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Intramolecular Cycloaddition of Geminal Dichloroazomethine Ylides to Multiple Carbon–Carbon Bonds

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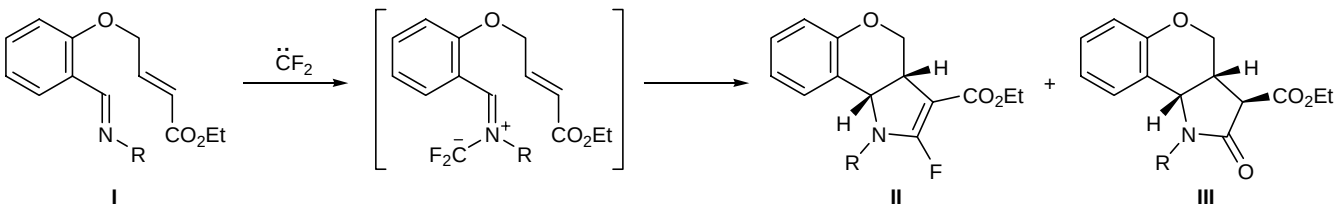
Abstract—Geminal dichloroazomethine ylides generated by reaction of dichlorocarbene with Schiff bases derived from *O*-alkenyl- or *O*-alkynylsalicylaldehyde undergo intramolecular [3+2]-cycloaddition with participation of the olefinic or acetylenic dipolarophile to afford chromeno[4,3-*b*]pyrrole and chromeno-[4,3-*b*]pyridine derivatives. The greatest yields of the intramolecular cycloaddition products were obtained from *N*-methyl-substituted dichloroazomethine ylides, whereas the main stabilization path of *N*-phenyl and *N*-*tert*-butyl derivatives was cyclization to geminal dichloroaziridines.

Intramolecular 1,3-dipolar cycloadditions of azomethine ylides provide a convenient method for the preparation of various fused and bridged nitrogen-containing polycyclic systems [1], including some natural compounds, e.g., (+)-α-lycorane [2] and lamellarin K [3]. Synthetic approaches were developed to building up martinelline skeleton, as well as those of physostigmine [4], erythrine [5], and other alkaloids [1]. The development of this synthetic strategy, among other lines, includes search for new functionalized azomethine ylides capable of transferring to the cycloadduct groups which can be useful for further transformations, e.g., halogen atoms or an oxo group. Synthetic equivalents of such reagents may be geminal dihalo-substituted azomethine ylides; the only example of intramolecular cycloaddition was reported for geminal difluoro-substituted ylides [6]. Despite dichloro derivatives are the most accessible from the synthetic viewpoint and the most studied among dihalo-substituted ylides, their intramolecular cycloadditions were not reported.

In the present work we examined transformations of geminal dichloroazomethine ylides generated from Schiff bases containing an olefinic or acetylenic dipolarophile fragment. We recently showed that Schiff bases **I** react with difluorocarbene to give difluoro ylides which undergo intramolecular ring closure involving the double C=C bond, yielding chromeno-[4,3-*b*]pyrrole derivatives **II** and **III** (Scheme 1) [6]. It should be noted that the cycloaddition readily occurs with difluoro ylides generated from both *N*-alkyl (R = Me, *t*-Bu) and *N*-aryl derivatives [6], though the transformation direction of halogenated ylides is known to depend on the substituent on the nitrogen atom [7].

We found that, unlike reactions with difluorocarbene, the substituent on the nitrogen atom in Schiff bases **Ia** and **Ib** strongly affected their reactions with dichlorocarbene generated by thermal decomposition of sodium trichloroacetate in chloroform in the presence of benzyltriethylammonium chloride (BTEAC). For example, ylide **IVa** generated from *N*-methyl-substituted Schiff base **Ia** and dichlorocarbene was trapped almost completely by the internal olefinic dipolarophile to afford two products: chromenopyrrole **Va** and chromenopyridine **VIa** in 34 and 26% yield, respectively (Scheme 2, see table). Compound **Va** is

Scheme 1.



