Russian Journal of Organic Chemistry, Vol. 41, No. 2, 2005, pp. 194–203. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 2, 2005, pp. 205–213.

Dipolar Cycloaddition of Carbonyl Ylides Generated from Methyl *cis*-2-Diazoacetyl-1-cyclopropanecarboxylates

A.P. Molchanov[1], V.V. Diev[1], J. Kopf[2], and R.R. Kostikov[1]

[1]*St. Petersburg State University, St. Petersburg, 198904 Russia*
[2]*Institut für Anorganische Chemie, Martin-Luter-King Platz 6, D-20146, Hamburg, Germany*

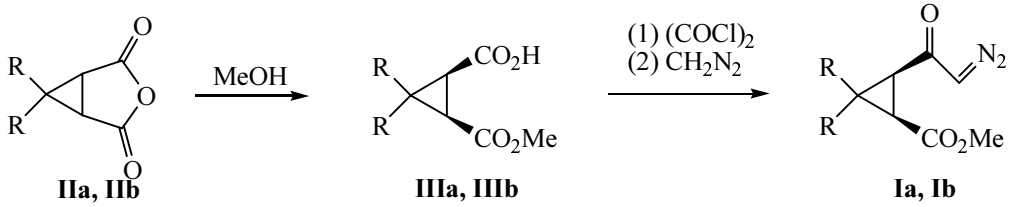
Received April 22, 2004

Abstract—Carbonyl ylide generated from methyl *cis*-3-diazoacetyl-2,2-diphenyl-1-cyclopropanecarboxylate in the presence of $Rh_2(OAc)_4$ when brought into reaction of 1,3-dipolar cycloadditionя with *N*-arylmaleimides afforded substituted 4-aryl-7-methoxy-9,9-diphenyl-12-oxa-4-azatetracyclo-[5.4.1.$0^{2,6}$.$0^{8,10}$]dodecene-3,5,11-triones. Concurrent processes resulted in formation of cycloheptatrienes, hydroxyacetylcyclopropanecarboxylates, and benzophenone. Carbonyl ylide generated from methyl *cis*-2-diazoacetyl-1-cyclopropanecarboxylate in the same reaction gave *rise to exo*- and *endo*-4-aryl-7-methoxy-12-oxa-4-azatetracyclo[5.4.1.$0^{2,6}$.$0^{8,10}$]dodecene-3,5,11-triones.

Nowadays several kinds of tandem transformations are developed, in particular, a cyclization of a metallocarbenoid formed from a diazo compound into a carbonyl ylide followed by 1,3-dipolar cycloaddition to a dipolarophiles. This method provides a possibility to prepare polysubstituted tetrahydrofuran derivatives that are structural elements of naturally occurring compounds [1]. The synthesis of some naturally occurring compounds was carried out applying this procedure [2]. The carbonyl ylides are involved into enantioselective transformations [3, 4], cyclizations of diazo compounds are described providing five-membered, six-membered, and seven-membered carbonyl ylides. In all cases the cyclization of carbonyl ylide and the subsequent dipolar cycloaddition are strongly affected by the structure of the initial diazo compound and the character of the carbonyl group [1]. In extension of our research concerning the application of carbonyl ylides reactions to the synthesis of cyclopropane compounds [5] we investigated in this study the opportunity of generating a six-membered carbonyl ylide with a fused three-carbon ring from *cis*-1,2-diazoketo-substituted cyclopropanes. The carbonyl ylide generated from *o*-methoxycarbonyl-α-diazoacetophenone and containing a fused benzene ring is known to be highly reactive in addition to a wide range of dipolarophiles [6]. At the same time attempts failed to obtain cycloadducts in reaction with methyl 5-diazo-4-oxopentane-1-carboxylate where the diazocarbonyl and ester groups are separated by a dimethylene chain [7]. No adducts formed also in reaction of some 1,2-disubstituted cyclopentanes possessing diazoketo and ester groups in a *cis*-position. The latter fact was ascribed to conformational reasons, namely, to cyclization of the rhodium carbenoid at the ester group oxygen instead of the carbonyl atom [8].

Diazoketone **Ia, Ib** were prepared from anhydrides **IIa, IIb** obtained by procedures [9, 10]. The anhydrides **IIa, IIb** obtained were boiled in anhydrous methanol to get partial esters **IIIa, IIIb** that were treated first with oxalyl chloride and then with diazomethane to afford diazoketones **Ia, Ib** (Scheme 1).

Scheme 1.

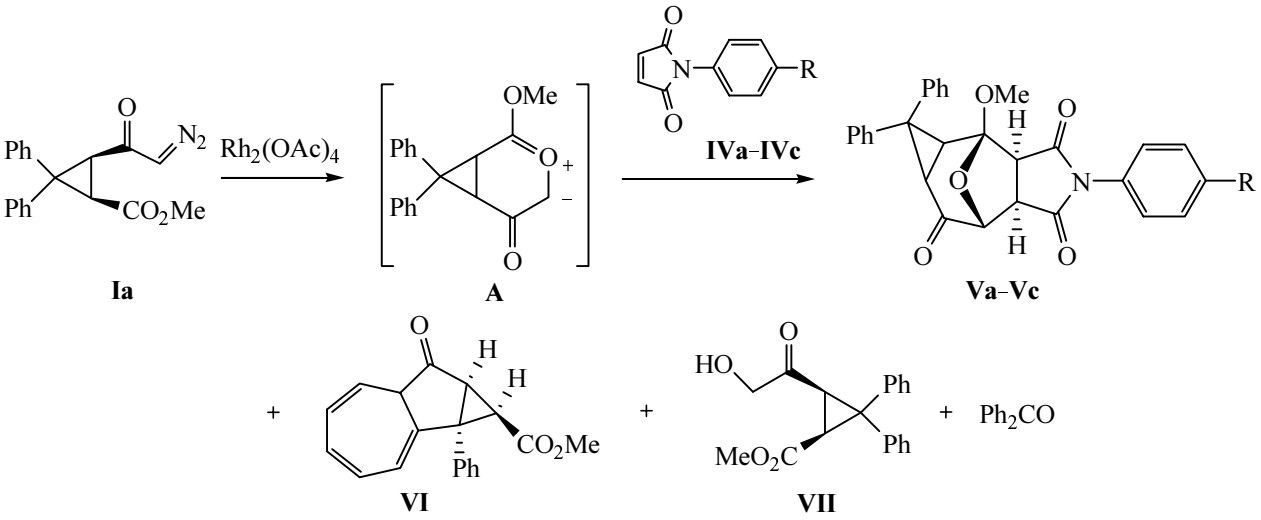


IIa, IIb **IIIa, IIIb** **Ia, Ib**

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

1070-4280/05/4102-0194©2005 Pleiades Publishing, Inc.

Scheme 2.



R = H (**a**), Me (**b**), Cl (**c**).

In the IR spectra of diazoketones **Ia, Ib** appear strong absorption bands at 2120 (C=N_2), 1740–1750 (ester C=O), and 1650–1660 cm^{-1} (C=O of diazoketo group). ^{1}H NMR spectra contain a broadened singlet belonging to the proton at the carbon attached to the diazo group in the region of 5.5 ppm, and proton signals of the cyclopropane ring in the region of 1.23–2.83 ppm. In the ^{13}C NMR spectra appear the signals from the carbons belonging to the ester groups (~170 ppm) and from that of diazoacetyl groups (~189 ppm), of carbonyl groups, and a broadened signal from the carbon attached to the diazo group at about 57 ppm.

The reaction of diazoketone **Ia** with N-aryl-substituted maleimides **IVa–IVc** in the presence of $Rh_2(OAc)_4$ afforded products of 1,3-dipolar cycloaddition of carbonyl ylide (**A**), 4-aryl-7-methoxy-9,9-diphenyl-12-oxa-4-azatetracyclo[5.4.1.$0^{2,6}$.$0^{8,10}$]dodecane-3,5,11-triones (**Va–Vc**) in 41–44% yields. Apart from these compounds we isolated from the reaction mixture a product of the carbenoid addition to the multiple bond of the phenyl group with a subsequent opening of the three-membered ring, methyl 2-oxo-1aα-phenyl-1aβ,6a,7,7aα-tetrahydro-1*H*-cyclopropa[*a*]azulene-1-carboxylate (**VI**) (26–28%), also methyl *cis*-3-glycoloyl-2,2-diphenyl-1-cyclopropanecarboxylate (**VII**), and benzophenone (3%) (Scheme 2).

