

Dedicated to Full Member of the Russian Academy of Sciences
N.S. Zefirov on His 70th Anniversary

Intramolecular 1,3-Dipolar Cycloaddition of Azomethine Ylides Generated from Ethoxycarbonylcarbenoids and Schiff Bases

A. F. Khlebnikov¹, M. S. Novikov¹, R. R. Kostikov¹, and J. Kopf²

¹ St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: Alexander.Khlebnikov@pobox.spbu.ru

² Institut für anorganische Chemie, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

Received April 7, 2005

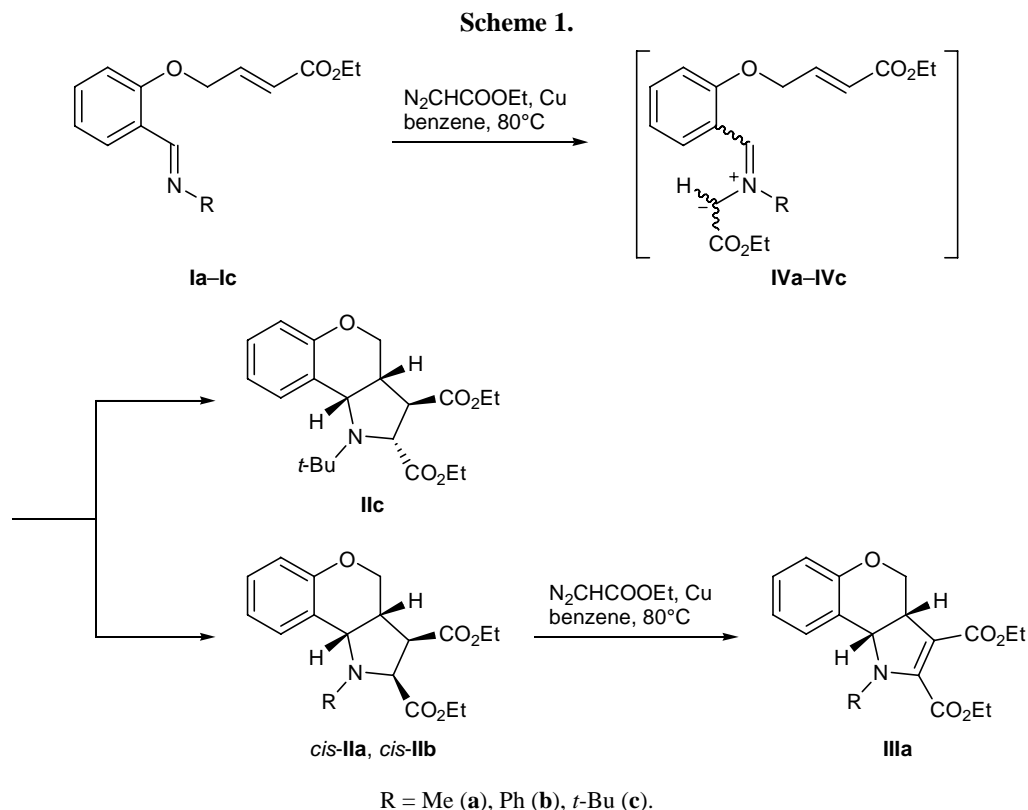
Abstract—Decomposition of ethyl diazoacetate in the presence of copper, copper acetylacetonate, or copper trifluoroacetylacetonate and ethyl 4-[2-(R-imino)phenoxyethyl]-2-butenolate leads to formation of chromeno[4,3-*b*]pyrrole-2,3-dicarboxylic acid derivatives. The reactions involve intermediate formation of azomethine ylides which undergo regio- and stereoselective intramolecular cycloaddition at the C=C bond to afford chromeno[4,3-*b*]pyrroles. The steric structure of the product depends on the configuration of intermediate ylide and nature of the substituent at the ylide nitrogen atom.

Metal carbenoids generated by catalytic decomposition of α -diazocarbonyl compounds are effective intermediates in the synthesis of various polycyclic systems. Several methods for building up nitrogen- and oxygen-containing polycyclic skeletons with participation of ylides have been developed in the framework of the general metal carbenoid strategy. These include cyclization of metal carbenoids to give azomethine or carbonyl ylides (cycloaddition), cyclization of metal carbenoids with formation of onium ylides (sigmatropic rearrangement), and intermolecular generation of cyclic iminium ylides (intermolecular cycloaddition) [1–7]. One more possible approach to heteropolycyclic systems via ylides generated from carbenes is based on intermolecular generation of azomethine ylide–intramolecular cycloaddition; it was implemented only with difluoro- and dichlorocarbenes [8–11]. In the present work we extended this approach to ylides generated from ethoxycarbonylcarbenoids and Schiff bases **Ia–Ic** derived from O-substituted salicylaldehydes containing a dipolarophilic olefin fragment in the side chain.