I **II** **III**

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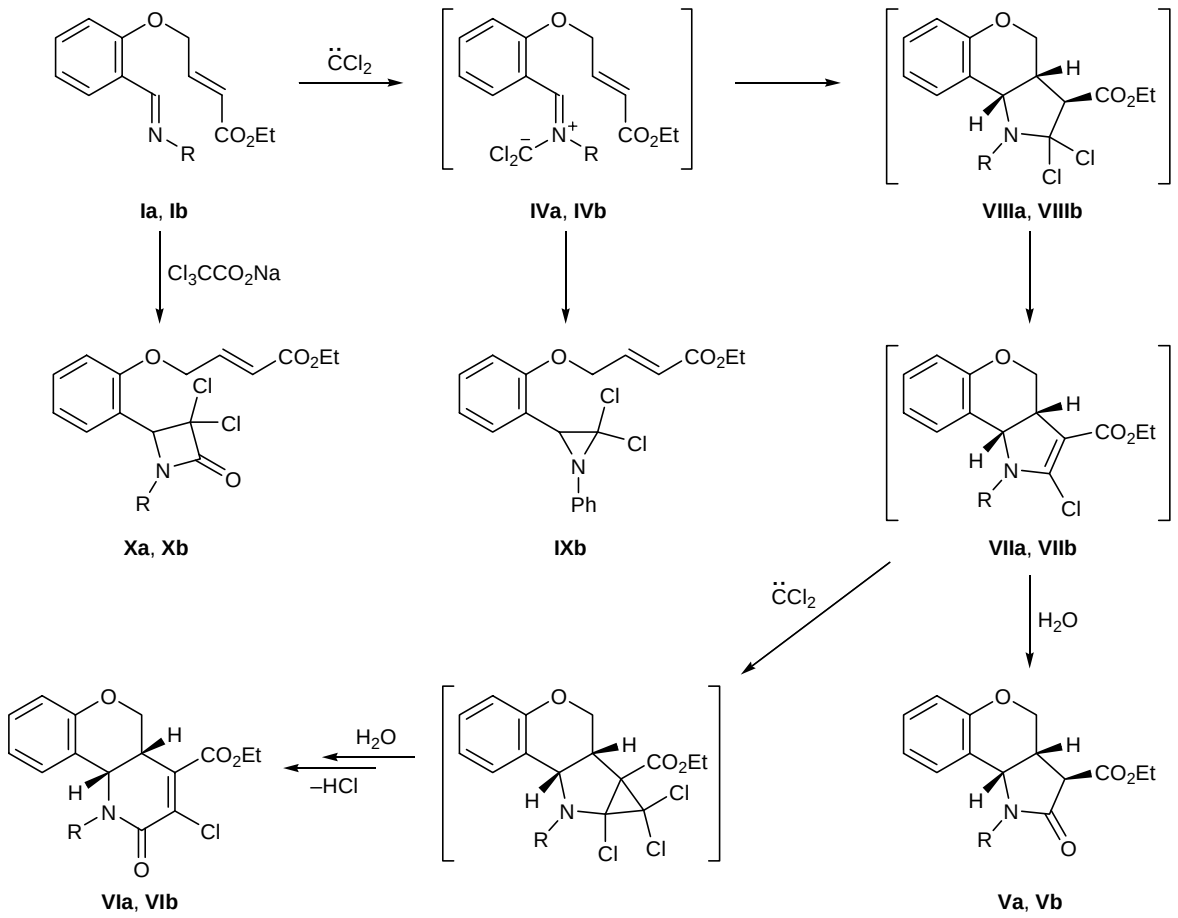
Scheme 2.



R = Me (**a**), Ph (**b**).

formed as a result of hydrolysis of intermediate chlorodihydropyrrole **VIIa** formed by dehydrochlorination of the primary cycloadduct, chromenopyrrole **VIIIa**. Dichlorocyclopropanation of compound **VIIa**, followed by ring expansion and hydrolysis (most probably, during chromatographic treatment of the reaction mixture), leads to chromenopyridine **VIa**.

