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Azirinium Ylides from Alkoxycarbonylcarbenoids and 2*H*-Azirines: Generation and Transformations

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Abstract—Dirhodium tetraacetate-catalyzed decomposition of diazo esters in the presence of 3-aryl-2*H*-azirines having no substituent in the 2-position gives rise to azirinium ylides which then undergo isomerization into 2-azabuta-1,3-diene derivatives or (in the presence of excess diazo ester) react with the corresponding rhodium carbenoid to form substituted 3,4-dihydro-2*H*-pyrroles. 2-Mono- and 2,2-disubstituted 3-phenyl-2*H*-azirines react with rhodium carbenoids generated from diazo esters to give azirinium ylides which are converted into the corresponding 2-azabuta-1,3-dienes.

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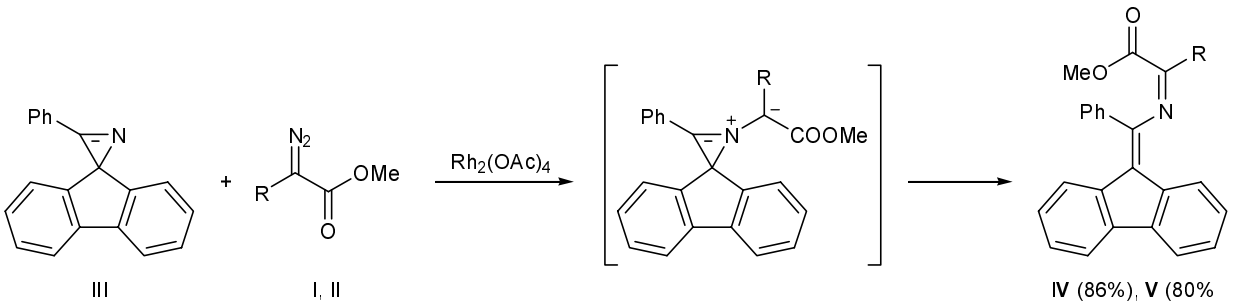
Progress in the carbene chemistry led to the development of an approach utilizing ylides as synthetic blocks generated by reactions of carbenes and carbenoid species with heteroelement-containing molecules [1–3]. Reactions involving carbenes open a way to unstable ylides which are often inaccessible via traditional methods. In the recent time, much attention was given to reactions of nitrogen-containing substrates having double C=N bonds with difluoro- [3, 4], dichloro- [2, 3], and arylhalocarbenes [3], as well as metal carbenoids, generated from diazo compounds [3], which gave rise to iminium ylides.

Structural specificity of 2*H*-azirines, in particular the presence in their molecules of a strongly strained double C=N bond, determines their high reactivity and versatile synthetic potential [5–8]. Despite much interest in the chemistry of 2*H*-azirines, their reactions with electrophilic carbenes have been studied poorly, though these reactions could lead to formation of unusual strained azomethine ylides. Hassner *et al*. [9] showed that reactions of dichlorocarbene with 2*H*-azirines involve opening of the three-membered ring with formation of *N*-(dichloromethylidene)-*N*-vinylamines, presumably through the corresponding aziriniodichloromethanides and their subsequent rearrangement with intermediate ring closure to 1-azabicyclobutane. Later on, we succeeded in detecting intermediate formation of fluoro-substituted azirinium ylides in reactions of 2*H*-azirines with difluorocarbene by trapping via 1,3-dipolar cycloaddition to dimethyl acetylenedicarboxylate and benzaldehyde [10, 11].

Only a few published data are available on reactions of 2*H*-azirines with diazo compounds, which can involve carbene intermediates. Nair [12, 13] reported that diazomethane and phenyldiazomethane react with 2*H*-azirines to give the corresponding vinyl azides. Presumably, these products are formed via ring opening in the adduct resulting from 1,3-dipolar cycloaddition of diazo compound at the azirine C=N bond [12, 13]. The reaction of diphenyldiazomethane with 3-phenyl-2*H*-azirine in boiling toluene afforded a mixture of *N*-(diphenylmethyl)-*N*-(1,3,3-triphenylprop-2-enylidene)amine, *N*-(diphenylmethylidene)-*N*-(1,3,3-triphenylprop-2-enyl)amine, and 2,2,3,3,5-pentaphenyl-3,4-dihydro-2*H*-pyrrole; these compounds may be regarded as 1:2 adducts of the azirine and diphenylcarbene, the latter being generated by thermal decomposition of diphenyldiazomethane [14].

In the present work we examined transformations of azirinium ylides formed by reactions of 2*H*-azirines with metal carbenoids which were generated *in situ* by decomposition of methyl 2-diazo-2-phenylacetate (**I**) in methylene chloride and dimethyl diazomalonate (**II**) in chloroform in the presence of $Rh_2(OAc)_4$ on heating. All newly synthesized compounds were characterized by standard set of spectral and analytical data.

Scheme 1.



I, **IV**, R = Ph; **II**, **V**, R = CO_2Me.