Ethyl diazoacetate was slowly added to a boiling solution of Schiff base **Ia** in benzene containing a catalytic amount of copper. As a result, two compounds were formed: hexahydrochromenopyrrole **IIa** (34%; product of intramolecular cycloaddition of intermediate azomethine ylide **IVa** at the C=C bond) and

tetrahydrochromenopyrrole **IIIa** (26%) (Scheme 1). Monitoring of the reaction course by thin-layer chromatography showed that initially compound **IIa** is formed exclusively. Tetrahydrochromenopyrrole **IIIa** appears in the reaction mixture later, the conversion of initial Schiff base **Ia** being incomplete. By special experiment we found that compound **IIIa** is formed by dehydrogenation of **IIa** during decomposition of ethyl diazoacetate in the presence of copper. Under analogous conditions, from Schiff base **Ib** we obtained only hexahydrochromenopyrrole **IIb**. It should be emphasized that intramolecular cycloaddition of ylides **IVa** and **IVb** is strictly stereoselective. Using the reaction of Schiff base **Ib** with ethyl diazoacetate as an example, we examined the effect of the catalyst on the yield of product **IIb**. The best results were obtained with copper acetylacetonate (Table 1). Surprisingly, decomposition of ethyl diazoacetate in the presence of copper and *N-tert*-butyl-substituted Schiff base **Ic** afforded stereoisomeric chromenopyrrole **IIc** in which the ethoxycarbonyl groups were arranged *trans*.

The structure of compounds **IIa–IIc** was confirmed by the IR and NMR spectra. The *cis*-junction of the dihydropyran and pyrrolidine rings in molecules **IIa–IIc** follows from the characteristic spin–spin coupling constant between 3a-H and 9c-H, which is equal to 7.5–8.8 Hz; the corresponding coupling constant for *trans*-fused rings is about ~11 Hz [12–16]. In addition,



the structure of chromenopyrroles **IIa–IIc** was unambiguously proved by X-ray analysis (Figs. 1–3).

Thus the intramolecular cycloaddition of ylides **IV** generated from copper-containing ethoxycarbonyl-carbenoids and Schiff bases **I** occurs with high regio- and stereoselectivity to give chromenopyrrole derivatives **II** with *cis*-fused dihydropyran and pyrrolidine rings, and the relative configuration at the C² and C³ atoms depends on the substituent on the nitrogen atom in the initial Schiff base.

It is known that ylides like **IV** can also be generated by condensation of the corresponding aldehydes with

Table 1. Catalytic decomposition of ethyl diazoacetate in the presence of Schiff bases **Ia–Ic**

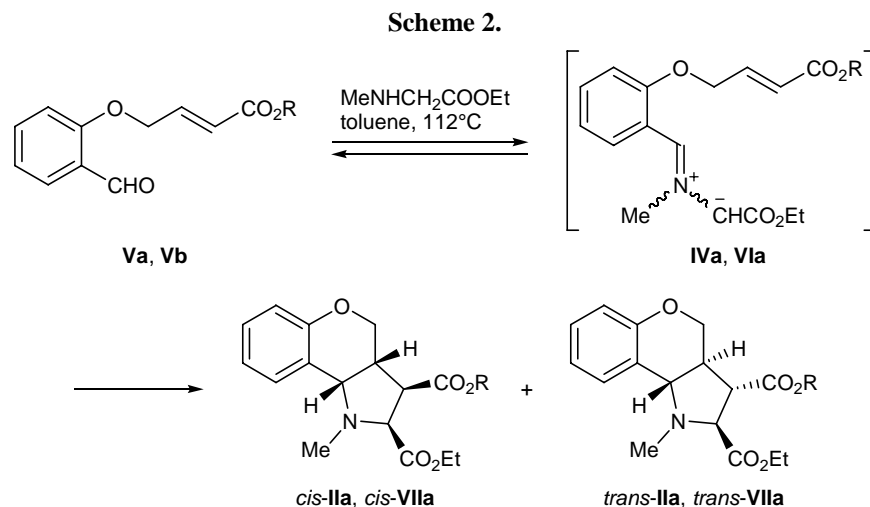
Schiff base	R	Catalyst	Yield of II , %
Ia	Me	Cu	34 ^a
Ib	Ph	Cu	16
Ib	Ph	Cu(tfacac) ₂	31
Ib	Ph	Cu(acac) ₂	37
Ib	Ph	Rh ₂ (OAc) ₄ ^b	0
Ic	<i>t</i> -Bu	Cu	25

^a Yield of **IIIa** 26%.

^b The reaction was carried out in methylene chloride at 20°C.

secondary amines [17]. Kanemasa *et al.* [16] showed that heating of an equimolar mixture of aldehyde **Vb** and ethyl 2-(methylamino)acetate in boiling toluene with simultaneous removal of water (deprotonation technique) leads to formation of almost equal amounts of *cis*- and *trans*-fused isomers of 1-methyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylic acid esters *cis*-**VIIa** and *trans*-**VIIa** (yield 42 and 44%, respectively; Scheme 2). In order to compare the data of [16] with our results obtained by generation of azomethine ylide **IVa** according to the carbene technique, we performed an analogous reaction of ethyl 2-(methylamino)acetate with aldehyde **Va**. By chromatographic treatment of the reaction mixture we isolated compounds *cis*-**IIa** and *trans*-**IIa** in 38% yield each.