The use of copper(II) acetylacetonate as catalyst resulted in decreased yield of adduct **Va** (15%) and in growing amount of azulenone **VI** to 45% apparently due to the higher electrophilicity of the carbenoid. The composition and structure of adducts **Va–Vc** were established from elemental analyses and spectral data. The IR spectra of compounds **Va–Vc** contain a strong absorption band characteristic of the stretching vibrations of C=O group in the region 1740–1720 cm^{-1}. In the ^{1}H NMR the following signals appear: a singlet of the proton attached to C^1 in the region 4.54–4.56 ppm, a singlet of the methoxy group at 3.6–3.7 ppm, two doublets from the cyclopropane protons in the region 2.5–2.8 ppm (*J* 8 Hz), and two doublets of protons at C^2 and C^6 in the region 3.4–3.7 ppm (*J* 8 Hz). The coupling constant of protons linked to C^1 and C^2 is close to zero; this value is characteristic of analogous compounds with an *exo*-configuration of the oxygen bridge, where the dihedral angle HC^1C^2H is equal approximately to 90° [11]. The ^{13}C NMR spectra of compounds **Va–Vc** contain

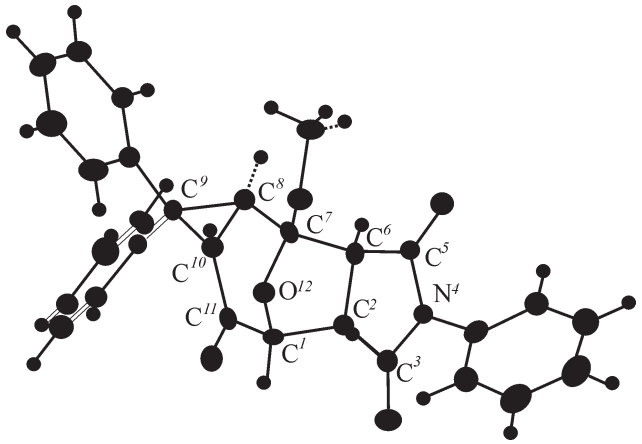


Fig. 1. Structure of compound **Va** according to X-ray diffraction data.

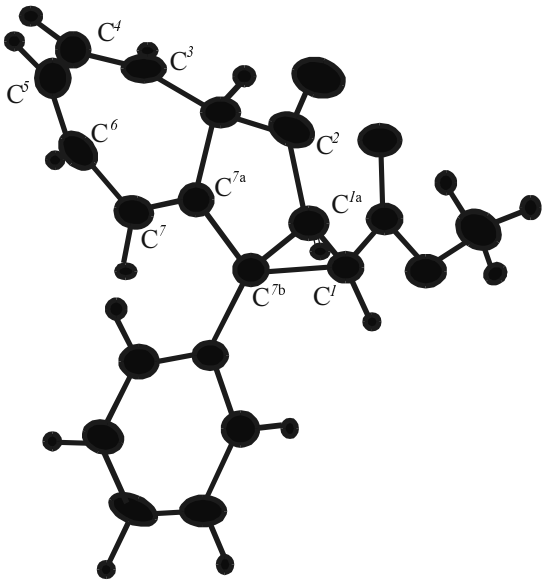


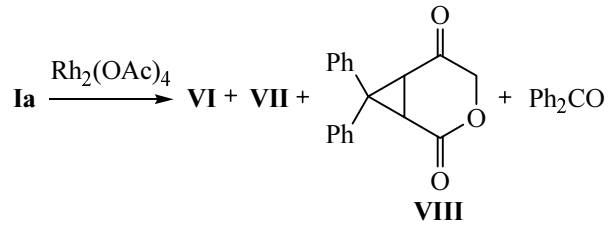
Fig. 2. . Structure of compound **VI** according to X-ray diffraction data.

signals from the carbons of three carbonyl groups: in the region 200 ppm (C^{11}) and within 171–174 ppm range (C^3, C^5); of a carbon atom in position *1* at 80 ppm, and of atom C^7 around 110 ppm. The structure of adduct **Va** was solved by X-ray diffraction analysis (Fig. 1).

In the IR spectrum of azulenone **VI** a strong absorption band is observed at 1750 cm^{-1} (C=O). The ^{1}H NMR spectrum contains multiplet signals of protons at the double bonds of the cycloheptatriene ring in the region of 5.5–6.5 ppm, doublets of the cyclopropane protons at 2.62 and 3.13 ppm (*J* 8.8 Hz), and a broadened singlet from the proton at C^{2a}, δ 3.15 ppm. In the ^{13}C NMR spectrum signals from two carbonyl carbons appear at 211.1 (ketone) and 169.7 ppm (ester). The carbon signals from the cycloheptatriene ring and from phenyl substituent are located in the region 120–139 ppm. The structure of azulenone **VI** was proved by X-ray diffraction analysis (Fig. 2). Azulenone **VI** presumabley forms as a result of concurrent intramolecular version of Buechner reaction, a cyclopropanation by rhodium carbenoid of a multiple bond in the phenyl group followed by isomerization of the norcaradiene into a cycloheptatriene. The processes of this sort in the presence of copper and rhodium catalysts are described in the literature [12].

The structure and composition of methyl *cis*-3-(2-hydroxyacetyl)-2,2-diphenyl-1-cyclopropanecarboxylate (**VII**) were established from the spectral data and elemental analysis. In the IR spectrum a broadened absorption band is present in the region 3420–3200 cm^{-1} characteristic of the stretching vibrations of a hydroxy group, and a strong broadened band at 1750 cm^{-1} (C=O). The ^{1}H NMR spectrum contains two doublets corresponding to the protons of a methylene group at 4.37 and 4.50 ppm (*J* 8.8 Hz), a broadened signal of the hydroxy group proton at 3.18 ppm, doublets of the cyclopropane protons at 2.86 and 2.97 ppm (*J* 9.8 Hz), and also a signal from methoxy group protons at 3.70 ppm. In the ^{13}C two signals from carbonyl carbons were observed at 204.7 (in hydroxyacetyl group) and 168.7 ppm (in methoxycarbonyl group), and the carbon atom of the methylene group gave rise to a signal at 70.1 ppm. Analogous reaction products presumably arising at hydrolysis of the reactive intermediates, like rhodium carbenoids, were described before [1].

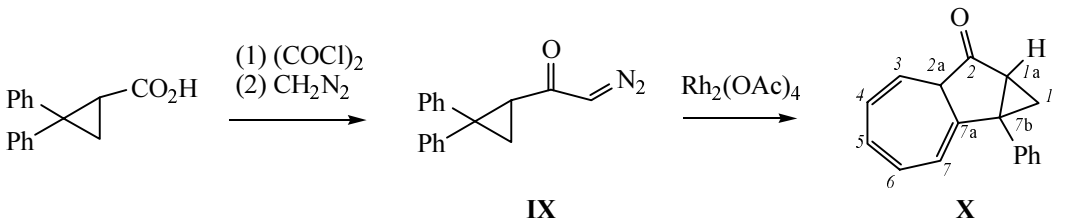
The catalytic decomposition of diazoketone **Ia** in the absence of dipolarophiles gave rise to azulenone **VI**, ester **VII**, 7,7-diphenyl-3-oxabicyclo-[4.1.0]-heptane-2,5-dione (**VIII**) in a 10% yield, and to benzophenone (~3%).