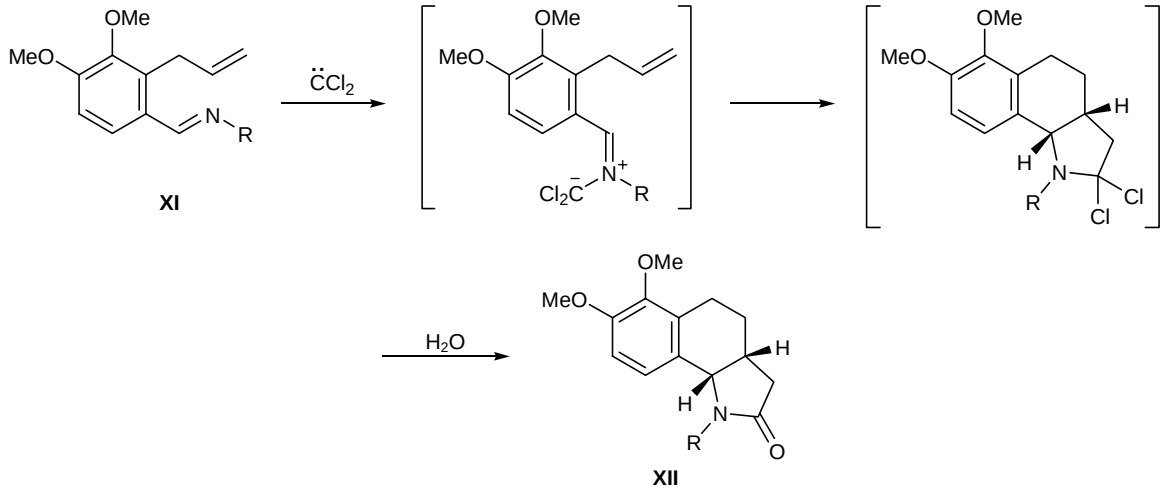
Under analogous conditions, the reaction of *N*-phenyl-substituted Schiff base **Ib** with dichlorocarbene afforded mainly 1,3-cyclization product of intermediate ylide **IVb**, aziridine derivative **IXb**, while the yield of chromenopyrrole **Vb** was as poor as 3%. Thus replacement of methyl group on the nitrogen atom in ylide intermediate **IV** by phenyl changes the direction of its stabilization: in the first case, intramolecular cycloaddition occurs exclusively, while in the second, the predominant reaction pathway is 1,3-cyclization to aziridine structure. Analogous effect of the substituent on the nitrogen atom in dichloroazomethine ylides was observed in their intra- and intermolecular cycloadditions at double C=C bonds: *N*-alkyl ylides underwent intramolecular cycloaddition, whereas *N*-aryl-substituted analogs gave rise to aziridine derivatives as a result of 1,3-cyclization [7]. It should be emphasized that the intramolecular cycloaddition of dichloroazomethine ylides generated from Schiff bases **Ia** and **Ib** is strictly stereoselective: the resulting chromenopyrrole derivatives are characterized exclusively by *cis*-junction of the pyran and pyrrolidine rings.

Apart from compounds **V**, **VI**, and **IX**, we isolated from the reaction mixtures azetidinones **Xa** and **Xb**; the latter are formed without participation of dichlorocarbene, via reaction of Schiff base with trichloro-

Reactions of Schiff bases **Ia** and **Ib** with dichlorocarbene

Schiff base	R	Yield, %			
		IX	**V**	**VI**	**X**
Ia	Me	0	34	26	19
Ib	Ph	60	3	2.5	5

Scheme 3.



XI **XII**

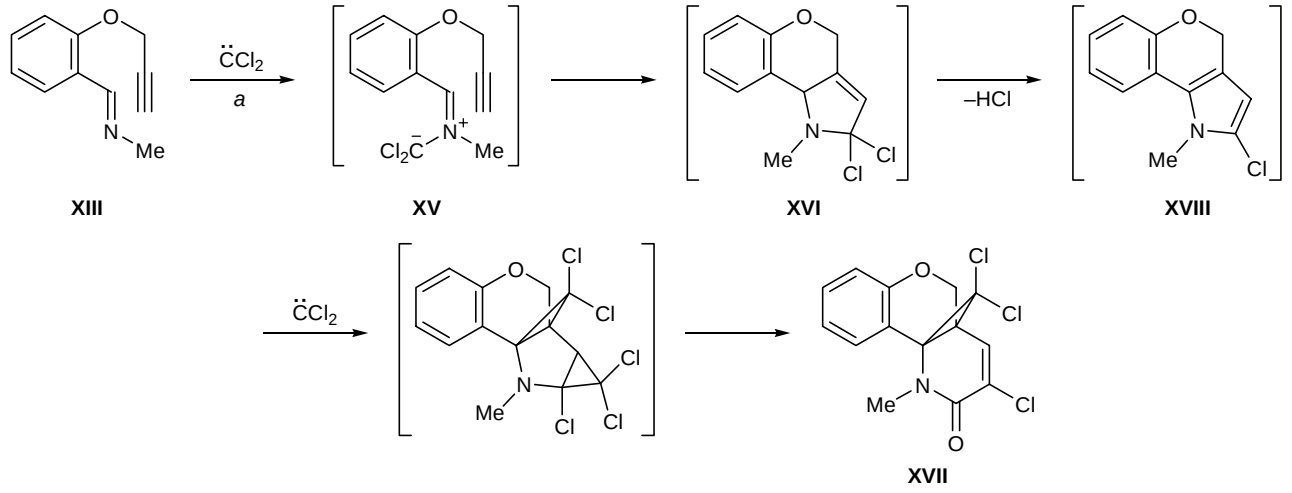
R = 4-BrC_6H_4.

