- and 4-bromo-3-ethynylcinnolines; the conditions of their synthesis were optimized. The possibility to use 4-bromo-3-ethynylcinnolines as substrates of electrophilic cyclization was demonstrated.

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In the last decade the chemistry of cinnoline and its derivatives has been essentially developed since these compounds possess diverse kinds of biological activity [1–7] and interesting optoelectronic characteristics [8, 9]. Among the methods of the synthesis of these compounds the main procedures should be mentioned applying as precursors the derivatives of arenediazonium salts (Richter, Widman–Stoermer, and Borsche–Herbert cyclizations), arylhydrazones and arylhydrazines, and nitro derivatives were also used for the synthesis of polyfused cinnolines by reductive methods [10–12].

Although the synthesis of the cinnoline core was first performed by the diazotization of *o*-aminophenylpropionic acid followed by the cyclization of the obtained salt [13] only to the end of the previous century the attention of researchers was turned to Richter reaction as the method of the synthesis of 4-halocinnolines [14]. Owing to the reactivity of the halogen atom in the nucleophilic substitution these compounds are convenient building blocks for the preparation of biologically active substances [15, 16], in particular, cinnoline 4-amino derivatives and their salts [17]. Also the development of the Pd-catalyzed cross-coupling made accessible starting *ortho*-ethynyl-substituted arenediazonium salts containing in the aromatic ring substituents of versatile character.

Along with the classic diazotization of *o*-ethynylarylamines [13, 14] Bräse et al. for the first time obtained 4-bromo-(chloro)cinnolines by the cyclization of *ortho*-ethynylarylaryltriaz-1-enes under the acid cleavage [18]. Depending on the structure of the starting substrates and the reaction conditions in both cases the process may occur by the *endo-dig* type with the formation of 4-halocinnolines and the side products of their hydrolysis, cinnolin-4-ones [14, 18, 19], as well as by the *exo-dig* type leading to indazoles [19–23].

Based on the cyclization of *o*-buta-1,3-diynylaryltriazenes under the action of HBr and HCl we formerly developed an approach to the synthesis of 4-bromo-(chloro)-3-ethynylcinnolines [24]. This approach is more advantageous than the diazotization of the diacetylene derivatives of arylamines [25, 26] for it makes it possible to avoid the side processes and provides better yields of the target products. However it was found that the cyclization rate of the *o*-buta-1,3-diynylaryltriazenes was affected by the concentration of the acid and the character of the substitutents in the aromatic ring. In the presence of the acceptor methoxycarbonyl substituent the side hydrolysis products were formed, and the yield of the target 3-alkynyl-4-bromocinnoline did not exceed 41% [26].

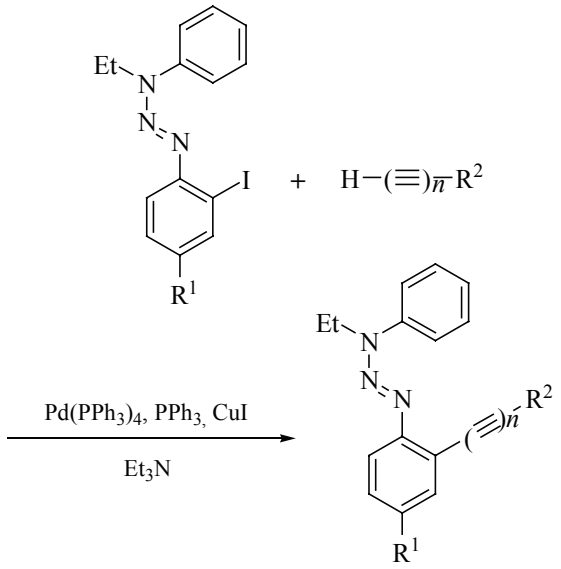
Since as the 4-bromo-3-ethynylcinnolines are of interest as building-blocks for the preparation of polyfused heterocycles and endiyne systems [24, 27] we have

investigated in this work the effect of the reaction conditions and the triazene structure on the course of Richter cyclization aiming at the optimization of the synthesis of 4-bromocinnolines.

We have chosen as the objects of the study the derivatives of *o*-(ethynyl)- and *o*-(1,3-butadiynyl)aryltriazenes **Ia–Ii** containing diverse substituents both in the aromatic ring in the *para*-position to the triazene function and at the triple bond. These compounds were synthesized by Sonogashira reaction [28] of 2-iodoaryltriazenes with the terminal mono- and diacetylenes [29] (Scheme 1).

We first studied the effect of the substituents in the aromatic ring on the rate of triazene **I** cyclization with the use of ^{1}H NMR spectroscopy. The cyclization of 0.1 M solutions of triazenes **Ib, Ic** in acetone-d_6 in the presence of 20-fold molar excess of 48% HBr was carried out in the NMR tubes (Scheme 2).

Scheme 1.



Ia–Ii

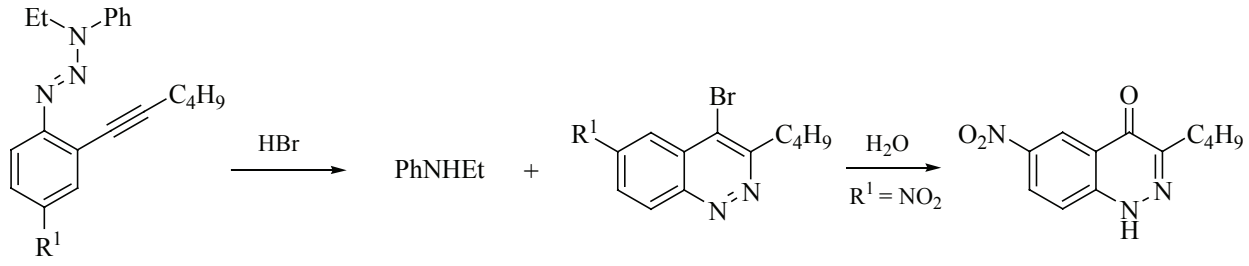
n = 1, R^2 = C_4H_9, R^1= CH_3 (**a**), Br (**b**), NO_2 (**c**), COOMe (**d**); n = 2, R^2 = C_8H_{17}, R^1= CH_3 (**e**), Br (**f**), COOMe (**g**); n = 2, R^2 = Ph, R^1= Br (**h**), COOMe (**i**).

It turned out that in the ^{1}H NMR spectra of the mixtures obtained 3 min after the addition of HBr only the signals of cyclization products 4-bromocinnolines **IIIb, IIIc** and of N-ethylaniline were observed. Besides in the ^{1}H NMR spectrum of the sample of the formed cinnoline **IIIc** registered 15 min later signals of its hydrolysis product, 6-nitrocinnolin-4-one (**IVc**) were appeared. The spectrum of this sample obtained after 2 days contained only the signals of cinnolinone **IVc**. 4-Bromo-6-nitrocinnoline **IIIc** also easily hydrolyzed at storage and even under the conditions of the registration of ESI MS (Electrospray Ionization Mass Spectrometry) spectra where a strong peak was observed belonging to the 6-nitrocinnolin-4-one. Thus the presence of a strong electron-acceptor substituent resulted in the substitution of bromine in the position *4* of the cinnoline skeleton for the hydroxy group. The acceleration of the nucleophilic substitution of halogens in the position *4* of cinnolines in strong acidic media we found earlier [26].

Although the ^{1}H NMR spectroscopy proved to be useful for establishing the fast proceeding of Richter cyclization of monoacetylene triazene derivatives **Ib, Ic**, this method possessed significant drawbacks. The presence of excess HBr not only complicated the assignment of the signals in the spectra of the reaction mixtures but also led to the broadening of the signals from the formed 4,6-dibromocinnoline **IIIb** due to the partial precipitation of its hydrobromide .