VIII

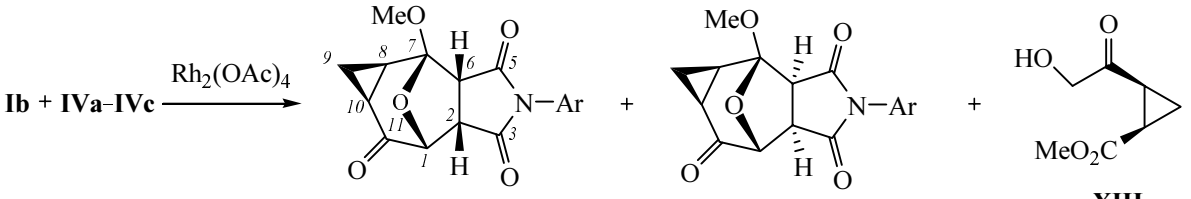
The decomposition of *o*-alkoxycarbonyl-α-diazoacetophenone was described in the literature, and a formation of a similar lactone as a result of a carbonyl ylides hydrolysis was presumed [6, 13]. The structure and composition of lactone **VIII** were established from elemental analysis and spectral data. In the ^{1}H NMR spectrum the methylene protons signal is present as a doublet of doublets at 4.36 ppm (*J* 18.5, 1.6 Hz), the resonances of the cyclopropane ring protons are located as a doublet of doublets at 3.12 ppm (*J* 7.5, 1.6 Hz) and as a doublet at 3.18 ppm (*J* 7.5 Hz). In the ^{13}C NMR spectrum are observed two signals of carbonyl carbon atoms at 197.8 (ketone) and 169.9 (lactone) ppm, and a resonance of methylene group carbon at 73.5 ppm. In the IR spectrum strong absorption bands of carbonyl groups appear at 1750 (lactone) and 1720 cm^{-1} (ketone). The benzophenone isolated from the reaction mixtures in ~3% yield originates from the oxidation of diazo compound **Ia** in the presence of rhodium salt or of intermediately formed carbonyl ylide. It should be noted that catalytic decomposition of diazoketone **IX** where the cyclization into a carbonyl ylide was impossible resulted in formation of only azulenone **X** in a ~70% yield (Scheme 3).

Scheme 3.



IX **X**

Scheme 4.



XIa–XIc **XIIa–XIIc** **XIII**

Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**).

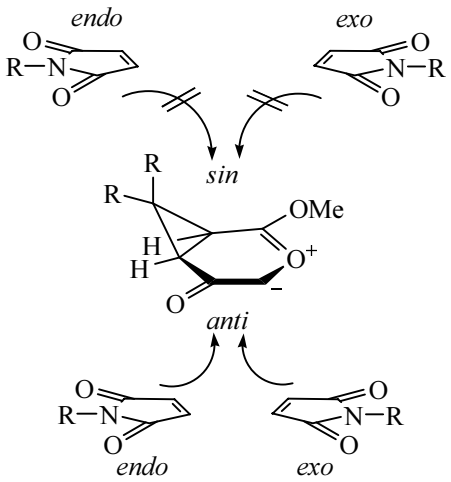
The structure of azulene **X** was derived from spectral data. In the ^{1}H NMR spectrum appear the multiplet signals from the protons of the cycloheptatriene ring in the region 5.43–6.36 ppm, resonances of the cyclopropane protons in the region 1.67–2.29 ppm, and a broadened singlet from the proton attached to C^{2a} in the region 3.14 ppm. In the ^{13}C NMR spectrum the signal of a carbonyl group carbon is located at 211.7 ppm.We failed to isolate azulenone **X** in a pure state for it suffered slight isomerization during chromatography on the silica gel.

The reaction of diazoketone **Ib** with N-aryl-substituted maleimides in the presence of $Rh_2(OAc)_4$ afforded a mixture of *endo*- **XIa–XIc** and *exo*- **XIIa–XIIc** isomers in a ratio 1.0:1.5–2.0 and an overall yield 41–45% (Scheme 4).

We did not find formation of two more probable isomers with respect to the position of the cyclopropane ring.. The structure and composition of adducts **XI** and **XII** were established from spectral data and elemental analyses. In the IR spectra strong absorption bands were observed at about 1730 cm^{-1} (C=O). The ^{1}H NMR spectra of *exo*-isomers **XIIa–XIIc** contain a singlet of the proton attached to C^1 in the region about 4.6 ppm, doublets of protons linked to C^2 and C^6 in the region 3.4–3.7 ppm (*J* 8 Hz), a singlet of the methoxy group at 3.6 ppm, and cyclopropane protons signals in the range of 1.45–2.40 ppm. In the ^{13}C NMR spectra the carbons of three carbonyl groups give rise to signals at about 200 ppm (ketone) and in the region 170–175 ppm (C^3 and C^5), the signals from the cyclopropane ring carbons are located upfield in the region 10–25 ppm, and the signals of atoms C^1 and C^7 appear at 80 and 110 ppm respectively. The *exo*-configuration was established from the lack of coupling between protons at C^1 and C^2 protons. In the ^{1}H NMR spectra of *endo*-isomers **XIa–XIc** were observed doublet signals of protons at C^1 (about 4.6 ppm), at C^6 (about 4.5 ppm, *J* 9 Hz), a triplet signal of proton at C^2 (about 4.0 ppm, *J* 9 Hz), and also signals of cyclopropane protons in the range of 1.2–2.3 ppm. The ^{13}C NMR spectra of the *endo*-isomers are similar to the spectra of the *exo*-isomers. The *endo*-configuration of adducts **XI** was established from the coupling constant between protons at C^1 and C^2 (*J* 9 Hz) [11]. The relative configuration of the cyclo-propane ring was assigned by analogy to adducts **V**. A side product of reaction, methyl *cis*-2-(2-hydroxy-acetyl)-1-cyclopropanecarboxylate **XIII** was detected in the reaction mixture by tits signals in the ^{1}H NMR spectrum: the methoxy group singlet at 3.69 ppm, the methylene protons doublets at 4.34 and 4.47 ppm (*J* 19 Hz), and multiplets of the cyclopropane protons in the range 1.3–2.3 ppm

Hence the reaction of 2,2-diphenyl-substituted diazoketone **Ia** in the presence of *N*-arylmaleimides gave rise to a product of 1,3-dipolar cycloaddition as an only stereoisomer of four possible structures whereas from diazoketone **Ib** unsubstituted in this position two isomers were obtained. The data obtained allow a suggestion that in the reaction under study the dipolarophile approaches from the *anti*-side of the carbonyl ylides (with respect to the cyclopropane ring), and therewith in the case of the ylide unsubstituted in the cyclopropane ring occurs both *exo*- and *endo*-approach, whereas with the diphenyl-substituted ylide (**A**) only the *exo*-approach is possible. The bulky phenyl groups prevent the *endo*-approach by the steric hindrances in the transition state (Scheme 5).

Scheme 5.



It should be noted that the carbonyl ylides under discussion did not react with diethyl fumarate or diethyl maleate.

EXPERIMENTAL

IR spectra were recorded from 2% solutions of compounds in chloroform on a spectrophotometer UR-20. NMR spectra were registered on spectrometer Bruker DPX-300 operating for ^{1}H at 300, for ^{13}C at 75 MHz. Elemental analyses were carried out on a CHN-analyzer HP-185B. Dichloromethane was distilled over P_2O_5. The progress of reactions was monitored by TLC on Silufol UV-254 plates