acetyl chloride arising from thermolysis of sodium trichloroacetate [8]. The formation of azetidin-2-ones usually accompanies transformations of *N*-alkyl-*N*-benzylideneamines with bulky secondary and tertiary alkyl groups on the nitrogen atom under conditions of thermocatalytic decomposition of sodium trichloroacetate in chloroform [9]. No examples of formation of such compounds from *N*-benzylideneanilines were reported. Presumably, an appreciable yield of azetidine derivatives **Xa** and **Xb** in the above reactions is explained by the presence of an *ortho* substituent in the benzene ring, which shields the nitrogen center thus hampering its reaction with dichlorocarbene and favoring concurrent processes.

The structure of compounds **VI**, **IX**, and **X** was determined on the basis of their ^1H and ^{13}C NMR spectra and elemental compositions. The *cis*-junction of the pyran and piperidine rings in **VIa** and **VIb** follows from the relatively small spin–spin coupling constant $^2J_{4a,10b}$ = 3.5–4.2 Hz; this is consistent with the proposed reaction mechanism according to which compounds **Va**, **Vb** and **VIa**, **VIb** are formed through a common dichloropyrrolidine intermediate **VIIIa** or **VIIIb** with the same mode of ring junction.

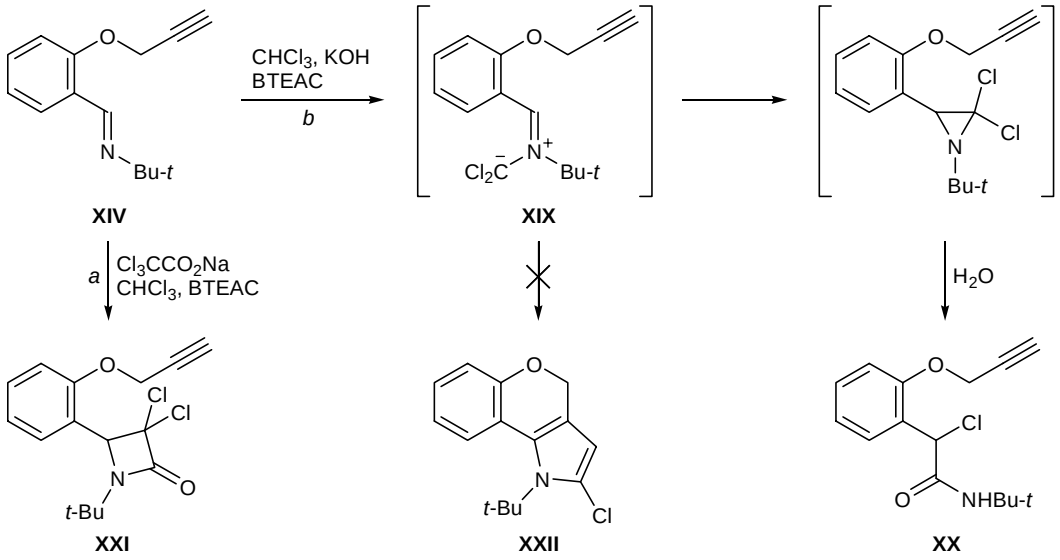
The reaction of dichlorocarbene (generated from sodium trichloroacetate) with Schiff base **XI** having a nonactivated C=C bond linked to the imine moiety through a three-atom fragment (C_{sp^2}–C_{sp^2}–C_{sp^3}) was accompanied by strong tarring, and the intramolecular cycloaddition product, lactam **XII**, was formed in 12% yield (Scheme 3). We failed to raise the yield by using the system $CHCl_3$–KOH–BTEAC for generation

Scheme 4.