We have decided to use in the monitoring of the reactions ESI MS which now becomes a frequent tool in the

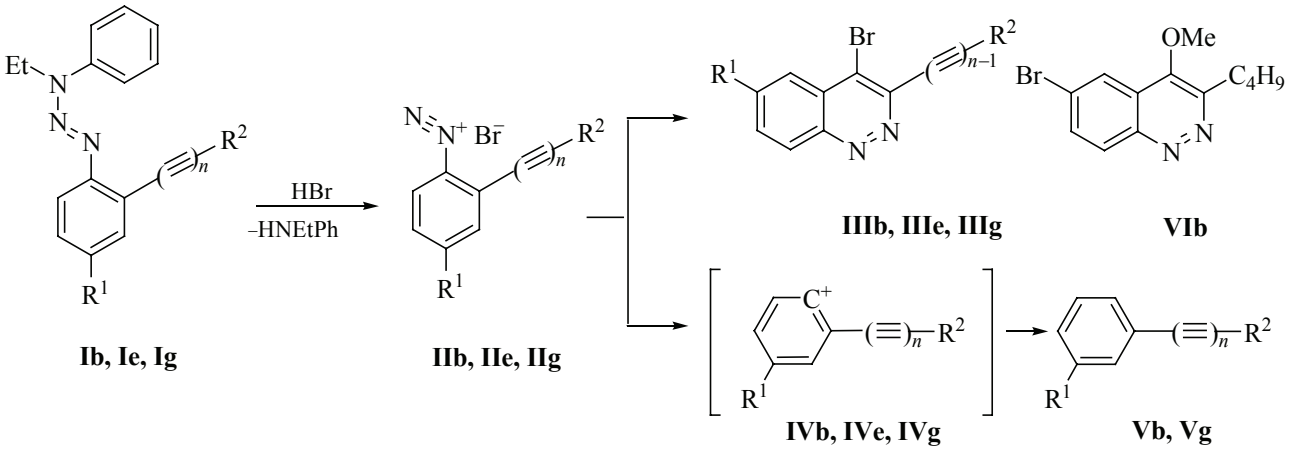
Scheme 2.



Ib, Ic **IIIb, IIIc** **IVc**

R^1 = Br (**b**), NO_2 (**c**).

Scheme 3.



Ib, Ie, Ig **IIb, IIe, IIg** **IIIb, IIIe, IIIg** **VIb** **IVb, IVe, IVg** **Vb, Vg**

n =0 (**IIb**), 1 (**IIe, IIg, IIIb, IVb**), 2 (**IIIe, IIIg, IVe, IVg**).

study of mechanisms of organic reactions [30, 31]. The spectra of triazene solutions after mixing with HBr solutions were registered on-line during continuous spraying of the reaction mixture. The spectra were registered in 40 s, 3, 6, or 8 min after the addition of the hydrobromic acid solution. The obtained data are presented in Schemes 3, 4 and in Tables 1, 2.

It was found that in the acetone medium Richter cyclization of triazene **Ie** (10^{-4} mol l^{-1}) with 48% HBr (10^{-1} mol l^{-1}) and the subsequent hydrolysis of 4-bromocinnoline **IIIe** proceeded so fast that already in the first spectrum of the reaction mixture only the signal with *m/z* 297.1958 $[M + H]^+$ was observed corresponding to the hydrolysis product 6-methyl-3-(1,3-decadiyn-1-yl) cinnolin-4-one (*M* + H 297.1967), or to the product of its further cyclization, furocinnoline [26, 29]. Test experiments demonstrated that the replacement of acetone by methanol provided the possibility to detect the intermediate reaction products, therefore all subsequent experiments were carried out in methanol.

The spectrum of the reaction mixture of triazene **Ib** with HBr already after 40 s lacked the peaks corresponding to the protonated form of the starting compound **Ib** and only signals belonging to the diazonium cation **IIb** and the products of its transformations were observed (Scheme 3, Table 1).

In the spectrum of diacetylene triazene **Ig** containing an electron-withdrawing methoxycarbonyl substituent (Scheme 3, Table 2) after 40 s the protonated form of the starting triazene was detected whose peak already in 3 min disappeared. The reaction mixture like that of the monoacetylene triazene **Ib** after 3 min contained the signals of

Table 1. Data of ESI MS spectra of the reaction mixture of triazene **Ib** with HBr[a]

Compound	*m/z* $[M + H]^+$		Time of the spectrum registration from the moment of HBr addition		
	Calculated	Found	40 s	3 min	8 min
Ib	384.1075		–	–	–
IIb	263.0184	263.0195	+	+	+
IIIb	342.9445	342.9454	+	+	+
PhNHEt	122.0970	122.0987	+	+	+
Vb	235.0122	235.0130	–	+	+
VIb	295.0446	295.0452	–	+	+

[a] Concentrations: **Ib** 10^{-5} mol l^{-1}, HBr 10^{-2} mol l^{-1}.

Table 2. ESI MS spectra of the reaction mixture of triazene **Ig** with HBr[a]

Compound	*m/z* $[M + H]^+$		Time of the spectrum registration from the moment of HBr addition		
	Calculated	Found	40 s	3 min	6 min
Ig	444.2651	444.2641	+	–	–
IIg	323.1760	323.1758	–	+	+
IIIg	403.1021	403.1009	–	+	+
PhNNEt	122.0970	122.0978	–	+	+
IVg	295.1698	295.1700	–	+	+
Vg	297.1855	297.1864	–	+	+

[a] Concentrations: **Ig** 10^{-5} mol l^{-1}, HBr 10^{-2} mol l^{-1}.

the diazonium cation and of its transformation products.

According to the data of mass spectrometry the main path of the transformation of diazonium cations **IIb**, **IIg** was the cyclization resulting in 4-bromocinnolines **IIIb, IIIg**. Besides it was possible to detect by ESI MS the ions corresponding to aryl cations **IVb–IVg** formed due to the reductive deamination of the diazonium cations. This transformation product **Vg** appeared in the mass spectra under the ESI conditions only in the case of the methoxycarbonyl derivative **Ig**.

The registration of a series of spectra of the reaction mixture of triazenes **Ie, Ig** (10^{-5} mol l^{-1}) with 48% HBr (10^{-1} mol l^{-1}) in the presence of an internal reference, *p*-toluidine (10^{-5} mol l^{-1}), for 10 min every ~20 s permitted the establishment of the parallel changes in the concentrations of the diazonium cation and the aryl cation indicating that the arenediazonium cation decomposed with the formation of the aryl cataion mainly directly in the spray chamber of the spectrometer after the spraying and desolvation processes.