Methyl *cis*-3-diazoacetyl-2,2-diphenyl-1-cyclopropanecarboxylate (Ia). In 20 ml of anhydrous methanol 1.00 g (3.79 mmol) of 3,3-diphenyl-1,2-cyclopropanedicarboxylic anhydride (**IIa**) was heated for 8 h. The methanol was evaporated, and *cis*-3,3-diphenyl-2-methoxycarbonyl-1-cyclopropanecarboxylic acid (**IIIa**) obtained was dried in a vacuum, mp 127–128°C. IR spectrum, cm^{-1}: 890, 950, 1020, 1150, 1260, 1300, 1420 s, 1450 v.s, 1500, 1605, 1710 v.s, 1750 v.s, 2690, 2770, 2960, 3050 br. ^{1}H NMR spectrum, δ, ppm: 2.86 d (1H, *J* 8.4 Hz), 2.99 d (1H, *J* 8.4 Hz), 3.93 s (3H), 7.18–7.45 m (10H). Found, %: C 72.89; H 5.42. $C_{18}H_{16}O_4$. Calculated, %: C 72.96; H 5.44. The acid was dissolved in 5 ml of CH_2Cl_2 and in a flow of dry argon while cooling with ice to the solution was added 0.96 g (7.6 mmol, 2 equiv) of oxalyl chloride and a drop of DMF. The mixture was stirred for 3.5 h at room temperature, the excess oxalyl chloride and dichloromethane were distilled off in a vacuum. The residue was dissolved in 10 ml of anhydrous THF and was added within 10 min to a cooled with ice ether solution of diazomethane prepared from 2.3 g (22.7 mmol, 6 equiv) of *N*-nitroso-*N*-methylurea. The reaction mixture was left standing for 10 h while slowly warming to room temperature. The solvent was evaporated in a vacuum, the residue was subjected to chromatography on a column packed with silica gel (5/40 mesh), eluent dichloromethane. Yield of diazoketone **Ia** 893 mg (74%), mp 160–164°C (decomp.). IR spectrum, cm^{-1}: 1020, 1060, 1085, 1145, 1180, 1330, 1375 s, 1410, 1450, 1500, 1605, 1660 s, 1750 v.s, 2120 v.s, 2930, 2960, 3005, 3040, 3070, 3120. ^{1}H NMR spectrum, δ, ppm: 2.76 d (1H, *J* 9.6 Hz), 2.83 d (1H, *J* 9.6 Hz), 3.69 s (3H), 5.53 s (1H), 7.15–7.50 m (10H). ^{13}C NMR spectrum, δ, ppm: 30.11 (CH), 33.83 (CH), 45.70 (C), 52.44 (CH_3), 57.61 (CHN_2), 127.50 (CH), 127.68 (CH), 127.78 (CH), 128.37 (CH), 129.24 (CH), 131.13 (C), 136.29 (C), 145.95 (C), 169.27 (C=O), 188.74 (C=O). Found, %: C 71.34; H 5.08; N 8.68. $C_{19}H_{16}N_2O_3$. Calculated, %: C 71.24; H 5.03; N 8.68.

Methyl *cis*-2-diazoacetyl-1-cyclopropanecarboxylate (Ib). A solution of 0.87 g (7.76 mmol) of 1,2-cyclopropanedicarboxylic anhydride (**IIb**) in 10 ml of anhydrous methanol was heated for 20 h. The methanol was distilled off, and the residue was dried in a vacuum. Without further purification the hemiester was dissolved in 5 ml of anhydrous dichloromethane, and to the solution obtained at cooling with ice while stirring was added in a flow of dry argon 1.97 g (15.5 mmol) of oxalyl chloride and a drop of DMF. The mixture was stirred at cooling with ice for 3 h, the excess oxalyl chloride and dichloromethane were distilled off in a vacuum. The residue dissolved in 5 ml of anhydrous dichloromethane was added at cooling with ice within 10 min to an ether solution of diazomethane prepared from 4.8 g (47 mmol, 6 equiv) of *N*-nitroso-*N*-methylurea. The reaction mixture was left standing for 10 h while slowly warming to room temperature. The solvent was evaporated in a vacuum, the residue was subjected to chromatography on a column packed with silica gel (5/40 mesh), eluent hexane–ethyl acetate mixture. Yield of diazoketone **Ib** 960 mg (75%), yellow oily substance. IR spectrum, cm^{-1}: 1060, 1110, 1150 s, 1160–1280 s, 1330 v.s, 1375 v.s, 1400 v.s, 1650 v.s, 1740 v.s, 2125 v.s, 2230, 2955, 3040, 3120. ^{1}H NMR spectrum, δ, ppm: 1.23–1.31 m (1H), 1.71–1.77 m (1H), 2.09–2.14 m (2H), 3.72 s (3H), 5.46 s (1H). ^{13}C, δ, ppm: 12.45 (CH_2), 23.18 (CH), 27.64 (CH), 52.54 (CH_3), 56.17 (CHN_2), 170.66 (C=O), 189.98 (C=O). Found, %: C 50.10; H 4.82; N 16.30. $C_7H_8N_2O_3$. Calculated, %: C 50.00; H 4.80; N 16.66.

General procedure of diazoketones Ia, Ib reaction with dipolarophiles in the presence of $Rh_2(OAc)_4$. To a 0.1–0.2 M solution of dipolarophile (1.2 equiv) and diazoketone (1 equiv) in anhydrous dichloromethane while stirring at room temperature was added ~0.5 mol% of $Rh_2(OAc)_4$. The reaction was carried out in a flow of dry argon. Within initial 10–15 min a vigorous evolution of nitrogen was observed. The reaction mixture was stirred for 30 min at room temperature, the solvent was evaporated in a vacuum, and the residue was subjected to a column chromatography on silica gel, eluent hexane–ethyl acetate mixture.

***rel*-(1*R*,2*R*,6*S*,7*R*,8*S*,10*R*)-7-Methoxy-4,9,9-triphenyl-12-oxa-4-azatetracyclo[5.4.1.$0^{2,6}$.$0^{8,10}$]dodecane-3,5,11-trione (Va)** was obtained from 150 mg (0.47 mmol) of diazoketone **Ia** and 102 mg (0.59 mmol, 1.26 equiv) of N-phenylmaleimide (**IVa**) in the presence of 1.2 mg (0.5 mol%) of $Rh_2(OAc)_4$ in 5 ml of dichloromethane. Yield 90 mg (41%), mp 215°C. IR spectrum, cm^{-1}: 1000, 1040, 1050, 1070, 1090, 1100, 1140–1280 s, 1300, 1390 s, 1450, 1500, 1600, 1720 v.s, 1790, 2950, 3050. ^1H NMR spectrum, δ, ppm: 2.65 d (1H, *J* 7.7 Hz), 2.77 d (1H, *J* 7.7 Hz), 3.43 d (1H, *J* 7.7 Hz), 3.61 s (3H), 3.68 d (1H, *J* 7.7 Hz), 4.55 s (1H), 7.19–7.52 m (15H). ^{13}C NMR spectrum, δ, ppm: 33.12 (CH), 36.21 (CH), 46.23 (C), 50.14 (CH), 52.00 (CH_3), 53.23 (CH), 81.88 (CH), 108.72 (C), 126.50 (CH), 127.44 (C), 127.79 (CH), 128.03 (CH), 129.00 (CH), 129.06 (CH), 129.35 (CH), 129.39 (CH), 129.68 (CH), 131.84 (C), 139.80 (C), 144.79 (C), 172.46 (CO), 174.07 (CO), 201.25 (CO). Found, %: C 74.63; H 5.22; N 2.73. $C_{29}H_{23}NO_5$. Calculated, %: C 74.83; H 4.98; N 3.01. Yield of azulenone **VI** 37 mg (28%).

***rel*-(1*R*,2*R*,6*S*,7*R*,8*S*,10*R*)-7-Methoxy-4-(4-methylphenyl)-9,9-diphenyl-12-oxa-4-azatetracyclo-[5.4.1.$0^{2,6}$.$0^{8,10}$]dodecane-3,5,11-trione (Vb)** was obtained from 146 mg (0.46 mmol) of diazoketone **Ia** and 108 mg (0.58 mmol, 1.26 equiv) of *N*-(4-methylphenyl)maleimide (**IVb**) in the presence of 1 mg (0.5 mol%) of $Rh_2(OAc)_4$ in 5 ml of dichloromethane. Yield 96 mg (44%), mp 165–166°C. IR spectrum, cm^{-1}: 1000, 1040, 1050, 1080, 1140–1290 s, 1300, 1330, 1380, 1450, 1490, 1520, 1730 v.s, 1800, 2960, 3050. ^1H NMR spectrum, δ, ppm: 2.38 s (3H), 2.65 d (1H, *J* 7.9 Hz), 2.77 d (1H, *J* 7.9 Hz), 3.41 d (1H, *J* 7.9 Hz), 3.59 s (3H), 3.66 d (1H, *J* 7.9 Hz), 4.54 s (1H), 7.09–7.45 m (14H). ^{13}C NMR spectrum, δ, ppm: 21.61 (CH_3), 33.20 (CH), 36.20 (CH), 46.22 (C), 50.12 (CH), 51.96 (CH_3), 53.17 (CH), 81.86 (CH), 108.67 (C), 126.29 (CH), 127.42 (CH), 127.78 (CH), 128.03 (CH), 128.99 (CH), 129.05 (CH), 129.18 (C), 129.35 (CH), 130.33 (CH), 139.56 (C), 139.83 (C), 144.81 (C), 172.58 (CO), 174.15 (CO), 201.27 (CO). Found, %: C 75.23; H 5.34; N 2.74. $C_{30}H_{25}NO_5$. Calculated, %: C 75.14; H 5.25; N 2.92. Yield of azulenone **VI** 34 mg (26%).