As shown in Schemes 3 and 4, isomer *cis*-**IIa** could be formed as a result of cycloaddition in *E,Z*-ylide through *endo*-transition state or cycloaddition in *Z,E*-ylide through *exo*-transition state. Isomer *trans*-**IIa** could be formed via cycloaddition in *E,Z*-ylide through *exo*-transition state or cycloaddition in *Z,E*-ylide through *endo*-transition state. According to Kanemasa *et al.* [16], the lack of stereoselectivity in the cycloaddition in ylide **VIa** is explained by similar energies of the *endo*- and *exo*-transition states in the reaction of *Z,E*-ylide (Scheme 3). When the ylide is generated by



Vb, VIa, VIIa, R = Me; IIa, Va, IVa, R = Et.

the carbene technique, attack by carbenoid species on the unshared electron pair on the nitrogen atom in Schiff bases **Ia** and **Ib** (which are *E* isomers) could give rise to only *E,Z*- and *Z,Z*-ylide. Among these, only the former is capable of being converted into adducts **IIa** and **IIb**, and the cycloaddition involves *endo*-transition state. No cycloaddition products derived from *Z,Z*-ylides were detected, presumably due to considerably lower stability of *Z,Z*-ylides as compared to *E,Z* isomers. This is confirmed by the results of quantum-chemical calculations of the enthalpy of formation of 2-[(*E*)-MeOCOCH=CHCH₂O]C₆H₄CH=N⁺(R)CH-CO₂Me (Table 2). The $\Delta H_{Z,Z}$ values for the *N*-phenyl- and *N*-methyl-substituted ylides are greater than $\Delta H_{E,Z}$ by 7–10 kcal/mol. By contrast, the enthalpies of formation of *N*-methyl-substituted *E,Z*- and *Z,E*-ylides differ

insignificantly; therefore, there are no reasons to believe that ylides **IVa** and **VIa** will be formed only as *Z,E* isomers under thermodynamically controlled conditions of the deprotonation technique. We can conclude that nonstereoselective reaction is most likely to result from cycloaddition in *E,Z*- and *Z,E*-ylides, which involves *endo*-transition state. This conclusion is supported by simple comparison of the structures of the corresponding transition states (Scheme 5). In the transition state responsible for formation of the observed products, the dihydropyran ring should adopt a *half-chair* conformation, while the *exo*-transition state for the reaction of *Z,E*-ylide should be destabilized due to *ax,ax'*-interaction. While studying the reaction of methyl 2-diazo-2-phenylacetate with Schiff bases [18], we also concluded that the *endo*-transition

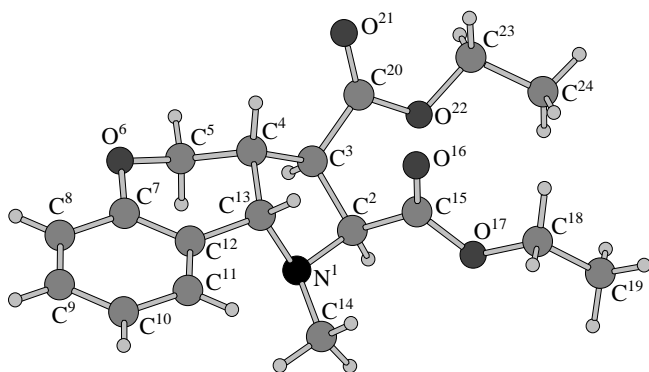


Fig. 1. Structure of the molecule of diethyl (*2RS,3RS,3aRS,9bSR*)-1-methyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylate (**IIa**) according to the X-ray diffraction data.