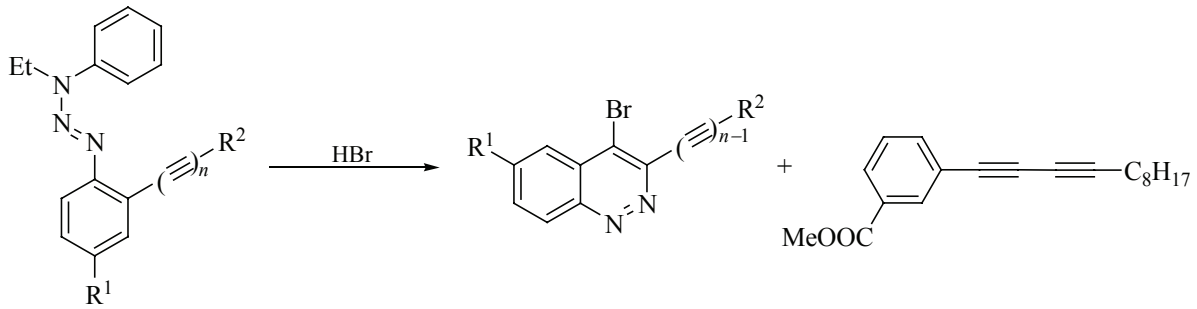
In the mass spectra of the reaction mixture of the bromoderivative **Ib** with HBr also a weak signal was observed corresponding to 4-methoxycinnoline **VIb**. The formation of 4-methoxycinnolines along with 4-chlorocinnolines was formerly observed at the diazotization and cyclization of diacetylene derivatives of arylamines in methanol saturated with HCl [26]. However in the spectra of the reaction mixtures of diacetylene derivatives **Ie, Ig** in methanol we did not find either signals of 4-methoxycinnolines, or 4-cinnolinones, or the products of cyclization of the latter, furocinnolines.

Therefore the application of the ESI MS method to the monitoring of Richter reaction made it possible to detect the diazonium cations formed at the triazenes decomposition under the action of HBr, and the products of their transformations. It was also found that the cyclization rate is affected by the nature of the solvent, and under equal conditions the conversion of alkynylaryltriazene **Ib** proceeded faster than that of alkadiynylaryltriazenes **Ie, Ig**.

On the second stage of the research we estimated the effect of substituents at the carbon atom of the triple bond and in the benzene ring on the cyclization rate of triazenes using the NMR spectroscopy. The cyclization of aryltriazenes **Ib, Id, If–Ii** under the treatment of concn. HBr was carried out in acetone (Scheme 4). After 3 min from the beginning of the reaction the water solution of triethylamine was added. After the treatment of the reaction mixtures the relative content of products was determined by ^{1}H NMR spectra. The results obtained are presented in Scheme 4 and Table 3. The relative content of compounds **I, III, V** was estimated by the comparison of the intensity of signals in the ^{1}H NMR spectra: of the protons of the aromatic ring H^5 (**Ib**), H^3 (**Id, If, Ig, Ii**), H^2 (**Vg**), of the CH_2 group adjacent to the triple bond (**Ih**), and of atom H^7 of cinnolines **III**.

The cyclization of alkynylaryltriazenes **Ib, Id** (Table 3, runs nos. *1*, *2*) proceeded considerably faster than that of *ortho*-(1,3-butadiynyl)aryltriazenes **If–Ii** (Table 3, runs nos. *3–6*), and after 3 min the reaction mixtures contained only cinnolines **IIIb, IIId**. With the diacetylene derivatives of aryltriazenes the conversion within 3 min was incomplete, and in the mixtures the signals appeared of starting compounds **I** alongside the signals of cinnolines **III**. The replacement in the aromatic ring of the substituent COOMe (**Ig**, **Ii**) by the weaker electron-acceptor bromine atom (**If, Ih**) resulted in an insignificant acceleration of the cyclization (cf. runs nos. *3* and *4*, *5* and *6*). At the same time the replacement of the alkyl substituent at the conjugated system of triple bonds in the triazenes **If, Ig** by the phenyl group in **Ih, Ii**

Scheme 4.



Ib, Id, If–Ii **IIIb, IIId, IIIf–IIIi** **Vg**

III, $n = 1$, $R^2 = C_4H_9$, R^1= Br (**b**), COOMe (**d**); $n = 2$, $R^2 = C_8H_{17}$, R^1= Br (**f**), COOMe (**g**); R^2 = Ph, R^1= Br (**h**), COOMe (**i**).

Table 3. Richter cyclization of *o*-(1-hexynyl)aryltriazenes **Ib, Id** and *ortho*-(1,3-butadiynyl)aryltriazenes **If–Ii** at the action of HBr

Run no.[a]	Compd. no.	Concentration of compound **I**, mol l^{-1}	Molar ratio **I**–conc. HBr	Content of compounds (by the data of ^{1}H NMR spectrum), %		
				III	**I**	**V**
1	**Ib**	0.1	1 : 20	100	–	–
2	**Id**	0.1	1 : 20	100	–	–
3	**Ig**	0.1	1 : 20	32	68	–
4	**If**	0.1	1 : 20	37	63	–
5	**Ii**	0.1	1 : 20	50	50	–
6	**Ih**	0.1	1 : 20	59	41	–
7	**Ig**	0.1	1 : 20	67	20	13
8	**Ig**	0.1	1 : 10	28	56	16
9	**Ig**	0.1	1 : 40	24	71	5
10	**Ig**	0.005	1 : 20	59	29	12
11	**Ig**	0.04	1 : 20	7	71	22

[a] Runs nos. *1–10* were carried out in acetone, run no. *11*, in a mixture MeOH–CH_2Cl_2, 5:1, at 20°C, run no. *7*, at 30°C.

resulted in a considerable acceleration of the cyclization (cf. runs nos. *3* and *5*, *4* and *6*).

The influence on the cyclization rate of the temperature, molar ratio triazene–HBr, triazene concentration and the solvent character was studied by an example of compound **Ig** (runs nos. *7–11*). Raising the temperature by 10°C resulted in an increased reaction rate and a greater fraction of the cyclization product **IIIg** (runs nos. *3*, *7*), but therewith formed the product of the reductive deamination **Vg**. The formation of this side product was also observed at the 2-fold decrease in the acid excess up to 10 equiv (run no. *8*); therewith the ratio of the cyclization product **IIIg** and the starting triazene did not change as compared with the run no. *3*. The increase in the HBr excess to 40 equiv (run no. *9*) in contrast to the expectations resulted in a considerable deceleration of the cyclization, and the dilution of the reaction mixture with acetone (run no. *10*) led to the increased rate of the cyclization (runs nos. *3*, *10*). The replacement in the run no. *11* of the aprotic solvent by a protic one (methanol) significantly decelerated the reaction (runs nos. *3*, *11*) and led to the formation of the fraction of the product of reductive deamination **Vg.**

Table 4. Richter cyclization of triazene **Ib**

Run no.	Acid	Molar ratio triazene–acid	Molar ratio triazene–Et_4NBr	Reaction time, min	Main reaction product (^{1}H NMR data)
1	H_2SO_4	1 : 2	[a]	3	**Ib**
2	H_2SO_4	1 : 2	1 : 20	60	**IIIb**
3	H_2SO_4	1 : 20	1 : 20	15	**IIIb**
4	HCl	1 : 2	1 : 2	1.5	**IIIj**[b]

[a] Without addition of Et_4NBr. [b]The reaction mixture contained only 4-chlorocinnoline **IIIj**.

The variations in the cyclization rate in the runs nos. *9–11* may be ascribed to the influence of the solvation effects on the cyclization of the diazonium cations suggesting that tight ion pairs are involved in the cyclization [26]. The increase in the excess of 48% HBr in the run no. *9* was accompanied also with the increased molar fraction of water in the reaction mixture; this fact same as the use of methanol (run no. *11*) might destroy the tight ion pairs. The dilution of the reaction mixture with acetone, a polar aprotic solvent, results in reducing the molar part of water, and this is favorable for the formation of tight ion pairs and results in the increase in the reaction rate (run no. *10*).

The influence of the acid and its concentration was investigated in the second set of experiments. The decomposition of 0.1 m solutions of triazene **Ib** in acetone was performed by the action of sulfuric and hydrochloric acids. After 3 min to the reaction mixture a solution of tetraethylammonium bromide in aqueous acetone (acetone–water 20:1 v/v) was added. The completeness of the reaction was monitored by TLC. On the completion of cyclization the reaction mixture was diluted with triethylamine water solution and after the treatment the ^{1}H NMR spectra of mixtures obtained were registered. The results are listed in Table 4.