XIII **XV** **XVI** **XVIII** **XVII**

Scheme 5.

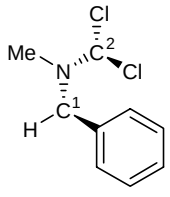


of dichlorocarbene; in this case, it was 10%. Nevertheless, in both cases the yield of lactam **XII** exceeded the overall yield of cycloaddition products **Vb** and **VIb** from ylide **IVb**. This means that increase in the rigidity of the linker (replacement of the four-atom C_{sp^2}–C_{sp^2}–C_{sp^3}–O fragment by three-atom C_{sp^2}–C_{sp^2}–C_{sp^3}) favors intramolecular cycloaddition to a grater extent than does activating alkoxycarbonyl group in the dipolarophile moiety.

Thus the transformation pathway of dichloro-substituted azomethine ylides having an olefinic dipolarophile moiety depends on the substituent on the nitrogen atom: the contribution of intramolecular cycloaddition becomes appreciable only for *N*-alkyl derivatives. Taking the above into account, we examined the possibility for intramolecular cycloaddition at the triple C≡C bond of dichloroazomethine ylides generated from *N*-methyl- and *N*-*tert*-butyl-2-(2-propynyloxy)-benzylideneamines **XIII** and **XIV** (Schemes 4, 5).

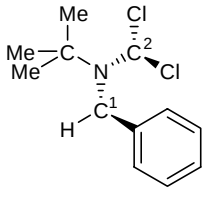
The reaction of Schiff base **XIII** with dichlorocarbene generated by thermocatalytic decomposition of sodium trichloroacetate gave compound **XVII** which was formed with participation of three dichlorocarbene molecules. The reaction sequence leading to product **XVII** is analogous to that shown in Scheme 2 for chromeno[4,3-*b*]pyridine **VIa**. We failed to isolate intermediate chloro-substituted chromenopyrrole **XVIII** because of its ready dichlorocyclopropanation at both double C=C bonds in the pyrrole ring; tetracyclic derivative **XVII** was isolated in 25% yield.

N-*tert*-Butyl-2-(2-propynyloxy)benzylideneamine (**XIV**) behaved differently, and the result depended on the dichlorocarbene generation mode. In the system $CHCl_3$–KOH–BTEAC, ylide **XIX** was formed initially, and the subsequent cyclization to aziridine derivative and hydrolysis of the latter gave 43% of α-chloro amide **XX**. When dichlorocarbene was generated from sodium trichloroacetate at higher temperature, decomposition of unstable *N*-alkyldichloroaziridine occurred, and we isolated only azetidinone **XXI** in 32% yield. In no case intramolecular cycloaddition product **XXII** or its cyclopropanated derivatives were detected. A probable reason for the observed behavior of *N*-*tert*-butyl-substituted ylide **XIX** could be shielding by the *tert*-butyl group of the carbon reaction centers in the dipole, which would inhibit cycloaddition at the C≡C bond. On the other hand, the ylide generated from Schiff base **XIV** and difluorocarbene readily undergoes intramolecular ring closure involving the triple carbon–carbon bond [6]. Another reason is that the presence of a bulky *tert*-butyl group on the nitrogen atom facilitates concurrent reaction, i.e., formation of aziridine structure. According to the results of PM3 calculations of the geometric parameters of *Z*-ylides **XXIII** and **XXIV** derived from the corresponding *E*-Schiff bases and dichlorocarbene, replacement of the



XXIII

$\angle C^1NC^2Cl = 9.4°$



XXIV

$\angle C^1NC^2Cl = 22.2°$

methyl group on the nitrogen by *tert*-butyl leads to a considerable rotation of the dichloromethylene fragment about the Cl_2C–N=C plane, which should reduce the energy of activation for conrotatory closure of the aziridine ring. This factor should be even stronger for *ortho*-substituted ylide **XIV**; therefore, its cyclization to aziridine should be accelerated, as is the case.