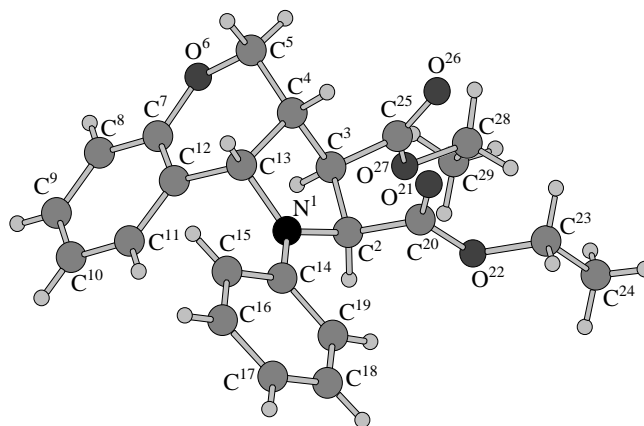
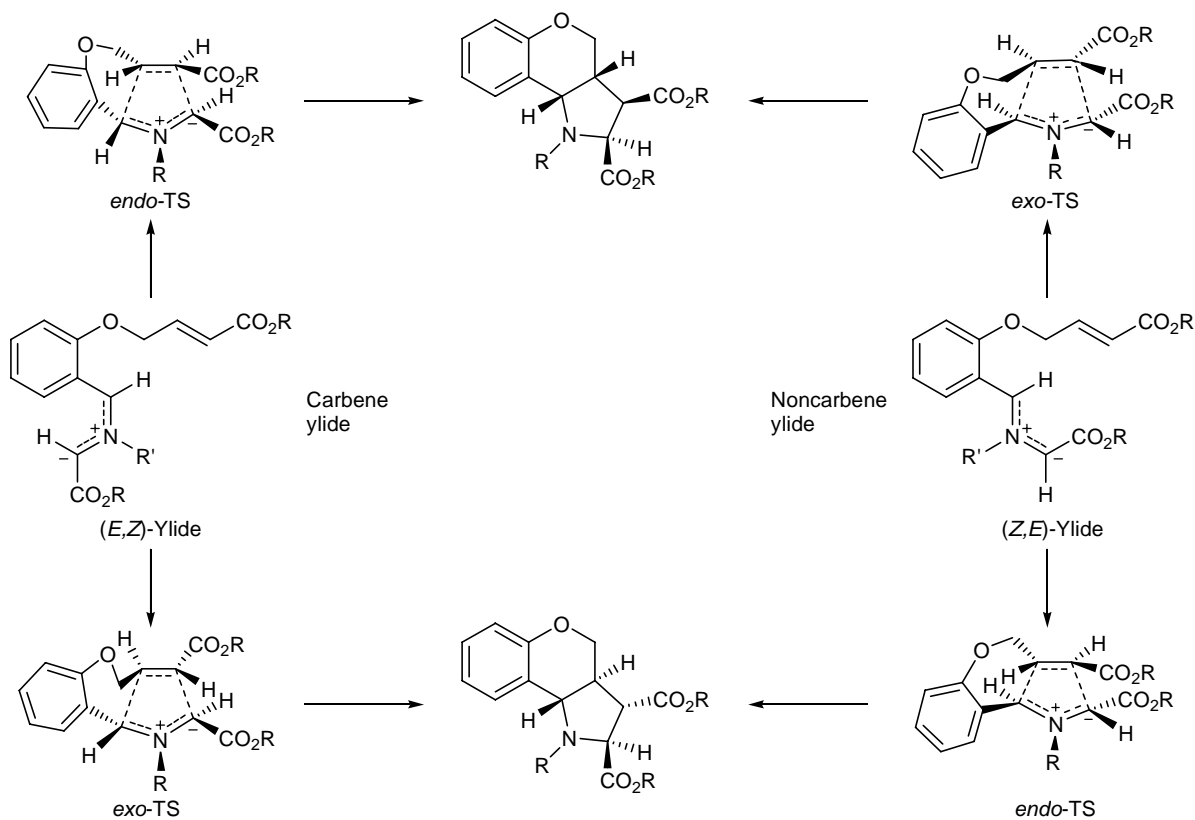
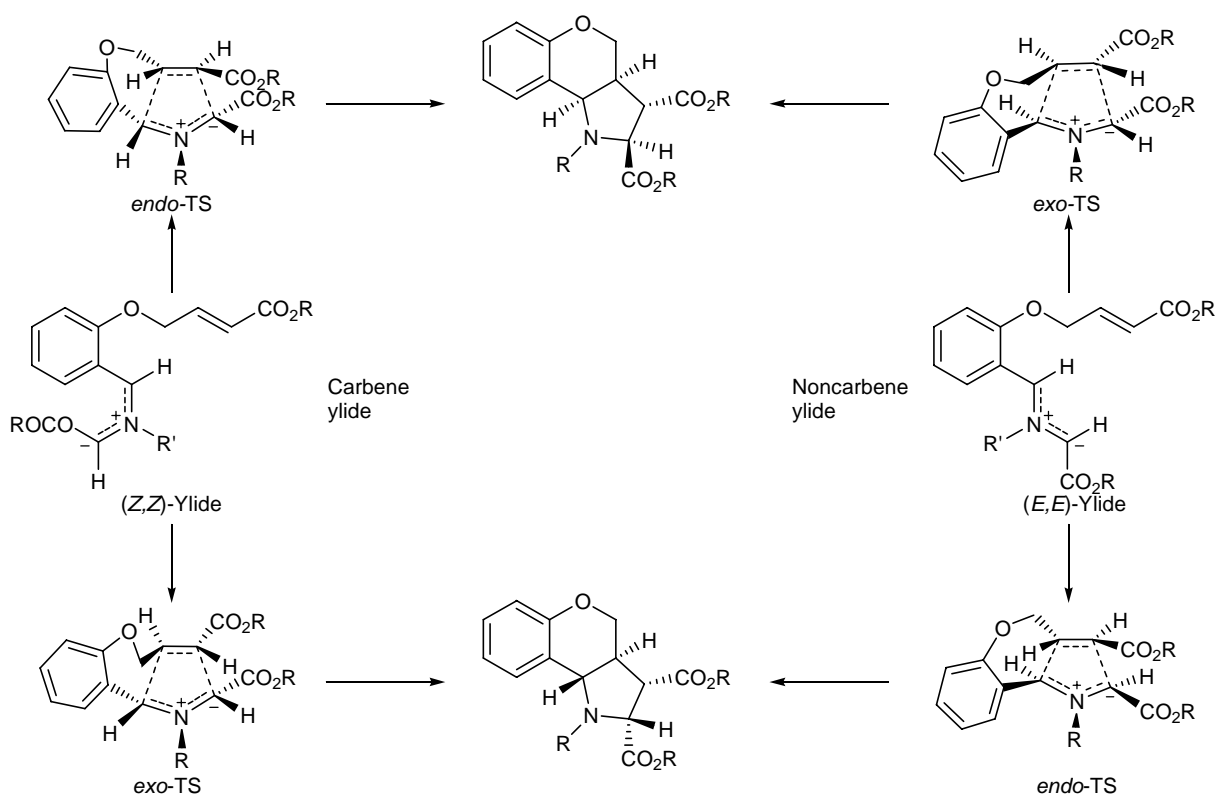


Fig. 2. Structure of the molecule of diethyl (*2RS,3SR,3aRS,9bSR*)-1-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylate (**IIb**) according to the X-ray diffraction data.