Unlike the reaction with HBr the treatment of 0.1 M solution of triazene **Ib** in acetone with 2 equiv of sulfuric acid did not result in the formation of the cyclization products, and after processing the reaction mixture with triethylamine the starting triazene was recovered (Table 4, run no. *1*). If after 3 min this reaction mixture was diluted with the Et_4NBr solution the formation of compound **IIIb** was observed, and in 1 h the triazene completely con-

verted into bromocinnoline **IIIb** (run no. *2*). The reaction rate grew with the increased excess of sulfuric acid (run no. *3*), but still the cyclization proceeded slower than in HBr (Table 3, run no. *1*). At the action on triazene **Ib** of 2 equiv of HCl with the subsequent addition to the reaction mixture of 2 equiv of tetraethylammonium bromide (run no. *4*) the only cyclization product according to the NMR and mass spectra was 4-chlorocinnoline **IIIj**.

Thus the data obtained confirm that the cyclization of *o*-ethynyl- and *o*-buta-1,3-diynylaryltriazenes at the acid treatment proceeds through the stage of formation of arenediazonium cations whose cyclization into the cinnolines occurs in the tight ion pair with the counter ion. The shift of the equilibrium in the first stage is favored by the increased acid concentration, but at the use of the acid with an anion of low nucleophilicity the cyclization of the formed diazonium salt into the cinnoline does not occur. At introducing into the system of an alien nucleophilic anion the anion exchange takes place, and the diazonium cation **II** is completely converted into bromocinnoline **III**.

The strongest effect on the cyclization rate produces the character of the substituent at the triple bond involved in the cyclization. The monoacetylene derivatives are essentially more reactive in Richter cyclization than 1,3-butadiynyltriazenes that may indicate the electrophilic character of the addition which has been regarded previously as the most probable reaction mechanism [14], for the conjugated system of two triple bonds is less reactive toward the electrophiles. Yet the electrocyclization mechanism of Richter reaction also cannot be excluded. The concerted mechanism is consistent with the fact that the replacement of the alkyl substituent at the triple bond by the ethynyl moiety would essentially decrease the contribution of the atomic orbitals of the *sp*-carbon atom into the HOMO of the diazonium cation because of the appearance of the nodal plane and this would decrease the rate of the allowed electrocyclic reaction. Besides a strong effect on the cyclization rate of *o*-(1-butadiyn-1-yl)triazenes produces the character of the substituent at the conjugated system of the triple bonds whereas the cyclization rate is weakly affected by the properties of the substituents in the aromatic ring.

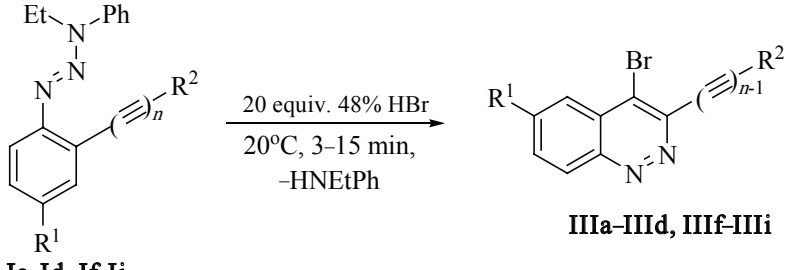
The data obtained have underlain the optimization of the procedures for the preparation of 4-bromocinnolines [18] and 4-bromo-3-ethynylcinnolines [24]. The reduction of the cyclization time of triazenes **Ia–Id** to 3 min made it possible to obtain bromocinnolines **IIIa–IIId** in 71–82% yields. The cyclization of the diacetylene derivatives **If–Ii** was carried out for 15 min, and 4-bromo-3-ethynylcinnolines **IIIf–IIIi** were isolated in 58–74% yields. Therewith even in the event of triazene **Ig** containing the methoxycarbonyl substituent no hydrolysis product cinnolin-4-one nor the furocinnoline was found (Scheme 5).

We formerly showed that 4-bromo-3-ethynylcinnolines could be used for the preparation of thienocinnolines, pyrrolocinnolines in the tandem reactions of the nucleophilic substitution-cyclization [24]. The replacement of the halogen by an ethynyl fragment in the cross-coupling reactions makes it possible to obtain endiyne systems fused with the cinnoline framework [27].

The additional opportunities of the synthetic application of 4-bromo-3-ethynylcinnolines in the electrophilic cyclization previously unknown for cinnolines [32] were demonstrated by the example of 4-bromocinnoline **IIIg** whose reaction with sodium methylsulfide led to the formation of 4-methylsulfanyl-3-(1-octynyl)cinnoline (**VII**). The sybsequent electrophilic cyclization of compound **VII** under the action of iodine in acetonitrile afforded iodothienocinnoline **IX** (Scheme 6).

Thus the separation of the stages of the nucleophilic

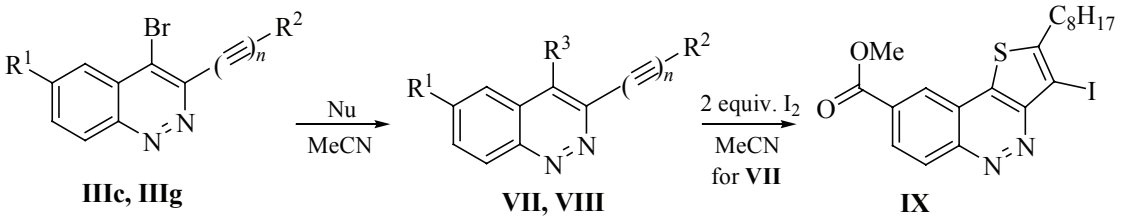
Scheme 5.



Ia–Id, If–Ii **IIIa–IIId, IIIf–IIIi**

III, n = 1, R^2 = C_4H_9, R^1= CH_3 (**a**), Br (**b**), NO_2 (**c**), COOMe (**d**); n = 1, R^2 = C_8H_{17}, R^1 = Br (**f**), COOMe (**g**); R^2 = Ph, R^1 = Br (**h**), COOMe (**i**).

Scheme 6.



IIIc, IIIg **VII, VIII** **IX**

n = 1, R^1 = COOMe, R^2 = C_8H_{17}, R^3 = NEt_2 (**VII**); n = 0, R^1 = NO_2, R^2 = C_4H_9, R^3 = SMe (**VIII**); Nu = Et_2NH (**IIIc**), MeSNa (**IIIg**).

substitution and the heterocyclization provided a possibility to easily introduce into the arising thiophene fragment the iodine atom, an important functional group for the modification of compounds obtained under the conditions of the Pd-catalyzed cross-coupling.

On 4-bromo-6-nitrocinnoline (**IIIc**) prone to hydrolysis we demonstrated the possibility to perform the nucleophilic substitution of bromine for diethylamino group without preliminary isolation of cinnoline **IIIc**. Thus from triazene **Ic** 3-butyl-4-diethylamino-6-nitrocinnoline (**VIII**) was obtained in an overall yield of 52%.

Hence we have demonstrated that along with the NMR spectroscopy the ESI MS method can be successfully used for the monitoring of Richter reaction. The application of the latter method provided valuable information on the intermediates formed in the course of the reaction. Based on the performed research we found optimal conditions of the synthesis of 4-bromo-3-ethynyl- and -3-alkylcinnolines containing both electron-donor and electron-acceptor substituents in the aromatic ring. We demonstrated the synthetic potential of 4-bromo-3-ethynylcinnolines as substrates for the electrophilic cyclization aiming at the preparation of iodine-containing polyheterocycles.