Thus azomethine ylides generated by reaction of dichlorocarbene with Schiff bases derived from *O*-alkenyl- or *O*-alkynylsalicylaldehyde are capable of undergoing intramolecular [3+2]-cycloaddition at the double or triple carbon–carbon bond. The yields of the cycloaddition products, chromeno[4,3-*b*]pyrrole and chromeno[4,3-*b*]pyridine derivatives, strongly depend on the substituent on the nitrogen atom. Intramolecular cycloaddition is the main stabilization pathway of *N*-methyl-substituted iminiodichloromethanides. In the transformations of *N*-aryl ylides, the contribution of intramolecular cycloaddition is small, while the major products (like in the transformations of *N*-*tert*-butyl analogs) are geminal dichloroaziridines or products of their hydrolysis.

EXPERIMENTAL

The melting points were determined on a Boetius device and were not corrected. The IR spectra were recorded on a Carl Zeiss UR-20 instrument using 400-μm cells. The NMR spectra were measured on a Bruker DPX 300 spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C. Elemental analysis was performed on an HP-185B CHN analyzer. The progress of reactions was monitored by TLC on Silufol UV-254 plates. The reaction mixtures were separated by column chromatography on LS 5/40 silica gel (Chemapol). Chloroform was washed with water and dried by distillation over P_2O_5.

Reactions of Schiff bases with dichlorocarbene (*general procedure*). *a*. A mixture of 1.4 mmol of the corresponding Schiff base and 1.6 g (0.7 mmol) of BTEAC in 40 ml of dry chloroform was heated to the boiling point, and 3.5 g (18.8 mmol) of sodium trichloroacetate was added in portions over a period of 1 h under stirring. The mixture was heated for an additional 1 h under reflux (TLC), cooled, and filtered. The filtrate was evaporated under reduced pressure, and the residue was subjected to column chromatography using hexane–ethyl acetate or hexane–diethyl ether as eluent. The product was additionally purified by recrystallization.

b. Powdered potassium hydroxide, 1.1–1.7 g (20–30 mmol), was added in portions over a period of 1–2 h under vigorous stirring to a mixture of 1.4 mmol of Schiff base and 0.16 g (0.7 mmol) of BTEAC in 40 ml of dry chloroform. When the reaction was complete (TLC), the mixture was diluted with 10 ml of hexane and filtered through a 5-mm layer of silica gel, the filtrate was evaporated under reduced pressure, and the residue was purified by recrystallization.

Following method *a*, from 1.0 g (0.004 mol) of Schiff base **Ia** (reaction time 2 h; eluent hexane–diethyl ether, 3:1) we obtained 0.375 g (34%) of compound **Va**, 0.33 g (26%) of **VIa**, and 0.277 g (19%) of **Xa**.

Ethyl (3*RS*,3a*RS*,9b*SR*)-2-oxo-1-methyl-1,2,3,-3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-3-carboxylate (Va). mp 97–98°C (from Et_2O) [10].

Ethyl (4a*RS*,10b*SR*)-3-chloro-1-methyl-2-oxo-1,4a,5,10b-tetrahydrochromeno[4,3-*b*]pyridine-4-carboxylate (VIa). mp 102–104°C (from Et_2O). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1725, 1660 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 t (3H, CCH_3, J = 7.1 Hz), 2.95 s (3H, NCH_3), 3.32 d.d.d (1H, 4a-H, J = 10.6, 4.0, 3.5 Hz), 4.17 t (1H, 5-H, J = 10.6 Hz), 4.38 d.d (2H, CH_2, J = 7.1 Hz), 4.36–4.40 m (1H, 5-H), 4.77 d (1H, 10b-H, J = 3.5 Hz), 6.92–7.36 m (4H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.7 (CH_3); 32.2, 35.5 (NCH_3, C^{4a}); 53.6 (C^{10b}); 61.9, 62.3 (CH_2, C^5); 116.2, 117.2, 120.1, 130.6, 131.7, 132.0, 133.8, 153.8 (C^3, C^4, C_{arom}); 159.0, 163.8 (C=O). Found, %: C 59.74; H 5.03; N 4.28. $C_{16}H_{16}ClNO_4$. Calculated, %: C 59.73; H 5.01; N 4.35.