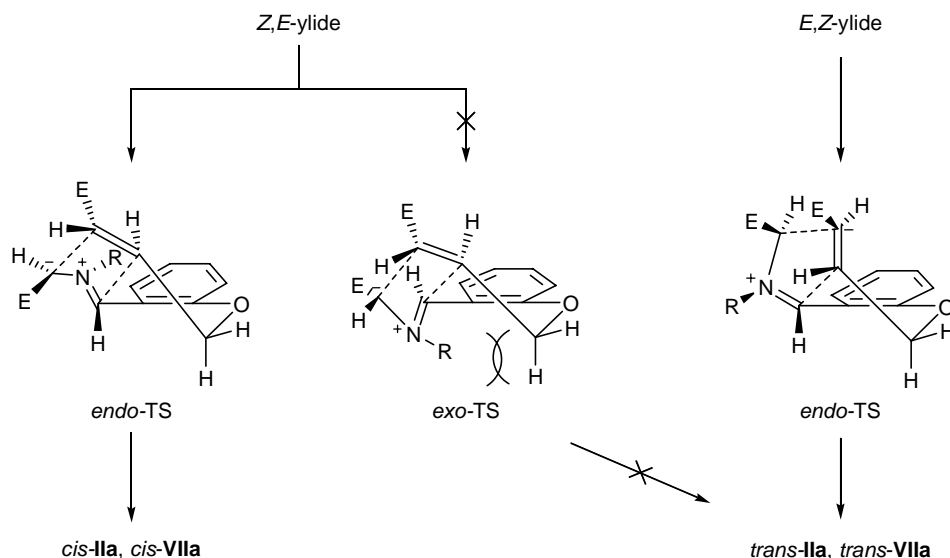
Scheme 3.



Scheme 4.



Scheme 5.



state is preferred in intramolecular 1,3-dipolar cycloaddition of azomethine ylides at activated C=C bond.

The data in Table 2 indicate increase in the stability of *Z,Z*-ylide relative to *E,Z*-ylide as the size of the R substituent increases. Presumably, this fact may be responsible for change in the stereoselectivity of cycloaddition in ylides **IV** in going from *N*-methyl and *N*-phenyl derivatives (generated by the carbene technique) to *N*-*tert*-butyl-substituted analog. In the latter case, the only product was chromenopyrrole **IIc** which can be formed via intramolecular 1,3-dipolar cycloaddition in ylide *Z,Z*-**IVc** through *endo*-TS (Scheme 4).

Thus we have effected intramolecular 1,3-dipolar cycloaddition of azomethine ylides generated by catalytic decomposition of ethyl diazoacetate in the presence of *ortho*-substituted benzylideneamines containing a dipolarophilic C=C fragment in the side chain. The cycloaddition stage is strictly regio- and stereoselective, and the products are hexahydrochromeno[4,3-*b*]pyrrole derivatives. The maximal yields of the products were obtained with the use of Cu(acac)₂ as catalyst. Analysis of the stereochemical results of the reaction of ylide **IVa** generated by two methods

(carbenoid and condensation of the aldehyde with amine) suggests that the cycloadducts are formed via *endo* approach of *E,Z*-ylides **IVa** and **IVb** to the C=C bond. Increase in the size of the substituent on the ylide nitrogen atom stabilizes the *Z,Z*-ylide, and *N*-*tert*-butyl derivative **IVc** gives rise to isomeric hexahydrochromeno[4,3-*b*]pyrrole with *trans*-oriented ethoxy-carbonyl groups.

EXPERIMENTAL

The melting points were determined on a Boetius microscope device and are uncorrected. The IR spectra were measured on a UR-20 instrument (Carl Zeiss) using 400- μ m cells. The ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300 and 75 MHz, respectively. The elemental compositions were determined on an Hewlett-Packard HP-185B CHN analyzer. The progress of reactions was monitored by TLC on Silufol UV-254 plates. Column chromatography was performed on LS silica gel (5–40 μ m, Chemapol).

Schiff bases **Ia–Ic** were synthesized by condensation of aldehydes with amines in ethanol. Copper

Table 2. Calculated enthalpies of formation ΔH (PM3, kcal/mol) of ylides 2-[(*E*)-MeOCOCH=CHCH₂O]C₆H₄CH=N⁺(R)-CHCO₂Me

R	Carbene <i>E,Z</i> -ylide		<i>E,E</i> -Ylide		<i>Z,E</i> -Ylide		Carbene <i>Z,Z</i> -ylide	
	ΔH	$\Delta\Delta H$	ΔH	$\Delta\Delta H$	ΔH	$\Delta\Delta H$	ΔH	$\Delta\Delta H$
Me	-129.03	1.35	-129.66	0.72	-130.38	0	-120.26	10.12
Ph	-94.47	2.88	-93.38	3.97	-97.35	0	-90.03	7.32
<i>t</i> -Bu	-137.22	6.00	-133.34	9.88	-143.22	0	-137.28	5.94

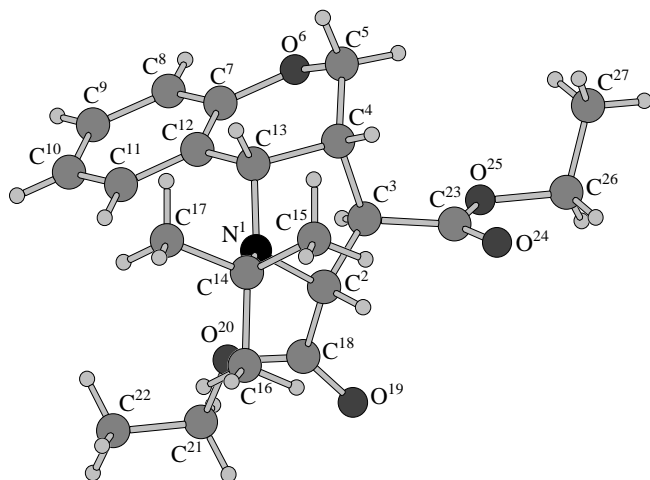


Fig. 3. Structure of the molecule of diethyl (2*RS*,3*SR*,3*aSR*,9*bRS*)-1-*tert*-butyl-1,2,3,3*a*,4,9*b*-hexahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylate (**IIIc**) according to the X-ray diffraction data.

powder for catalytic decomposition of ethyl diazoacetate was kept for 2 h in glacial acetic acid, filtered off, washed with methanol and diethyl ether, and dried for 0.5 h at 60°C under reduced pressure (1 mm).