EXPERIMENTAL

The elemental analysis was carried out on an instrument EuroVector 3000. ^{1}H (300.13 MHz) and ^{13}C (75.5 MHz) NMR spectra were registered on a spectrometer Bruker DPX 300. The chemical shifts were measured with respect to the residual signals of the solvent $CDCl_3$ (δ_H 7.26, δ_C 77.00 ppm). High resolution mass spectra with electrospray ionization were recorded on a spectrometer Bruker MicroTOF in the mode of positive ions registration (solvent methanol, ionizing additive 30% formic acid, ionization potential 70 V, voltage on the capillary 4500 V, drying gas temperature 180°C).

Study of Richter cyclization of triazenes Ib,Ic by ^{1}H NMR spectroscopy. To a solution of 0.07 mmol of triazene in 0.7 ml of acetone-d_6 in an NMR tube was fast added 1.4 mmol (0.16 ml) of 48% HBr, the tube was thoroughly shaken, and the ^{1}H NMR spectra were registered. The first spectrum was registered 3 min after the addition of HBr, the subsequent spectra, with 2–3 min interval. The overall time of the experiment was 15 min.

Study of Richter cyclization of triazenes Ib,Id, Ig by ESI MS method. To a solution of triazene **Ib** (Table 1), **Ig** (Table 2), or a mixture of triazenes **Ie, Ig** and *p*-toluidine in methanol was added a solution of concn. HBr in methanol. The time from HBr addition to the registration of the first spectrum was ~40 s. The time of observation in the continuous mode was 6–8 min (the admission of the sample flow into the spectrometer by a syringe pump at a rate 180 μl h^{-1}).

Study of Richter cyclization of triazenes Ib,If by ^{1}H NMR spectroscopy. To a solution of 0.05 mmol of triazene in an appropriate volume of the solvent was quickly added at vigorous stirring a calculated quantity of concn. hydrobromic acid (Table 3). The reaction mixture was stirred at a controlled temperature for 3 min and was poured into 10 ml of water solution of Et_3N (equivalent to the amount of HBr), the product was extracted into dichloromethane, the extract was washed with a saturated solution of NH_4Cl and with water, the organic layer was separated, dried with anhydrous sodium sulfate, the solvent was removed in a vacuum, the residue was dissolved in 0.6 ml of $CDCl_3$, and the ^{1}H NMR spectrum was registered.

***ortho*-(1-Hexyn-1-yl)aryltriazenes Ia–Id and *ortho*-(dodeca-1,3-diynyl)aryltriazenes Ie–Ig. General procedure**. To a solution of 1.5 mmol of 1-(2-iodophenyl)-3-phenyl-3-ethyltriaz-1-ene [33, 34] in 15 ml of Et_3N

and 5 ml of dichloromethane were added in succession 2.25 mmol of an appropriate terminal alkyne or diyne [29], 0.075 mmol (0.087 g) of $Pd(PPh_3)_4$, and 0.15 mmol (0.039 g) of PPh_3. For 5 min the reaction mixture was flushed with argon, then 0.225 mmol (0.043 g) of CuI was added, and the stirring in an argon flow at 50°C (for compounds **Ia–Id**) or at 40°C (for compounds **Ie–Ig**) was continued till the complete conversion of the starting iodotriazenes (1– 24 h). The reaction mixture was poured into a saturated solution of NH_4Cl (~50 ml), extracted with dichloromethane (3 × 15 ml), the organic layer was washed with the saturated solution of NH_4Cl (2 × 20 ml) and water (30 ml), dried with Na_2SO_4, dichloromethane was removed in a vacuum. The reaction products were isolated by column chromatography on silica gel.

1-[2-(1-Hexynyl)-4-methylphenyl]-3-phenyl-3-ethyltriaz-1-ene (Ia). Yield 31% (eluent petroleum ether–ethyl acetate, 40:1), bright-orange oily substance. ^{1}H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3, *J* 7.3 Hz), 1.37 t (3H, CH_3, *J* 7.3 Hz), 1.46–1.67 m (4H, $2CH_2$), 2.34 s (3H, CH_3), 2.49 t (2H, CH_2, *J* 7.3 Hz), 4.36 q (2H, CH_2, *J* 7.3 Hz), 7.09–7.11 m ($2H_{arom}$), 7.31 d ($1H_{arom}$, *J* 1.5 Hz), 7.36–7.51 m ($5H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.9, 13.7, 19.4, 20.8, 22.0, 30.9, 39.9 (Bu, Et, Me), 78.5 (C_{sp}), 94.5 (C_{sp}), 116.5, 117.5, 119.8, 123.1, 129.1, 129.2, 133.4, 135.8, 144.3, 149.2 (C_{arom}). Found: *m/z* 320.2088 $[M + H]^+$. $C_{21}H_{25}N_3$. Calculated (*M* + H) 320.2127.

1-[4-Bromo-2-(1-hexyn-1-yl)phenyl]-3-phenyl-3-ethyltriaz-1-ene (Ib). Yield 80% (eluent petroleum ether–ethyl acetate, 20:1), bright-orange oily substance. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 0.94 t (3H, CH_3, *J* 7.3 Hz), 1.37 t (3H, CH_3, *J* 7.3 Hz), 1.47–1.63 m (4H, $2CH_2$), 2.50 t (2H, CH_2, *J* 7.3 Hz), 4.44 q (2H, CH_2, *J* 7.3 Hz), 7.15–7.20 m ($1H_{arom}$), 7.41–7.50 m ($4H_{arom}$), 7.58–7.59 m ($3H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.58, 13.63, 18.87, 19.40, 21.99, 30.77 (Bu, Et), 76.50 (C_{sp}), 96.28 (C_{sp}), 116.88, 118.94, 119.01, 121.81, 123.73, 129.25, 131.16, 135.47, 144.03, 150.41 (C_{arom}). Found, %: C 62.67; H 5.89; N 11.00. $[M + H]^+$ 384.1079. $C_{20}H_{22}BrN_3$. Calculated, %: C 62.50; H 5.77; N 10.93. (*M* + H) 384.1074.

1-[2-(1-Hexynyl)-4-nitrophenyl]-3-phenyl-3-ethyltriazene (Ic). After the chromatographic isolation (eluent petroleum ether–ethyl acetate, 20:1) the product was crystallized from hexane. Yield 71%, mp 49–51°C. ^{1}H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3, *J* 7.3 Hz), 1.40 t (3H, CH_3, *J* 7.3 Hz), 1.47–1.67 m (4H, $2CH_2$), 2.50 t (2H, CH_2, *J* 7.3 Hz), 4.43 q (2H, CH_2, *J* 7.3 Hz), 7.20–7.24 m ($1H_{arom}$), 7.40–7.52 m ($4H_{arom}$), 7.61 d [1H, H^6, ^3J (H^6–H^5) 8.8 Hz], 8.10 d.d [1H, H^5, ^3J(H^5–H^6) 8.8, ^4J(H^5–H^3) 2.4 Hz], 8.33 d [1H, H^3, ^4J(H^3–H^5) 2.4 Hz]. ^{13}C NMR spectrum, δ, ppm: 10.9, 13.6, 19.4, 22.0, 30.7, 41.4 (Bu, Et), 76.8 (C_{sp}), 97.3 (C_{sp}), 117.6, 117.9, 120.8, 123.3, 124.9, 128.7, 129.4, 143.6, 145.1, 156.0 (C_{arom}). Found, %: C 68.32; H 3.38; N 16.00. $[M + H]^+$ 351.1851. $C_{20}H_{22}N_4O_2$. Calculated, %: C 68.55; H 6.33; N 15.99. (*M* + H) 351.1821.