Ethyl (*E*)-4-[2-(3,3-dichloro-1-methyl-4-oxoazetidin-2-yl)phenoxy]-2-butenoate (Xa). mp 98–100°C (from Et_2O). IR spectrum (CCl_4), ν, cm^{-1}: 1790, 1720 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (3H, CH_3, J = 7.1 Hz), 3.02 s (3H, NCH_3), 4.22 q (2H, CH_2, J = 7.1 Hz), 4.72–4.90 m (2N, C^4H_2), 5.49 s (1H, CHN), 6.31 d.t (1H, 2-H, J = 15.6, 1.9 Hz), 6.95–7.45 m (5H, 3-H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.8 (CH_3); 28.0 (NCH_3); 60.2, 66.6 ($O\mathbf{C}H_2CH_3$, C^4); 70.0 (CHN); 84.6 (CCl_2); 111.6, 120.9, 121.3, 122.0, 126.7, 130.3, 141.0, 156.2 (C^2, C^3, C_{arom}); 161.9, 165.5 (C=O). Found, %: C 53.76; H 4.89; N 3.87. $C_{16}H_{17}Cl_2NO_4$. Calculated, %: C 53.65; H 4.78; N 3.91.

Following method *a*, from 0.433 g (0.0014 mol) of Schiff base **Ib** (reaction time 2 h; eluent hexane–diethyl ether, 3:1) we obtained 0.014 g (3%) of com-

pound **Vb**, 0.014 g (2.5%) of **VIb**, 0.33 g (60%) of **IXb**, and 0.028 g (5%) of **Xb**.

Ethyl (3*RS*,3a*RS*,9b*SR*)-2-oxo-1-phenyl-1,2,3,-3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-3-carboxylate (Vb). mp 148–150°C (from Et_2O) [6].

Ethyl (4a*RS*,10b*SR*)-3-chloro-2-oxo-1-phenyl-1,4a,5,10b-tetrahydrochromeno[4,3-*b*]pyridine-4-carboxylate (VIb). mp 143–145°C (from Et_2O). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1730, 1680 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 t (3H, CH_3, J = 7.0 Hz), 3.45–3.52 m (1H, 4a-H), 4.42 q (2H, CH_2, J = 7.0 Hz), 4.44–4.52 m (2H, 5-H), 5.20 d (1H, 10b-H, J = 4.2 Hz), 6.46–7.30 m (9H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.6 (CH_3); 35.9 (C^{4a}), 55.4 (C^{10b}); 61.8, 62.6 (CH_2, C^5); 116.4, 119.7, 127.3, 128.0, 128.7, 129.8, 131.4, 131.9, 134.7, 138.7, 153.2 (C^3, C^4, C_{arom}); 158.6, 163.8 (C=O). Found, %: C 65.56; H 4.73; N 3.47. $C_{21}H_{18}ClNO_4$. Calculated, %: C 65.61; H 4.73; N 3.65.

Ethyl (*E*)-4-[2-(3,3-dichloro-1-phenylaziridin-2-yl)phenoxy]-2-butenoate (IXb). Oily substance. IR spectrum (CCl_4): ν(C=O) 1720 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (3H, CH_3, J = 7.2 Hz), 4.01 s (1H, CHN), 4.23 q (2H, CH_2, J = 7.2 Hz), 4.87 m (2H, CH_2), 6.33 d (1H, 2-H, J = 16.4 Hz), 6.95–7.47 m (10H, 3-H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.9 (CH_3); 51.1 (CHN); 60.2, 66.5 (CH_2, C^4); 75.1 (CCl_2); 111.0, 119.5, 121.0, 121.8, 122.1, 123.9, 128.2, 128.7, 129.6, 141.5, 145.0, 156.7 (C^2, C^3, C_{arom}); 165.7 (C=O).

Ethyl (*E*)-4-[2-(3,3-dichloro-4-oxo-1-phenylazetidin-2-yl)phenoxy]-2-butenoate (**Xb**). mp 127–128°C (from Et_2O). IR spectrum (CCl_4), ν, cm^{-1}: 1780, 1715 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t (3H, CH_3, J = 7.1 Hz), 4.25 q (2H, CH_2, J = 7.1 Hz), 4.88 m (2H, CH_2), 5.93 s (1H, CHN), 6.36 d (1H, 2-H, J = 15.9 Hz), 6.88–7.51 m (10H, 3-H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.9 (CH_3); 60.3, 66.7 (OCH_2, C^4); 68.9 (CHN); 83.5 (CCl_2); 111.5, 117.7, 120.6, 120.9, 122.2, 125.1, 127.4, 129.0, 130.4, 135.8, 141.0, 156.0 (C^2, C^3, C_{arom}); 158.3, 165.5 (C=O). Found, %: C 59.80; H 4.57; N 3.13. $C_{21}H_{19}Cl_2NO_4$. Calculated, %: C 60.01; H 4.56; N 3.33.