Diethyl (2*RS*,3*RS*,3*aRS*,9*bSR*)-1-methyl-1,2,3,3*a*,4,9*b*-hexahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylate *cis*-(IIa**) and diethyl (3*aRS*,9*bSR*)-1-methyl-1,3*a*,4,9*b*-tetrahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylate (**IIIa**).** A solution of 1.38 g (12.1 mmol) of ethyl diazoacetate in 9 ml of benzene was added dropwise over a period of 2.5 h to a mixture of 1 g (4.0 mmol) of Schiff base **Ia** and 0.129 g (2.0 mmol) of copper powder in 12 ml of anhydrous benzene under stirring at 80°C. The progress of the reaction was monitored by TLC following the disappearance of initial Schiff base **Ia**. The mixture was cooled, diluted with 20 ml of hexane, and filtered through a 0.5-cm layer of silica gel, and the sorbent was additionally washed with a 4:1 hexane–diethyl ether mixture. The solvent was evaporated under reduced pressure, and the residue was recrystallized from hexane–diethyl ether to isolate 0.189 g of compound **IIIa**. The mother liquor was evaporated, and the residue was subjected to column chromatography using hexane–diethyl ether as eluent to isolate an additional portion of compound **IIIa** (0.155 g, overall yield 26%) and 0.460 g (34%) of compound **IIa** as colorless crystals.

Compound *cis*-**IIa**. mp 39–41°C (from hexane). IR spectrum (CCl₄): $\nu(\text{C}=\text{O})$ 1735 cm⁻¹. ¹H NMR spectrum (CDCl₃), δ , ppm: 1.28 t (3H, CCH₃, $J = 7.1$ Hz),

1.33 t (3H, CCH₃, $J = 7.1$ Hz), 2.41 s (3H, NCH₃), 3.41 d.d.d (1H, 3*a*-H, $J = 2.2, 3.5, 8.8, 9.3$ Hz), 3.48 d.d (1H, 3-H, $J = 6.6, 9.3$ Hz), 3.90 d.d (1H, 4-H, $J = 3.5, 11.4$ Hz), 4.02 d (1H, 9*b*-H, $J = 8.8$ Hz), 4.04 d (1H, 2-H, $J = 6.6$ Hz), 4.10–4.31 m (5H, CH₂, 4-H), 6.96–7.28 m (4H, H_{arom}). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 13.8 (CH₃); 14.1 (CH₃); 35.3 (NCH₃); 41.4 (C^{3*a*}); 47.4 (C³); 59.5 (C^{9*b*}); 60.1 (CH₂); 60.7 (CH₂); 67.4 (C²); 69.6 (C⁴); 117.7, 121.1, 125.0, 128.3, 129.5, 156.9 (C_{arom}); 170.7, 171.0 (C=O). Found, %: C 64.85; H 7.00; N 3.13. C₁₈H₂₃NO₅. Calculated, %: C 64.85; H 6.95; N 4.20.

Compound **IIIa**. mp 87–89°C (from hexane–diethyl ether). IR spectrum (CCl₄), ν , cm⁻¹: 1755, 1705 (C=O). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.26 t (3H, CCH₃, $J = 7.1$ Hz), 1.39 t (3H, CCH₃, $J = 7.1$ Hz), 2.82 s (3H, NCH₃), 3.34 d.d.d (1H, 3*a*-H, $J = 5.1, 8.4, 10.6$ Hz), 3.80 d.d (1H, 4-H, $J = 10.6, 10.8$ Hz), 4.30 d.d (1H, 4-H, $J = 5.1, 10.8$ Hz), 4.37 d (1H, 9*b*-H, $J = 8.4$ Hz), 4.40 q (2H, CH₂, $J = 7.1$ Hz), 6.94–7.00 m and 7.21–7.30 m (4H, H_{arom}). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 13.7 (CH₃); 14.0 (CH₃); 32.7 (NCH₃); 37.3 (C^{3*a*}); 59.2, 62.0, 62.9, 64.2 (C³, C^{9*b*}, CH₂); 99.4 (C³); 116.8, 117.5, 120.2, 129.5, 130.9 (C_{arom}); 153.8, 155.7 (C², C_{arom}); 162.8, 163.9 (C=O). Found, %: C 65.48; H 7.38; N 3.98. C₁₈H₂₁NO₅. Calculated, %: C 65.24; H 6.39; N 4.23.

Dehydrogenation of compound IIa. Copper powder, 20 mg (0.32 mmol), was added to a solution of 20 mg (0.06 mmol) of compound **IIa** in 2 ml of anhydrous benzene, and the mixture was heated for 0.5 h under reflux. According to the TLC data, no reaction occurred. A solution of ethyl diazoacetate in benzene was then added until the initial compound disappeared. The product was isolated by column chromatography using hexane–diethyl ether as eluent. Yield of **IIIa** 7 mg (35%), colorless crystals.