***rel*-(1*R*,2*R*,6*S*,7*R*,8*S*,10*R*)-7-Methoxy-4-(4-chlorophenyl)-9,9-diphenyl-12-oxa-4-azatetracyclo[5.4.1.$0^{2,6}$.$0^{8,10}$]dodecane-3,5,11-trione (Vc)** was obtained from 111 mg (0.35 mmol) of diazoketone **Ia** and 91 mg (0.44 mmol, 1.26 equiv) of *N*-(4-chlorophenyl)-maleimide (**IVc**) in the presence of 1 mg (0.5 mol%) of $Rh_2(OAc)_4$ in 5 ml of dichloromethane. Yield 71 mg (41%), mp 164–167°C. IR spectrum, cm^{-1}: 1000, 1040, 1200 s, 1270, 1300, 1380 s, 1450, 1500 s, 1735 v.s, 1800, 2940, 3050. ^1H NMR spectrum, δ, ppm: 2.66 d (1H, *J* 8.0 Hz), 2.77 d (1H, *J* 8.0 Hz), 3.43 d (1H, *J* 8.0 Hz), 3.63 C (3H), 3.69 d (1H, *J* 8.0 Hz), 4.54 s (1H), 7.20–7.42 m (14H). ^{13}C NMR spectrum, δ, ppm: 32.92 (CH), 36.24 (CH), 46.30 (C), 50.15 (CH), 52.06 (CH_3), 53.36 (CH), 81.91 (CH), 108.80 (C), 127.49 (CH), 127.71 (CH), 127.85 (CH), 127.98 (CH), 128.97 (C), 120.08 (CH), 129.38 (CH), 129.87 (CH), 130.25 (CH), 135.20 (C), 139.69 (C), 144.69 (C), 172.11 (CO), 173.79 (CO), 201.09 (CO). Found, %: C 69.68; H 4.42; N 2.55. $C_{29}H_{22}ClNO_5$. Calculated, %: C 69.67; H 4.44; N 2.80. Yield of azulenone **VI** 29 mg (29%).

Methyl *rel*-(1*R*,1a*S*,6a*S*,7a*R*)-7-oxo-1aα-phenyl-1aβ,6a,7,7aα-tetrahydro-1*H*-cyclopropa[*a*]-azulene-1-carboxylate (VI), mp 108–110°C (from ether). IR spectrum, cm^{-1}: 1020, 1170 s, 1240 br, 1320, 1350, 1410, 1450, 1750 v.s, 2950, 3040. ^1H NMR spectrum, δ, ppm: 2.62 d (1H, *J* 8.8 Hz), 3.13 d (1H, *J* 8.8 Hz), 3.15 s (1H), 3.77 s (3H), 5.41 d.d (1H, *J* 9.3, 4.5 Hz), 5.97 d (1H, *J* 4.5 Hz), 6.23–6.28 m (1H), 6.38–6.49 m (2H), 7.25–7.38 m (5H). ^{13}C NMR spectrum, δ, ppm: 38.12 (CH), 42.96 (CH), 50.52 (C), 53.27 (CH_3), 120.56 (CH), 124.01 (CH), 128.10 (CH), 128.39 (CH), 129.14 (CH), 129.75 (CH), 129.81 (CH), 131.10 (CH), 136.27 (C), 138.90 (C), 169.74 (CO), 211.08 (CO). Found, %: C 78.05; H 5.41. $C_{19}H_{16}O_3$. Calculated, %: C 78.06; H 5.52.

Reaction of methyl *cis*-2-diazoacetyl-3,3-diphenyl-1-cyclopropanecarboxylate (Ia) with *N*-phenylmaleimide (IVa) in the presence of copper acetylacetonate. To a solution of 217 mg (0.68 mmol) of diazoketone **Ia** and 143 mg (0.81 mmol) of imide **IVa** in 5 ml of dichloromethane was added in a flow of dry argon 3.5 mg (2 mol%) of copper(II) acetylacetonate.

The reaction mixture was stirred at room temperature for 20 h, the solvent was evaporated in a vacuum, and the residue was subjected to column chromatography, eluent hexane–ethyl acetate mixture.. Yield of adduct **Va** 47 mg (15%) of azulenone **VI** 90 mg (45%).

Decomposition of diazoketone Ia at treatment with $Rh_2(OAc)_4$ in the absence of dipolarophiles. To a stirred solution of 97 mg (0.30 mmol) of diazoketone **Ia** in 2 ml of dichloromethane was added in an argon flow 0.8 mg (0.6 mol%) of $Rh_2(OAc)_4$. Within initial 10 min a vigorous nitrogen evolution was observed. The reaction mixture was stirred at room temperature for 30 min more, then the solvent was evaporated in a vacuum, and the residue was subjected to column chromatography (eluent hexane–ethyl acetate mixture). We isolated 3 mg (5%) of benzophenone, 16 mg (18%) of azulenone **VI,** 14 mg (15%) of ester **VII**, and 8 mg (10%) of lactone **VIII**.

Methyl *cis*-2-glycoloyl-3,3-diphenyl-1-cyclopropanecarboxylate (VII), amorphous substance. IR spectrum, cm^{-1}: 1060, 1140, 1150–1280, 1360, 1400, 1450, 1750 v.s, 2930, 2950, 3070, 3200–3420. ^1H NMR spectrum, δ, ppm: 2.86 d (1H, *J* 9.8 Hz), 2.97 d (1H, *J* 9.8 Hz), 3.18 s (1H), 3.70 s (3H), 4.37 d (1H, *J* 18.8 Hz), 4.50 d (1H, *J* 18.8 Hz), 7.20–7.45 m (10H). ^{13}C NMR spectrum, δ, ppm: 34.86 (CH), 35.23 (CH), 46.32 (C), 52.62 (CH_3), 70.06 (CH_2), 127.68 (CH), 127.72 (CH), 127.87 (CH), 128.46 (CH), 129.33 (CH), 130.94 (CH), 136.02 (C), 145.27 (C), 168.66 (CO), 204.14 (CO).

7,7-Diphenyl-3-oxabicyclo[4.1.0]heptane-2,5-dione (VIII), mp 142–143°C. IR spectrum, cm^{-1}: 1040, 1095, 1120, 1290 s, 1335, 1395, 1435, 1450, 1720 v.s, 1750 v.s, 2930, 3070. ^1H NMR spectrum, δ, ppm: 3.12 d.d (1H, *J* 7.5 , 1.6 Hz), 3.18 d (1H, *J* 7.5 Hz), 3.46 d (1H, *J* 18.5 Hz), 4.36 d.d (1H, *J* 18.5, 1.6 Hz), 7.25–7.50 m (10H). ^{13}C NMR spectrum, δ, ppm: 33.17 (CH), 39.04 (CH), 45.41 (C), 73.45 (CH_2), 127.49 (CH), 128.39 (CH), 129.33 (CH), 129.47 (CH), 129.52 (CH), 130.20 (CH), 136.26 (C), 142.15 (C), 165.94 (CO), 197.84 (CO). Found, %: C 77.58; H 5.29. $C_{18}H_{14}O_3$. Calculated, %: C 77.68; H 5.07.