(3a*RS*,8b*SR*)-1-(4-Bromophenyl)-5,6-dimethoxy-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole-2-one (XII) was obtained from 0.54 g (1.50 mmol) of Schiff base **XI** according to method *a* (reaction time 2 h) or from 0.52 g (1.44 mmol) of **XI** according to method *b* (reaction time 3.5 h); the product was isolated by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.068 g (12%) (*a*) or 0.057 g (10%) (*b*). mp 157–160°C (from CH_2Cl_2–Et_2O) [10].

3-Chloro-4a,10b-dichloromethano-1-methyl-1,5-dihydrochromeno[4,3-*b*]pyridine-2-one (XVII) was synthesized from 0.378 g (2.2 mmol) of Schiff base **XIII** according to method *a* (reaction time 3 h); the product was purified by column chromatography using hexane–diethyl ether (3:1) as eluent. Yield 0.180 g (25%). mp 190–192°C (from hexane–Et_2O). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1680 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.34 s (3H, NMe), 4.25 d (1H, 5-H, J = 12.4 Hz), 4.55 d (1H, 5-H, J = 12.4 Hz), 6.75 s (1H, 4-H), 7.02–7.61 m (4H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 33.6 (NMe); 34.9 (C^{4a}); 48.9 (C^{10b}); 67.2 (CCl_2); 71.9 (CH_2); 117.7, 118.6, 121.8, 130.1, 130.5, 131.3, 131.4, 157.2 (C^3, C^4, C_{arom}); 157.7 (C=O). Found, %: C 50.88; H 3.10; N 4.00. $C_{14}H_{10}Cl_3NO_2$. Calculated, %: C 50.86; H 3.05; N 4.24.

***N*-*tert*-Butyl)-2-chloro-2-[2-(2-propynyloxy)-phenyl]acetamide (XX)** was obtained from 0.640 g (3.0 mol) of Schiff base **XIV** according to method *b* (reaction time 5.5 h); the product was isolated by column chromatography using hexane–diethyl ether (3:1) as eluent. Yield 0.273 g (43%). Oily substance. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3420 (NH); 3320 (≡C–H); 2140 (C≡C); 1760, 1715 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 s (9H, *t*-Bu), 2.55 t (1H, ≡CH, J = 2.2 Hz), 4.74 d (2H, CH_2, J = 2.2 Hz), 5.64 s (1H, CHCl), 6.63 br.s (1H, NH), 6.99–7.41 m (4H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 28.0 (C**C**H_3); 51.4 (**C**CH_3); 55.9 (CH_2); 56.4 (CHCl); 75.6 (≡CH); 77.8 (–C≡); 112.2, 121.5, 126.4, 128.9, 129.8, 154.5 (C_{arom}); 166.0 (C=O). In addition, 0.240 g (50%) of 2-(2-propynyloxy)benzaldehyde was isolated.

1-*tert*-Butyl-3,3-dichloro-4-[2-(2-propynyloxy)-phenyl]azetidin-2-one (XXI) was obtained from 0.377 g (1.8 mmol) of Schiff base **XIV** according to method *a* (reaction time 5 h); the product was isolated by column chromatography using hexane–diethyl ether (3:1) as eluent. Yield 0.188 g (32%). Oily substance. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3320 (≡C–H), 2130 (C≡C), 1790 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 s (9H, *t*-Bu), 2.56 t (1H, ≡CH, J = 2.4 Hz), 4.81 t (2H, OCH_2, J = 2.4 Hz), 5.58 s (1H, CHN), 7.09–7.41 m (4H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.4 (C**C**H_3); 55.1 (**C**CH_3); 56.2 (CH_2); 66.7 (CHN); 75.6 (≡CH); 77.8 (–C≡); 83.0 (CCl_2); 112.2, 120.9, 123.9, 127.9, 129.9, 155.4 (C_{arom}); 161.9 (C=O).

In addition, 0.066 g (25%) of 2-(2-propynyloxy)-benzaldehyde was isolated.

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