Diethyl (2*RS*,3*RS*,3*aRS*,9*bSR*)-1-phenyl-1,2,3,3*a*,4,9*b*-hexahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylate (IIb**).** *a.* A solution of 0.7 g (9.14 mmol) of ethyl diazoacetate in 12 ml of benzene was added dropwise over a period of 2.5 h to a mixture of 0.7 g (2.26 mmol) of Schiff base **Ib** and 0.1 g (1.57 mmol) of copper powder in 10 ml of anhydrous benzene under stirring at 80°C. The solvent was evaporated, and the residue was subjected to column chromatography using hexane–ethyl acetate as eluent to isolate 0.117 g (13%) of compound **IIIb** as colorless crystals. mp 101–103°C (from diethyl ether). IR spectrum

(CCl₄): $\nu(\text{C}=\text{O})$ 1750 cm⁻¹. ¹H NMR spectrum (CDCl₃), δ , ppm: 1.14 t (3H, CCH₃, $J = 7.1$ Hz), 1.33 t (3H, CCH₃, $J = 7.1$ Hz), 3.38 d.d.d.d (1H, 3a-H, $J = 2.3, 2.7, 8.4, 12.4$ Hz), 3.67 d.d (1H, 3-H, $J = 8.4, 12.4$ Hz), 4.08 m (2H, CH₂), 4.22 m (2H, CH₂), 4.30–4.34 m (2H, CH₂), 4.80 d (1H, 2-H, $J = 8.4$ Hz), 5.50 d (1H, 9b-H, $J = 8.4$ Hz), 6.79–6.92 m (5H, C₆H₅), 7.12–7.45 m (4H, H_{arom}). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 13.7 (CH₃); 13.8 (CH₃); 37.7 (C^{3a}); 45.8 (C³); 53.2 (C^{9b}); 60.8 and 61.0 (CH₂); 63.2 and 64.3 (C², C⁴); 113.8, 116.8, 117.7, 121.3, 124.9, 128.3, 128.5, 129.0, 146.2, 153.2 (C_{arom}); 169.6, 170.9 (C=O). Found, %: C 69.98; H 6.44; N 3.45. C₂₃H₂₅NO₅. Calculated, %: C 69.86; H 6.37; N 3.54.

b. A solution of 0.2 g (1.75 mmol) of ethyl diazoacetate in 12 ml of anhydrous benzene was added dropwise over a period of 2.5 h to a mixture of 0.3 g (0.97 mmol) of Schiff base **Ib** and 0.025 g (0.10 mmol) of copper acetylacetonate in 5 ml of benzene under stirring at 80°C (after addition of 1 equiv of ethyl diazoacetate, products with small R_f values appeared in the mixture). The mixture was evaporated, and the residue was subjected to column chromatography using hexane–ethyl acetate as eluent to isolate 206 mg of an oily substance. The product was dissolved in diethyl ether, and the solution was left to stand for 24 h in a refrigerator. The crystals were filtered off and recrystallized from diethyl ether. Yield of **IIIb** 0.142 g (37%), colorless crystals.

c. A solution of 0.9 g (7.89 mmol) of ethyl diazoacetate in 3.1 ml of anhydrous benzene was added dropwise over a period of 4 h to a mixture of 0.927 g (3.0 mmol) of Schiff base **Ib** and 0.111 g (0.3 mmol) of copper trifluoroacetylacetonate in 15 ml of benzene under stirring at 80°C. After appropriate treatment, we isolated 0.37 g (31%) of compound **IIIb** as colorless crystals.

Diethyl (2RS,3SR,3aSR,9bRS)-1-tert-butyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylate (IIc). Ethyl diazoacetate, 1.2 g (10.5 mmol), was added dropwise over a period of 5 h to a mixture of 0.572 g (1.98 mmol) of Schiff base **Ic** and 0.3 g (0.47 mmol) of copper powder in 10 ml of benzene under stirring at 80°C. The mixture was evaporated, and the residue was subjected to column chromatography using hexane–diethyl ether as eluent to isolate 0.19 g (25%) of compound **IIc** as colorless crystals. mp 118–120°C (from hexane–diethyl ether). IR spectrum (CCl₄), ν , cm⁻¹: 1745, 1760 (C=O). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.03 t (3H, CH₃,

$J = 7.1$ Hz), 1.26 s (9H, *t*-Bu), 1.33 t (3H, CCH₃, $J = 7.1$ Hz), 2.65 d.d.d.d (1H, 3a-H, $J = 2.2, 2.2, 7.5, 11.5$ Hz), 3.45 d.d (1H, 3-H, $J = 8.4, 11.5$ Hz), 3.90 q (2H, CH₂, $J = 7.1$ Hz), 4.20 d (1H, 2-H, $J = 8.4$ Hz), 4.23 q (2H, CH₂, $J = 7.1$ Hz), 4.27 d.d (1H, 4-H, $J = 2.2, 7.1$ Hz), 4.23 q (2H, CH₂), 4.24 (1H, 4-H, $J = 2.2, 11.9$ Hz), 4.30 (1H, 4-H, $J = 2.2, 11.9$ Hz), 4.44 d (1H, 9b-H, $J = 7.5$ Hz), 6.73–7.56 m (4H, H_{arom}). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 13.5 (CH₃); 13.9 (CH₃); 28.0 (*t*-Bu); 42.5 (C^{3a}); 48.2 (C³); 55.0 (CMe₃); 56.5 (C^{9b}); 60.2 and 60.8 (CH₂); 63.8 (C⁴); 64.0 (C²); 115.9, 120.6, 124.9, 127.5, 130.7, 153.5 (C_{arom}); 172.9, 173.7 (C=O). Found, %: C 67.06; H 7.72; N 3.47. C₂₁H₂₉NO₅. Calculated, %: C 67.18; H 7.78; N 3.73.