2-Diazo-1-(2,2-diphenylcyclopropyl)-1-ethanone (IX). To a solution of 0.92 g (9.2 mmol) of ethyl acrylate in 5 ml of anhydrous benzene was added a solution of 1.78 g (9.2 mmol) of diphenyldiazomethane in 5 ml of anhydrous benzene. In 10 min the nitrogen started to liberate, the color of diphenyldiazomethane gradually disappeared. The mixture was heated for 2 h, benzene was distilled off in a vacuum, to the residue was added 5 ml of ethanol, 2 ml of water, 1 g of NaOH, and the mixture was boiled for 6 h. Water and ethanol were distilled off in a vacuum, the solid residue was dissolved in 50 ml of water, the solution was acidified with hydrochloric acid, and the precipitated 2,2-diphenyl-1-cyclopropanecarboxylic acid was filtered off. Yield 1.6 g (73%) [14] The acid obtained was used without further purification. To a stirred suspension of 824 mg (3.46 mmol) of the acid in 6 ml of dichloromethane cooled with ice was added under an argon atmosphere 0.8 ml (2 equiv) of oxalyl chloride and a drop of DMF. The mixture was stirred at cooling with ice for 2.5 h, the excess oxalyl chloride and dichloromethane were evaporated in a vacuum. The residue was dissolved in 5 ml of dichloromethane and was added at cooling with ice within 5 min to an ether solution of diazomethane prepared from 1.8 g (17 mmol, 5 equiv) of *N*-nitroso-*N*-methylurea. The reaction mixture was left standing and slowly warming to room temperature. The solvent was evaporated in a vacuum, the residue was subjected to column chromatography on silica gel (5/40 mesh), eluent hexane–ethyl acetate mixture. Yield of diazoketone **IX** 0.79 mg (87%), mp 121–124°C (decomp.). IR spectrum, cm^{-1}: 1040, 1080, 1100, 1140 C, 1250, 1340 v.s, 1390 v.s, 1450, 1500, 1600, 1650 v.s, 1710, 2120 v.s, 2370, 3020, 3040, 3070. ^1H NMR spectrum, δ, ppm: 1.65–1.73 m (1H), 2.33–2.40 m (1H), 2.53–2.65 m (1H), 5.4 C (1H), 7.17–7.40 m (10H). ^{13}C NMR spectrum, δ, ppm: 21.32 (CH_2), 35.71 (CH), 56.36 (CH), 126.99 (CH), 127.52 (CH), 127.79 (CH), 128.81 (CH), 128.94 (CH), 130.46 (CH), 139.82 (C), 145.49 (C), 190.03 (CO). Found, %: C 77.79; H 5.44; N 10.39. $C_{17}H_{14}N_2O$. Calculated, %: C 77.84; H 5.38; N 10.68.

1aα-Phenyl-1a,6a,7,7aβ-tetrahydro-1*H*-cyclopropa[*a*]azulen-7-one(X). To a stirred solution of 150 mg (0.57 mmol) of diazoketone **IX** in 2 ml of dichloromethane was added in a flow of dry argon 0.7 mg (0.3 mol%) of $Rh_2(OAc)_4$. Within initial 10 min a vigorous evolution of nitrogen was observed. The reaction mixture was stirred at room temperature for 30 min, the solvent was evaporated in a vacuum. The residue at applying on silica gel turned dark According to the ^1H NMR data the reaction mixture contained azulenone **X** which formed in nearly 70% yield. ^1H NMR spectrum, δ, ppm: 1.67 t (1H, *J* 4.0 Hz), 2.11–2.20 m (2H), 2.29 d.d (1H, *J* 9.5, 3.6 Hz), 5.43 d.d (1H, *J* 8.3, 3.3 Hz), 5.88–5.90 m (1H), 6.18–6.25 m (1H), 6.29–6.36 m (2H), 7.28–7.37 m (5H). ^{13}C NMR spectrum, δ, ppm: 21.37 (CH_2),

42.98 (C), 48.35 (CH), 119.75 (CH), 121.52 (CH), 128.15 (CH), 128.23 (CH), 128.94 (CH), 128.99 (CH), 130.20 (C), 130.56 (C), 211.70 (C).

***rel*-(1*R*,2*S*,6*R*,7*R*,8*R*,10*S*)- (XIa) and *rel*-(1*R*,2*R*,6*S*,7*R*,8*R*,10*S*)-7-Methoxy-4-phenyl-12-oxa-4-azatetracyclo[5.4.1.0^{2,6}.0^{8,10}]dodecane-3,5,11-triones (XIIa).** The reaction was performed using 167 mg (0.99 mmol) of diazoketone **Ib**, 203 mg (1.17 mmol) imide **IVa,** and 1.4 mg (0.3 mol%) of $Rh_2(OAc)_4$. $(OAc)_4$ in 5 ml of dichloromethane. The products were subjected to column chromatography on silica gel (5/40 mesh), eluent hexane–ethyl acetate.

I fraction. Isomer **XIa**, yield 49 mg (16%), mp 169–172°C. IR spectrum, cm^{-1}: 960, 1020, 1040, 1060, 1150, 1160, 1185 s, 1260, 1305, 1380 s, 1470, 1500, 1735 v.s. 1800, 2950, 3050. ^{1}H NMR spectrum, δ, ppm: 1.40–1.45 m (1H), 1.85–1.94 m (2H), 2.00–2.07 m (1H), 3.61 C (3H), 3.83 d (1H, *J* 10 Hz), 4.01 d.d (1H, *J* 10, 9 Hz), 4.80 d (1H, *J* 9 Hz), 7.22 m (2H), 7.42–7.49 m (3H). ^{13}C NMR spectrum, δ, ppm: 11.08 (CH_2), 16.76 (CH), 25.30 (CH), 49.53 (CH), 52.73 (CH_3), 54.30 (CH), 82.30 (CH), 106.41 (C), 126.59 (CH), 129.45 (CH), 129.74 (CH), 131.55 (C), 171.24 (CO), 172.66 (CO), 200.43 (CO). Found, %: C 65.05; H 4.99; N 4.29. $C_{17}H_{15}NO_5$. Calculated, %: C 65.15; H 4.83; N 4.47.

II fraction. Isomer **XIIa**, yield 78 mg (25%), mp 178–181°C. IR spectrum, cm^{-1}: 965, 1030, 1080, 1150–1280, 1300, 1380 s, 1460, 1500, 1600, 1730 v.s, 1795, 2950, 3050. ^{1}H NMR spectrum, δ, ppm: 1.48–1.53 m (1H), 1.87–1.99 m (3H), 3.43 d (1H, *J* 7.6 Hz), 3.62 s (3H), 3.66 d (1H, *J* 7.6 Hz), 4.81 s (3H), 7.28–7.51 m (5H). ^{13}C NMR spectrum, δ, ppm: 11.94 (CH_2), 19.97 (CH), 23.78 (CH), 50.79 (CH), 52.66 (CH_3), 53.86 (CH), 83.88 (CH), 106.79 (C), 126.78 (CH), 129.26 (CH), 129.57 (CH), 132.03 (C), 171.88 (CO), 174.40 (CO), 201.99 (CO). Found, %: C 65.02; H 4.92; N 4.43. $C_{17}H_{15}NO_5$. Calculated, %: C 65.17; H 4.83; N 4.47.

***rel*-(1*R*,2*S*,6*R*,7*R*,8*R*,10*S*)- (XIb) and *rel*-(1*R*,2*R*,6*S*,7*R*,8*R*,10*S*)-4-(4-Methylphenyl)-7-methoxy-12-oxa-4-azatetracyclo[5.4.1.0^{2,6}.0^{8,10}]-dodecane-3,5,11-triones (XIIb).** The reaction was performed using 194 mg (1.16 mmol) of diazoketone **Ib**, 253 mg (1.35 mmol) of imide **IVb**, and 1.9 mg (0.3 mol%) of $Rh_2(OAc)_4$ in 5 ml of dichloromethane. The reaction products were subjected to column chromatography on silica gel (5/40 mesh), eluent hexane–ethyl acetate.