Methyl 3-(1-hexynyl)-4-[(3-phenyl-3-ethyl)triazen-1-yl]benzoate (Id). Yield 86%, orange crystals (eluent petroleum ether–ethyl acetate, 20:1, then 10:1), mp 44–45°C. ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, CH_3, *J* 7.3 Hz), 1.40 t (3H, CH_3, *J* 7.3 Hz), 1.49–1.66 m (4H, $2CH_2$), 2.50 t (2H, CH_2, *J* 7.3 Hz), 3.93 s (3H, OCH_3), 4.42 q (2H, CH_2, *J* 7.3 Hz), 7.18 t ($1H_{arom}$, *J* 7.3 Hz), 7.40–7.58 m ($5H_{arom}$), 7.94 d.d [1H, H^5, ^3J(H^5–H^6) 8.7, ^4J(H^5–H^3) 1.5 Hz], 8.18 d [1H, H^3, ^4J(H^3–H^4) 1.5 Hz]. ^{13}C NMR spectrum, δ, ppm: 11.3, 14.1, 19.8, 22.4, 31.3, 41.2 (Bu, Et), 52.5 (OMe), 78.1 (C_{sp}), 96.1 (C_{sp}), 117.6, 118.0, 120.5, 124.6, 127.8, 129.72, 129.74, 135.3, 144.3, 155.1, 166.9 (COOMe). Found, %: C 72.81; H 6.86; N 11.62. $[M + Na]^+$ 386.1840. $C_{22}H_{25}N_3O_2$. Calculated, %: C 72.70; H 6.93; N 11.56. (*M* + Na) 386.1844.

1-[2-(Dodeca-1,3-diynyl)-4-methylphenyl]-3-phenyl-3-ethyltriazene (Ie). Yield 19%, orange oily substance (eluent petroleum ether–ethyl acetate, 40:1). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3, *J* 7.3 Hz), 1.29–1.40 m [13H, $(CH_2)_5$, CH_3], 1.53–1.60 m (2H, CH_2), 2.33–2.39 m (5H, CH_2, CH_3), 4.37 q (2H, CH_2, *J* 7.3 Hz), 7.10–7.15 m ($2H_{arom}$), 7.35–7.50 m ($6H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.8, 14.1, 19.7, 20.8, 22.6, 28.3, 28.8, 29.06, 29.15, 31.8, 40.4 (C_8H_{17}, C_2H_5, CH_3), 65.5, 73.2, 78.3, 85.0 (C_{sp}), 116.7, 117.7, 117.8, 123.4, 129.17, 129.22, 130.3, 134.1, 135.8, 150.8. Found: *m/z* 400.2759 $[M + H]^+$. $C_{27}H_{34}N_3$. Calculated: (*M* + H) 400.2759.

1-[2-(Dodeca-1,3-diynyl)-4-bromophenyl]-3-phenyl-3-ethyltriazene (**If**) and methyl 3-(dodeca-1,3-diynyl)-4-[(3-phenyl-3-ethyl)triazene-1-yl]benzoate (**Ig**) were obtained as described in [24], yields 69 and 90% respectively.

1-[2-(4-Phenylbuta-1,3-diynyl)-4-bromophenyl]-3-phenyl-3-ethyltriaz-1-ene (Ih). The phenyldiacetylene was obtained from 2.0 mmol (0.368 g) of 2-methyl-6-phenylhexa-3,5-diyn-2-ol in 10 ml of toluene [35], the obtained toluene solution was added at stirring to a mixture of 1 mmol (0.351 g) of 1-(4-bromophenyl)-3-

phenyl-3-ethyltriaz-1-ene, 0.1 mmol (0.026 g) of PPh_3, and 0.05 mmol (0.058 g) of $Pd(PPh_3)_4$. For 5 min the reaction mixture was flushed with argon, then 0.15 mmol (0.028 g) of CuI was added, and the stirring in an argon flow at 40°C was continued for 23 h. The reaction mixture was poured into a saturated solution of NH_4Cl (~40 ml), extracted with dichloromethane (3 × 15 ml), the organic layer was washed with the saturated solution of NH_4Cl (2 × 20 ml) and water (30 ml), dried with Na_2SO_4, dichloromethane was removed in a vacuum. The residue was subjected to column chromatography on silica gel (eluent petroleum ether–ethyl acetate, 50:1). Yield 55%, bright-orange oily substance. ^{1}H NMR spectrum, δ, ppm: 1.40 t (3H, CH_3, *J* 7.3 Hz), 4.39 q (2H, CH_2, *J* 7.3 Hz), 7.14–7.19 m (1H$_{arom}$), 7.34–7.55 m (11H$_{arom}$), 7.70 s (1H$_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.8 (CH_3), 41.0 (CH_2), 74.1 (C_{sp}), 78.5 (C_{sp}), 79.2 (C_{sp}), 82.7 (C_{sp}), 117.2, 118.9, 119.3, 119.5, 121.8, 124.1, 128.4, 129.2, 129.3, 134.5, 132.8, 136.0, 143.9, 152.1. Found, %: C 67.61; H 4.35; N 9.53. $[M + H]^+$ 428.0748. $C_{24}H_{18}BrN_3$. Calculated, %: C 67.30; H 4.24; N 9.87. (*M* + H) 428.0762.

Methyl 3-(phenylbuta-1,3-diynyl)-4-(3-ethyl-3-phenyltriaz-1-ene-1-yl)benzoate (Ii) was obtained similarly from 1 mmol (0.409 g) of methyl 3-iodo-4-(3-ethyl-3-phenyltriaz-1-ene-1-yl)benzoate. Yield 71%, bright-yellow oily substance (eluent petroleum ether–ethyl acetate, 20:1). ^{1}H NMR spectrum, δ, ppm: 1.43 t (3H, CH_3, *J* 7.3 Hz), 3.93 s (3H, OCH_3), 4.43 q (2H, CH_2, *J* 7.3 Hz), 7.15–7.21 m (1H$_{arom}$), 7.32–7.44 m (5H $_{arom}$), 7.51–7.55 m (4H$_{arom}$), 7.60 d [1H, H^6, ^3J(H^6–H^5) 8.7 Hz], 8.00 d.d [1H, H^5, ^3J(H^5–H^6) 8.7, ^4J(H^5–H^3) 2.2 Hz], 8.27 d [1H, H^3, ^4J(H^3–H^5) 2.2 Hz]. ^{13}C NMR spectrum, δ, ppm: 10.8 (CH_3), 41.3 (CH_2), 52.2 (OCH_3), 74.2 (C_{sp}), 78.6 (C_{sp}), 79.2 (C_{sp}), 82.2 (C_{sp}), 117.4, 117.5, 117.9, 121.9, 124.5, 127.4, 128.4, 129.1, 129.3, 130.8, 132.5, 135.6, 143.7, 156.1, 166.1 (COOMe). Found: *m/z* 408.1682 $[M + H]^+$. $C_{26}H_{21}N_3O_2$. Calculated: (*M* + H) 408.1712.

4-Bromocinnolines IIIa–IIId, IIIg–IIIi. General procedure. To a solution of (0.25 mmol) of triazene in 2.5 ml of acetone at vigorous stirring was quickly added 5 mmol (0.843 g, 0.57 ml) of 48% HBr. The reaction mixture was stirred at 20°C for 3 min in the case of triazenes **Ia–Id** or for 15 min in the case of triazenes **Ig–Ii**, the mixture was poured into 10 ml of water solution containing 5 mmol (0.505 g, 0.70 ml) of Et_3N, the product was extracted into dihloromethane (3 × 10 ml), the extract was washed with saturated solution of NH_4Cl and water, dried with Na_2SO_4, the solvent was removed in a vacuum. The residue was subjected to column chromatography on silica gel (eluent petroleum ether– ethyl acetate 20:1, then 10:1).