Reaction of ethyl 4-(2-formylphenoxy)methyl)-2-butenolate (VI) with ethyl 2-(methylamino)acetate. A mixture of 0.35 g (1.5 mmol) of aldehyde **VI**, 0.51 g (3.32 mmol) of ethyl 2-(methylamino)acetate hydrochloride, and 0.4 g (3.95 mmol) of triethylamine in 10 ml of toluene was heated for 2 h under reflux. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography using hexane–ethyl acetate as eluent to isolate 0.18 g (38%) of diethyl (2RS,3RS,3aRS,9bSR)-1-methyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylate (*cis*-**IIa**) and 0.18 g (38%) of diethyl (2RS,3SR,3aSR,9bSR)-1-methyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylate (*trans*-**IIa**).

Compound *trans*-**IIa**. mp 36–37°C (from pentane). IR spectrum (CCl₄): $\nu(\text{C}=\text{O})$ 1735 cm⁻¹. ¹H NMR spectrum (CDCl₃), δ , ppm: 1.30 t (3H, CCH₃, $J = 7.1$ Hz), 1.33 t (3H, CCH₃, $J = 7.1$ Hz), 2.56 s (3H, NCH₃), 2.67 d.q (1H, 3a-H, $J = 11.3, 4.4$ Hz), 3.11 d.d (1H, 3-H, $J = 11.3, 5.9$ Hz), 4.00 d (1H, 9b-H, $J = 11.3$ Hz), 4.17 d (1H, 2-H, $J = 5.9$ Hz), 4.22 q (2H, CH₂, $J = 7.1$ Hz), 4.25 q (2H, CH₂, $J = 7.1$ Hz), 4.66 d.d (1H, 4-H, $J = 10.2, 5.9$ Hz), 4.21 d.d (1H, 4-H, $J = 11.3, 10.2$ Hz), 6.83–7.35 m (4H, H_{arom}). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 13.9 (CH₃); 38.1 (NCH₃); 41.0 (C^{3a}); 48.9 (C³); 61.0 (C^{9b}); 64.2 (CH₂); 64.3 (CH₂); 69.5 and 71.2 (C², C⁴); 116.2, 119.9, 122.9, 125.5, 127.9, 153.7 (C_{arom}); 171.8, 172.2 (C=O). Found, %: C 64.83; H 6.94; N 3.96. C₁₈H₂₃NO₅. Calculated, %: C 64.85; H 6.95; N 4.20.

This study was performed under financial support by the Program “Universities of Russia” (project no. ur.05.01.316) and by the Russian Foundation for Basic Research (project no. 05-03-33257).

REFERENCES

1. Doyle, M., McKervey, M., and Ye, T., *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*, New York: Wiley, 1998.
2. Padwa, A. and Hornbuckle, S.F., *Chem. Rev.*, 1991, vol. 91, p. 263.
3. Padwa, A. and Krumpke, K.E., *Tetrahedron*, 1992, vol. 48, p. 5385.
4. Ye, T. and McKervey, M.A., *Chem. Rev.*, 1994, vol. 94, p. 1091.
5. Khlebnikov, A.F., Novikov, M.S., and Kostikov, R.R., *Adv. Heterocycl. Chem.*, 1996, vol. 65, p. 93.
6. Davies, H.M.L. and Beckwith, R.E.J., *Chem. Rev.*, 2003, vol. 103, p. 2861.
7. Khlebnikov, A.F., Novikov, M.S., and Kostikov, R.R., *Usp. Khim.*, 2005, vol. 74, p. 183.
8. Voznyi, I.V., Novikov, M.S., Khlebnikov, A.F., Kostikov, R.R., and Kopf, J., *J. Chem. Soc., Perkin Trans. 1*, 2002, p. 1628.
9. Voznyi, I.V., Novikov, M.S., Khlebnikov, A.F., Kopf, J., and Kostikov, R.R., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 199.
10. Voznyi, I.V., Novikov, M.S., Khlebnikov, A.F., and Kostikov, R.R., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2004, p. 1044.
11. Khlebnikov, A.F., Voznyi, I.V., Novikov, M.S., and Kostikov, R.R., *Russ. J. Org. Chem.*, 2005, vol. 41, p. 560.
12. Tsuge, O., Ueno, K., and Ueda, I., *Heterocycles*, 1981, vol. 16, p. 1503.
13. Armstrong, P., Grigg, R., Jordan, M.W., and Malone, J.F., *Tetrahedron*, 1985, vol. 41, p. 3547.
14. Grigg, R., Donegan, G., Gunaratne, H.Q.N., Kennedy, D.A., Malone, J.F., Sridharan, V., and Thianpatanagul, S., *Tetrahedron*, 1989, vol. 45, p. 1723.
15. Barr, D.A., Grigg, R., Gunaratne, H.Q.N., Kemp, J., McMeekin, P., and Sridharan, V., *Tetrahedron*, 1988, vol. 44, p. 557.
16. Kanemasa, S., Sakamoto, K., and Tsuge, O., *Bull. Chem. Soc. Jpn.*, 1989, vol. 62, p. 1960.
17. Tsuge, O. and Kanemasa, S., *Adv. Heterocycl. Chem.*, 1989, vol. 45, p. 231.
18. Khlebnikov, A.F., Novikov, M.S., Bespokoiev, A.A., Kostikov, R.R., Kopf, J., Starikova, Z.A., and Antipin, M.Yu., *Russ. J. Org. Chem.*, 2005, vol. 41, p. 922.