I fraction. Isomer **XIb**, yield 59 mg (16%), mp 179°C. IR spectrum, cm^{-1}: 990, 1020, 1030, 1040, 1070, 1120, 1130, 1155, 1160, 1195, 1255, 1380 s, 1510, 1735 v.s, 1800, 3020, 3040. ^{1}H NMR spectrum, δ, ppm: 1.40–1.47 m (1H), 1.83–1.92 m (2H), 1.99–2.06 m (1H), 2.39 s (3H), 3.61 s (3H), 3.81 d (1H, *J* 10 Hz), 3.98 d.d (1H, *J* 10, 9 Hz), 4.78 d (1H, *J* 9 Hz), 7.09 d (2H, *J* 8 Hz), 7.28 d (2H, *J* 8 Hz). ^{13}C NMR spectrum, δ, ppm: 11.00 (CH_2), 16.71 (CH), 21.62 (CH_3), 25.32 (CH), 49.52 (CH), 52.69 (CH_3), 54.21 (CH), 82.25 (CH), 106.36 (C), 126.54 (CH), 129.40 (C), 130.33 (CH), 139.58 (C), 171.41 (CO), 172.81 (CO), 200.41 (CO). Found, %: C 65.87; H 5.57; N 4.10. $C_{18}H_{17}NO_5$. Calculated, %: C 66.05; H 5.23; N 4.28.

II fraction. Isomer **XIIb**, yield 116 mg (31%), mp 179°C. IR spectrum, cm^{-1}: 970, 1040, 1095, 1170, 1200, 1280, 1390 s, 1510, 1735 v.s, 1800, 2960, 3050. ^{1}H NMR spectrum, δ, ppm: 1.47–1.54 m (1H), 1.85–2.01 m (3H), 2.40 s (3H), 3.41 d (1H, *J* 8 Hz), 3.63 s (3H), 3.65 d (1H, *J* 8 Hz), 4.82 s (1H), 7.19 d (2H, *J* 8 Hz), 7.29 d (2H, *J* 8 Hz). ^{13}C NMR spectrum, δ, ppm: 11.91 (CH_2), 19.97 (CH), 21.62 (CH_3), 23.76 (CH), 50.77 (CH), 52.64 (CH_3), 53.84 (CH), 83.86 (CH), 106.76 (C), 126.57 (CH), 129.39 (C), 130.21 (CH), 139.37 (C), 171.97 (CO), 174.50 (CO), 201.99 (CO). Found, %: C 65.94; H 5.36; N 4.35. $C_{18}H_{17}NO_5$. Calculated, %: C 66.05; H 5.23; N 4.28.

***rel*-(1*R*,2*S*,6*R*,7*R*,8*R*,10*S*)- (XIc) and *rel*-(1*R*,2*R*,6*S*,7*R*,8*R*,10*S*)-7-Methoxy-4-(4-chlorophenyl)12-oxa-4-azatetracyclo[5.4.1.0^{2,6}.0^{8,10}]-dodecane-3,5,11-triones (XIIc).** The reaction was performed using 193 mg (1.15 mmol) of diazoketone **Ic**, 281 mg (1.36 mmol) of imide **IVc**, and 1.6 mg (0.3 mol%) of $Rh_2(OAc)_4$ in 5 ml of dichloromethane. The reaction products were subjected to column chromatography on silica gel (5/40 mesh), eluent hexane–ethyl acetate.

I fraction. Isomer **XIc**, yield 64 mg (17%), mp167–168°C. IR spectrum, cm^{-1}: 980, 1030, 1060, 1105, 1160, 1180, 1270, 1380 s, 1495, 1735 v.s, 1800, 3060. ^{1}H NMR spectrum, δ, ppm: 1.40–1.49 m (1H), 1.81–2.09 m (3H), 3.61 s (3H), 3.83 d (1H, *J* 10 Hz), 3.99 d.d (1H, *J* 10, 9 Hz), 4.79 d (1H, *J* 9 Hz), 7.19 d (2H, *J* 8 Hz), 7.45 d (2H, *J* 8 Hz). ^{13}C NMR spectrum, δ, ppm: 11.18 (CH_2), 16.88 (CH), 25.39 (CH), 49.50 (CH), 52.79 (CH_3), 54.43 (CH), 82.30 (CH), 106.41 (C), 127.80 (CH), 129.96 (CH), 131.35 (C), 135.32 (C), 170.91 (CO), 172.36 (CO), 200.46 (CO). Found, %: C 58.69; H 4.22; N 4.04. $C_{17}H_{14}ClNO_5$. Calculated, %: C 58.72; H 4.06; N 4.03.

II fraction. Isomer **XIIc**, yield 95 mg (25%), mp 164°C. IR spectrum, cm^{-1}: 970, 1040, 1100, 1110, 1210 s, 1385 s, 1500 s, 1740 v.s, 1800, 3050. ^{1}H NMR

spectrum, δ, ppm: 1.49–1.56 m (1H), 1.86–2.02 m (3H), 3.43 d (1H, *J* 8.0 Hz), 3.63 s (3H), 3.66 d (1H, *J* 8.0 Hz), 4.82 s (1H), 7.29 d (2H, *J* 8.0 Hz), 7.46 d (2H, *J* 8.0 Hz). ^{13}C NMR spectrum, δ, ppm: 11.95 (CH_2), 19.95 (CH), 23.78 (CH), 50.79 (CH), 52.67 (CH_3), 53.90 (CH), 83.84 (CH), 106.81 (C), 128.02 (CH), 129.76 (CH), 130.48 (C), 135.03 (C), 171.57 (CO), 174.17 (CO), 201.10 (CO). Found, %: C 58.66; H 4.14; N 3.94. $C_{17}H_{14}ClNO_5$. Calculated, %: C 58.72; H 4.06; N 4.03.

X-ray diffraction study of compound Va. $C_{29}H_{23}NO_5$. *M* 465.48. Monoclinic space group $P1\,2_1/c1$ (*no* 14); *a* 8.8729(7), *b* 28.764(2), *c* 8.6987(7) Å, β 96.06°, *V* 2207.7(3) Å^3, *Z* 4, d_c 1.400 g/cm^3, μ 0.078 mm^{-1}, F(000) 912, radiation source MoK_a, λ 0.71073 Å, graphite monochromator. Further are given some bond lengths (Å) and bond angles (deg): C^1–C^2 1.530(2), C^2–C^3 1.512(2), C^3–N^4 1.390(2), N^4–C^5 1.386(2), C^5–C^6 1.507(2), C^6–C^2 1.526(2), C^6–C^7 1.574(2), C^7–C^8 1.511(2), C^8–C^9 1.501(2), C^9–C^{10} 1.520(2), C^8–C^{10} 1.517(2), C^{10}–C^{11} 1.482(2), C^1–C^{11} 1.516(2), C^7–O^{12} 1.420(2), C^1–O^{12} 1.423(2); C^{2}C^{3}N^4 108.48(11), C^{3}N^{4}C^5 112.37(11), N^{4}C^{5}C^6 108.51(11), C^{5}C^{6}C^2 104.77(10), C^{6}C^{2}C^3 104.65(11), C^{1}C^{2}C^6 103.86(10), C^{2}C^{6}C^7 103.26(10), C^{6}C^{7}O^{12} 103.37(10), C^{7}O^{12}C^1 105.49(9), O^{12}C^{1}C^2 102.61(10), O^{12}C^{7}C^8 109.78(10), C^{7}C^{8}C^{10} 114.1(1), C^{8}C^{10}C^{11} 118.06(11), C^{10}C^{11}C^1 116.06(11), C^{11}C^{1}O^{12} 110.73(10), C^{8}C^{9}C^{10} 60.27(9), C^{9}C^{8}C^{10} 60.49(9), C^{8}C^{10}C^9 59.24(9). Complete set of crystallographic parameters is deposited in the Database of the Cambridge Crystallographic Centre (CCDC-254381).