4-Bromo-3-butyl-6-methylcinnoline (IIIa). Yield 80%, orange oily substance. ^{1}H NMR spectrum, δ, ppm: 0.99 t (3H, CH_3, *J* 7.3 Hz), 1.50 sextet (2H, CH_2, *J* 7.3 Hz), 1.88 m (2H, CH_2), 2.62 s (3H, CH_3), 3.39 t (2H, CH_2, *J* 8.0 Hz), 7.62 d.d [1H, H^7, ^3J(H^7–H^8) 8.7, ^4J(H^7–H^5) 2.2 Hz], 7.87 C (1H, H^5), 8.36 d [1H, H^8, ^3J(H^8–H^7) 8.7 Hz]. ^{13}C NMR spectrum, δ, ppm: 13.9, 22.3, 22.6, 31.2, 36.0 (Me, Bu), 124.2, 126.3, 126.9, 129.7, 132.6, 143.1 148.7, 157.2. Found: *m/z* 279.0556 $[M + H]^+$. $C_{13}H_{15}BrN_2$. Calculated: (*M* + H) 279.0497.

3-Butyl-4,6-dibromocinnoline (IIIb). Yield 82%, mp 59–61°C. ^{1}H NMR spectrum, δ, ppm: 0.99 t (3H, CH_3, *J* 7.3 Hz), 1.50 sextet (2H, CH_2, *J* 7.3 Hz), 1.83–1.93 m (2H, CH_2), 3.41 t (2H, CH_2, *J* 8.0 Hz), 7.88 d.d [1H, H^7, ^3J(H^7–H^8) 8.7, ^4J(H^7–H^5) 1.5 Hz], 8.32 d [1H, H^5, ^4J(H^5–H^7) 1.5 Hz], 8.36 d [1H, H^8, ^3J(H^8–H^7) 8.7 Hz]. ^{13}C NMR spectrum, δ, ppm: 13.9, 22.6, 31.1, 36.0 (Bu), 125.5, 127.7, 127.9, 128.1, 131.6, 134.1, 148.0, 158.0. Found, %: C 42.11; H 3.79; N 8.09. $[M + H]^+$ 342.9419. $C_{12}H_{12}Br_2N_2$. Calculated, %: C 41.89; H 3.52; N 8.14. (*M* + H) 342.9445.

3-Butyl-4,6-dibromocinnoline hydrobromide (IIIb). Yield 39%, mp 137–140°C. ^{1}H NMR spectrum, δ, ppm: 0.99 t (3H, CH_3, *J* 7.3 Hz), 1.53 sextet (2H, CH_2, *J* 7.3 Hz), 1.85–1.95 m (2H, CH_2), 3.64 t (2H, CH_2, *J* 8.0 Hz), 7.22 d.d (1H$_{arom}$, *J* 8.7 Hz), 8.55 s (1H, H^5), 8.84 d (1H$_{arom}$, *J* 8.7 Hz), 11.61 br.s (1H, HBr). ^{13}C NMR spectrum, δ, ppm: 13.6, 22.4, 30.8, 33.6 (Bu), 128.4, 128.6, 132.0, 133.7, 134.5, 139.4, 143.5, 157.5 (C_{arom}). Found, %: C 33.72; H 3.23; N 6.32. $[M + H]^+$ 342.9397. $C_{12}H_{12}Br_2N_2$. Calculated, %: C 33.92; H 3.08; N 6.59. (*M* + H) 342.9445.

4-Bromo-3-butyl-6-nitrocinnoline (IIIc). Yield 71%, mp 75–77°C. ^{1}H NMR spectrum, δ, ppm: 1.01 t (3H, CH_3, *J* 7.3 Hz), 1.46–1.58 m (2H, CH_2), 1.86–1.97 m (2H, CH_2), 3.48 t (2H, CH_2, *J* 8.0 Hz), 8.54 d.d [1H, H^7, ^3J(H^7–H^8) 8.7, ^4J(H^7–H^5) 2.2 Hz], 8.71 d [1H, H^8, ^3J(H^8–H^7) 8.7 Hz], 9.07 d [1H, H^5, ^4J(H^5–H^7) 2.2 Hz]. ^{13}C NMR spectrum, δ, ppm: 13.8, 22.6, 31.0, 36.1 (Bu), 123.4, 123.5, 126.4, 128.2, 132.7, 149.0, 149.5, 159.3 (C_{arom}).

3-Butyl-6-nitrocinnoline-4-one (IVc) was obtained after treating the reaction mixture in the course of the study of triazene **Ic** cyclization by ^{1}H NMR spectroscopy.

^{1}H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3, *J* 7.3 Hz), 1.36–1.48 m (2H, CH_2), 1.64–1.72 m (2H, CH_2), 2.85 t (2H, CH_2, *J* 8.0 Hz), 8.63 d [1H, H^8, $^3J(H^8–H^7)$ 8.7 Hz], 8.46 d.d [1H, H^7, $^3J(H^7–H^8)$ 8.7, $^4J(H^7–H^5)$ 2.2 Hz], 9.2 d [1H, H^5, $^4J(H^5–H^7)$ 2.2 Hz]. Found, %: C 57.92; H 5.07; N 17.21. $[M + H]^+$ 248.1117. $C_{12}H_{14}N_2O_3$. Calculated, %: C 58.29; H 5.30; N 16.99. (*M* + H) 248.1035.

Methyl 4-bromo-3-butyl-6-cinnolinecarboxylate (IIId). Yield 52%, mp 104–106°C. ^{1}H NMR spectrum, δ, ppm: 1.00 t (3H, CH_3, *J* 7.3 Hz), 1.51 sextet (2H, CH_2, *J* 7.3 Hz), 1.85–1.95 m (2H, CH_2), 3.44 t (2H, CH_2, *J* 8.0 Hz), 4.04 s (3H, OCH_3), 8.34 d.d [1H, H^7, $^3J(H^7–H^8)$ 7.3, $^4J(H^5–H^3)$ 2.2 Hz], 8.54 d [1H, H^8, $^3J(H^8–H^7)$ 7.3 Hz], 8.34 d [1H, H^5, $^4J(H^5–H^7)$ 2.2 Hz]. ^{13}C NMR spectrum, δ, ppm: 13.8, 22.6, 31.1, 36.0 (Bu), 52.9 (OMe), 126.2, 128.1, 129.1, 130.5, 133.0, 150.1 (one signal overlapped with the others) (C_{arom}), 158.3 (COOMe). Found: *m/z* 323.0374 $[M + H]^+$. $C_{14}H_{15}BrN_2O_2$. Calculated: (*M* + H) 323.0395. 4,6-Dibromo-3-(dec-1-yn-1-yl)cinnoline (**IIIf**) [24]. Yield 66%.

Methyl 4-bromo-3-(dec-1-yn-1-yl)-6-cinnolinecarboxylate (**IIIg**) [24]. Yield 74%.

4,6-Dibromo-3-(phenylethynyl)cinnoline (IIIh). Yield 52%, mp 206–209°C. ^{1}H NMR spectrum, δ, ppm: 7.40–7.45 m ($3H_{arom}$), 7.71–7.74 m ($2H_{arom}$), 7.94 d.d [1H, H^7, $^3J(H^7–H^8)$ 8.7, $^4J(H^7–H^5)$ 2.2 Hz], 8.34 d [1H, H^5, $^4J(H^5–H^7)$ 2.2 Hz], 8.41 d [1H, H^8, $^3J(H^8–H^7)$ 8.7 Hz]. ^{13}C NMR spectrum, δ, ppm: 86.0 (C_{sp}), 98.1 (C_{sp}), 121.6, 127.0, 127.7, 128.3, 128.4, 128.6, 129.8, 132.0, 132.3, 135.1, 143.4 147.0. Found: *m/z* 386.9126 $[M + H]^+$. $C_{16}H_8Br_2N_2$. Calculated: (*M* + H) 386.9132.