X-ray diffraction study of compound VI. $C_{19}H_{16}O_3$. *M* 292.32. Triclinic space group *P*-1 (*no* 2); *a* 10.8897(13), *b* 11.5437(14), *c* 11.7311(14) Å, α 91.98, β 98.82, γ 90.34°, *V* 1456.26(30) Å^3, *Z* 4, d_c 1.333 γ/cm^3, μ 0.078 mm^{-1}, F(000) 912, radiation source MoK_a, λ 0.71073 A, graphite monochromator. Further are given some bond lengths (Å) and bond angles (deg): C^1–C^{1a} 1.524(2), C^1–C^{7a} 1.512(3), C^{1a}–C^{1b} 1.504(2), C^{1b}–C^2 1.334(2), C^2–C^3 1.443(2), C^3–C^4 1.342(2), C^4–C^5 1.441(3), C^5–C^6 1.330(3), C^6–C^{6a} 1.498(2), C^{6a}–C^7 1.522(3), C^7–C^{7a} 1.490(3); C^{1}C^{7a}C^{1a} 60.14(9), C^{1}C^{1a}C^{7a} 59.36(9), C^{1a}C^{1}C^{7a} 60.50(9), C^{1a}C^{7a}C^7 107.44(11), C^{1a}C^{1b}C^{6a} 111.02(11), C^{1b}C^{1a}C^{7a} 106.31(11), C^{1b}C^{2}C^3 125.51(12), C^{1b}C^{6a}C^7 104.51(10), C^{1b}C^{6a}C^6 111.17(11), C^{2}C^{1b}C^{6a} 124.66(12), C^{2}C^{3}C^4 126.91(13), C^{3}C^{4}C^5 126.18(14), C^{4}C^{5}C^6 126.63(14), C^{5}C^{6}C^{6a} 123.28(14), C^{6a}C^{7}C^{7a} 110.61(12). Complete set of crystallographic parameters is deposited in the Database of the Cambridge Crystallographic Centre (CCDC-254380).

The study was carried out under financial support of the Ministry of Education of the Russian Federation (grant no. A03.-2.11-116) and INTAS program (grant no. 00-0549).

REFERENCES

1. Padwa, A. and Weingarten, M.D., *Chem. Rev*., 1996, p. 223; Mehta, G. and Muthusamy, S., *Tetrahedron,* 2002, vol. 58, p. 9477.
2. Padwa, A., Curtis, E.A., and Sandanayaka, V.P., *J. Org. Chem*., 1997, vol. 62, p. 1317; Curtis, E.A., Sandanayaka, V.P., and Padwa, A., *Tetrahedron Lett.,* 1995, vol. 36, p. 1989; McMorris, T.C., Hu, Y., Yu, J., and Kelner, M.J., *Chem. Commun*., 1997, 315; Kinder, F.R. and Bair, K.W., *J. Org. Chem*., 1994, vol. 59, p. 6965; McMills, M.C., Zhuang, L., Wright, D.L., and Watt, W., *Tetrahedron Lett.,* 1994, vol. 35, p. 8311; Dauben, W.G., Dinges, J., and Smith, T.C., *J. Org. Chem*., 1993, vol. 58, p. 7635; Padwa, A., Precedo, L., and Semones, M.A., *J. Org. Chem*., 1999, vol. 64, p. 4079; Padwa, A, Harring, S.R., and Semones, M, A., *J. Org. Chem.,* 1998, vol. 63, p. 44; Padwa, A., Broadney, M.A., Marino, J.P., and Sheehan, S.M., *J. Org. Chem*., 1997, vol. 62, 78; Padwa, A., and Price, A.T., *J. Org. Chem*., 1998, vol. 63, p. 556; Kissel, W.S. and Padwa, A., *Tetrahedron Lett.,* 1999, vol. 40, p. 4003.
3. Hodgson, D.M., Stupple, P.A., and Johnstone, C., *Tetrahedron Lett.,* 1997, vol. 38, p. 6471; Doyle, M.P. and Forbes, D.C., *Chem. Rev*., 1998, vol. 98, p. 911; Suga, H., Ishida, H., and Ibata, T., *Tetrahedron Lett.,* 1998, vol. 39, 3165; Kitagaki, S., Anada, M., Kataoka, O., Matsuno, K., Umeda, C., Watanabe, N., and Hashimoto, S., *J. Am. Chem. Soc*., 1999, vol. 121, p. 1417; Hodgson, D.M., Stupple, P.A., and Johnstone, C., *Chem. Commun.,* 1999, p. 2185; Hodgson, D.M., Stupple, P.A., Pierard, F.Y.T.M., Labande, A.H., and Johnstone, C., *Chem. Eur. J*., 2001, vol. 7, p. 4465; Hodgson, D.M., Glen, R., Grant, G.H., and Redgrave, A.J., *J. Org. Chem*., 2003, vol. 68, p. 581.
4. Padwa, A., Curtis, E.A., and Sandanayaka, V.P., *J. Org. Chem*., 1996, vol. 61, p. 73.
5. Molchanov, A.P., Diev, V.V., Kopf, Yu., and Kostikov, R.R., *Zh. Org. Khim.*, 2004, vol. 40, p. 258.
6. Ueda, K., Ibata, T. and Takebayashi, M., *Bull. Chem. Soc. Jpn*., 1972, vol. 45, p. 2779; Ibata, T. and Jitsuhiro, K., *Bull. Chem. Soc. Jpn*., 1979, vol. 52, p. 3582; Ibata, T., Jitsuhiro, K., and Tsubokura, Y., *Bull. Chem. Soc. Jpn*., 1981, vol. 54, p. 240; Ibata, T. and Toyoda, J., *Bull. Chem. Soc. Jpn*., 1985, vol. 58, p. 1787; Ibata, T., Nakano, H., and Tamura, H., *Bull. Chem. Soc. Jpn*., 1992, vol. 65, p. 1362.
7. Kitagaki, S., Yasugahira, M., Anada, M., Nakajima, M., and Hashimoto, S., *Tetrahedron Lett.,* 2000, vol. 41, p. 5931.

8. Padwa, A., Hornbuckle, S.F., Fryxell, G.E., and Stull, P.D., *J. Org. Chem.,* 1989, vol. 54, p. 817.
9. Baltzly, R., Mehta, N.B., Russel, P.B., Brooks, R.E., Grivsky, E.M., and Steinberg, A.M., *J. Org. Chem.,* 1961, vol. 26, p. 3669.
10. McCoy, L.L., *J. Am. Chem. Soc.,* 1958, vol. 80, p. 6568.
11. Padwa, A., Fryxell, G., and Zhi, L., *J. Org. Chem.,* 1990, vol. 112, p. 3100.
12. Maas, G., *Top. Cur. Chem.,* 1987, vol. 137, p. 75; Scott, L.T., *Chem. Commun.,* 1973, p. 882; Anciaux, A.J., Demonceau, A., Hubert, A.J., Noels, A.F., Petiniot, N., and Teyssie, P., *Chem. Commun.,* 1980, p. 765; Kennedy, M., McKervey, M.A., Maguire, A.R., Tuladhar, S.M., and Twohig, M.F., *J. Chem. Soc., Perkin Trans. I,* 1990, p. 1047; Ye, T. and McKervey, M.A., *Chem. Rev.,* 1994, vol. 94, p. 1091; Maguire, A.R., O'Leary, P., Harrington, F., Lawrence, S.E., and Blake, A.J., *J. Org. Chem.,* 2001, vol. 66, p. 7166; Merlic, C.A., Zechman, A.L., and Miller, M.M., *J. Am. Chem. Soc.,* 2001, vol. 66, p. 7166; Pirrung, M.C., Liu, H., and Morehead, A.T., *J. Am. Chem. Soc.,* 2002, vol. 124, p. 1014.
13. Padwa, A., Carter, S.P., Nimmesgern, H., and Stull, P., *J. Am. Chem. Soc.,* 1988, vol. 110, p. 2894.
14. Tomioka, H. and Miyagawa, H., *Chem. Commun.,* 1988, p. 1183.