Methyl 4-bromo-3-(2-phenylethynyl)-6-cinnolinecarboxylate (IIIi). After chromatographing (eluent petroleum ether–ethyl acetate, 10:1, then 5:1) the product was crystallized from acetonitrile. Yield 58%, mp 157–158°C. ^{1}H NMR spectrum, δ, ppm: 4.04 s (3H, OCH_3), 7.42–7.44 m ($3H_{arom}$), 7.71–7.74 m ($2H_{arom}$), 8.42 d.d [1H, H^7, $^3J(H^7–H^8)$ 8.7, $^4J(H^7–H^5)$ 1.5 Hz], 8.61 d [1H, H^8, $^3J(H^8–H^7)$ 8.7 Hz], 8.85 d [1H, H^5, $^4J(H^5–H^7)$ 1.5 Hz]. ^{13}C NMR spectrum, δ, ppm: 53.0 (OCH_3), 85.9 (C_{sp}), 98.1 (C_{sp}), 121.5, 125.5, 128.5, 128.98, 129.1, 129.8, 130.7, 130.9, 132.2, 133.7, 143.6, 149.0 (two overlapping signals), 165.2 (COOMe). Found, %: C 59.05; H 2.82; N 7.54. $[M + H]^+$ 367.0092. $C_{18}H_{11}BrN_2O_2$. Calculated, %: C 58.88; H 3.02; N 7.63. (*M* + H) 367.0082.

Methyl 3-(dec-1-yn-1-yl)-4-(methylsulfanyl) cinnoline-6-carboxylate (VII). To a solution of 0.060 g (0.148 mmol) of bromocinnoline **IIId** in 2 ml of acetonitrile at 0°C was added 0.010 g (0.147 mmol) of $NaSCH_3$. The reaction mixture was stirred at 0°C for 2 h and then 0.5 h at room temperature. The solvent was removed at a reduced pressure, the residue was chromatographed on silica gel (eluent petroleum ether–ethyl acetate, 10 : 1, then 7:1). Yield 73%, mp 44–46°C. ^{1}H NMR spectrum, δ, ppm: 0.87 t (3H, CH_3, *J* 7.5 Hz), 1.24–1.30 m (8H, $4CH_2$), 1.48–1.57 m (2H, CH_2), 1.74 quintet (2H, CH_2, *J* 7.3 Hz), 2.64 t (2H, CH_2, *J* 7.3 Hz), 2.74 c (3H, SCH_3), 4.02 s (3H, OCH_3), 8.34 d.d [1H, H^7, $^3J(H^7–H^8)$ 8.7, $^4J(H^7–H^5)$ 1.5 Hz], 8.55 d [1H, H^8, $^3J(H^8–H^7)$ 8.7 Hz], 9.13 d [1H, H^5, $^4J(H^5–H^7)$ 1.5 Hz]. ^{13}C NMR spectrum, δ, ppm: 14.0, 18.0, 20.0, 22.6, 28.2, 29.0, 29.07, 29.15, 31.8, 52.8 (OCH_3), 78.2 (C_{sp}), 101.1 (C_{sp}), 126.4, 127.7, 129.8, 130.8, 132.4, 138.5, 144.3, 148.2, 165.7 (COOMe). Found: *m/z* 371.1790 $[M + H]^+$. $C_{21}H_{26}N_2O_2S$. Calculated: (*M* + H) 371.1793.

3-Butyl-4-*N*,*N*-diethylamino-6-nitrocinnoline (VIII). To a solution in 2 ml of acetonitrile of 4-bromo-5-nitrocinnoline obtained by the above described procedure 0.123 mmol (0.07 g) of triazene **Ic** not subjected to the chromatography was added 1.84 mmol (0.135 g, 0.2 ml) of diethylamine. The reaction mixture was heated at 50°C over 48 h, poured into 10 ml of water, the product was extracted into dichloromethane (3 × 7 ml), the combined organic solutions were washed with the saturated solution of NH_4Cl, with water till pH 7, the extract was dried with Na_2SO_4, the solvent was removed in a vacuum, the residue was subjected to chromatography (eluent petroleum ether–ethyl acetate, 5 : 1). Yield 52%, mp 204–206°C. ^{1}H NMR spectrum, δ, ppm: 1.00 t (3H, CH_3, *J* 7.3 Hz), 1.14 t (6H, $2CH_3$, *J* 7.3 Hz), 1.51 sextet (2H, CH_2, *J* 7.3 Hz), 1.90–2.00 m (2H, CH_2), 3.19 t (2H, CH_2, *J* 8.0 Hz), 3.47 q (4H, $2CH_2$, *J* 7.3 Hz), 8.40 d.d [1H, H^7, $^3J(H^7–H^8)$ 9.5, $^4J(H^7–H^5)$ 2.2 Hz], 8.58 d [1H, H^8, $^3J(H^8–H^7)$ 9.5 Hz], 9.02 d [1H, H^5, $^4J(H^5–H^7)$ 2.2 Hz]. ^{13}C NMR spectrum, δ, ppm: 14.0, 14.1, 23.1, 31.6, 32.9, 47.9 (2Et, Bu) 121.7, 122.3, 125.7, 132.3, 144.1, 147.2, 150.5, 157.5. Found: *m/z* 303.1739 $[M + H]^+$. $C_{16}H_{22}N_2O_4$. Calculated: (*M* + H) 303.1821.

Methyl 3-iodo-2-octylthieno[3,2-*C*]cinnoline-8-carboxylate (IX). To a solution of 0.068 mmol (0.025 g) of 4-methylsulfanylcinnoline **VII** in 1.5 ml of acetonitrile was added at stirring 0.136 mmol (0.034 g) of iodine preliminary thoroughly ground in a mortar. The reaction mixture was stirred for 15 h at room temperature, the formed precipitate was filtered off and washed with acetonitrile, with 5% solution of sodium sulfite, with water

and again with acetonitrile. The filtrate was diluted with water (20 ml), extracted with dichloromethane, washed with water, and the extract was dried with anhydrous sodium sulfate. The solvent was removed at a reduced pressure, the residue was combined with the previously obtained precipitate and recrystallized from acetonitrile. Yield 70%, mp 134–136°C. ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, J 6.6 Hz), 1.29–1.48 m (10H, $5CH_2$), 1.80–1.89 m (2H, CH_2), 3.14 t (2H, CH_2, J 7.3 Hz), 4.05 s (3H, OCH_3), 8.39 d.d [1H, H^7, $^3J(H^7–H^6)$ 8.6, $^4J(H^7–H^9)$ 1.3 Hz], 8.74–8.78 m (2H, H^6, H^9). ^{13}C NMR spectrum, δ, ppm: 14.1, 22.6, 29.07, 29.14, 29.3, 30.4, 31.8, 32.9 (C_8H_{17}), 52.9 (OCH_3), 82.9 (CI) 120.9, 125.2, 128.7, 131.6, 132.3, 132.8, 146.7, 147.9, 154.1 (C_{arom}), 165.7 (COOMe). Found: m/z 483.0566 $[M + H]^+$. $C_{20}H_{24}IN_2O_2S$. Calculated: (M + H) 483.0603.

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