We previously found that the most typical transformation of intermediate aziriniodifluoromethanides formed in reactions of 2-mono- and 2,2-disubstituted 3-aryl-2*H*-azirines with difluorocarbene [10, 11] is their isomerization into the corresponding 2-azadienes. Analogous results were obtained in the reactions of structurally related azirines with metal carbenoids. Spiro azirine **III** reacted with methyl 2-diazo-2-phenylacetate (**I**) in the presence of a catalytic amount of $Rh_2(OAc)_4$ in boiling methylene chloride to give 86% of aza diene **IV** (Scheme 1). Likewise, the reaction of **III** with diazomalonate **II** in the presence of $Rh_2(OAc)_4$ in boiling chloroform afforded aza diene **V** in a high yield (Scheme 1).

Compounds **IV** and **V** are stable substances: they do not decompose during chromatographic purification and can be stored at –20°C for several months. Molecules **IV** and **V** possess an extended conjugated bond system which endows them with orange color. The UV spectrum of **IV** contains a long-wave absorption maximum at λ 405 nm (logε 3.79). In the IR spectra of **IV** and **V** we observed absorption bands due to stretching vibrations of the ester carbonyl (1750 cm^{-1}). The ^{13}C NMR spectra of these compounds contained signals from aromatic carbon atoms, methoxy groups [δ_C 51.9 ppm (**IV**); δ_C 52.0, 53.0 ppm (**V**)], carbon atom at the double C=N bond (δ_C ~147 ppm), and carbonyl carbon atoms [δ_C 164.4 ppm (**IV**); δ_C 162.1, 162.4 ppm (**V**)].

The molecular and crystalline structure of compound **IV** was determined by X-ray analysis (Fig. 1). Molecules **IV** in crystal exist as two rotamers differing by orientation of the carbonyl fragment with respect to the C^1–C^2 or C^{33}–C^{34} bond. The aza diene fragment in

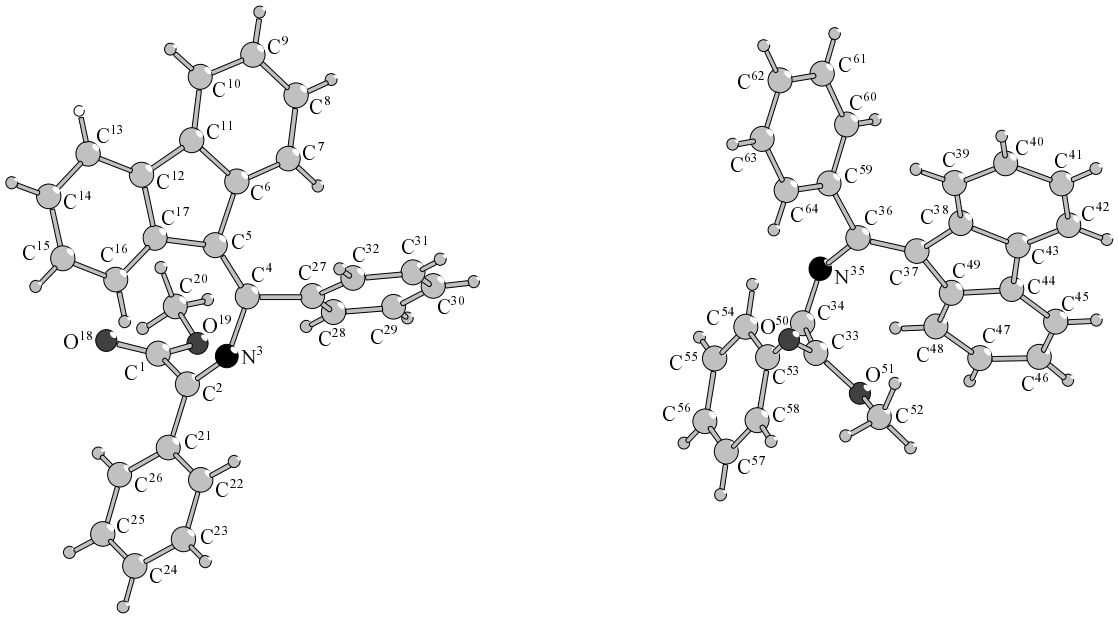
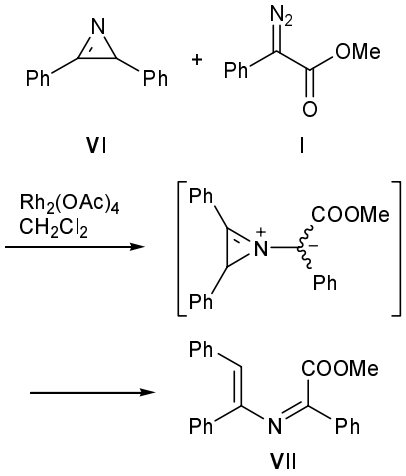


Fig. 1. Structure of the molecule of methyl 2-phenyl-2-[phenyl(fluoren-9-ylidene)methylimino]acetate (**IV**) according to the X-ray diffraction data.

IV is characterized by a considerable deviation from the planar *s-cis* conformation (the angle of rotation about the ordinary C–N bond is 73–75°).

The reaction of 2,3-diphenyl-2*H*-azirine (**VI**) with methyl 2-diazo-2-phenylacetate (**I**) also led to formation of the corresponding aza diene **VII** with high stereoselectivity (Scheme 2). The product was isolated as a single stereoisomer in 68% yield.

Scheme 2.



Compound **VII** showed in the IR spectrum absorption bands belonging to stretching vibrations of the ester carbonyl group (1745 cm^{-1}) and C=N bond (1620 cm^{-1}). Its ^1H NMR spectrum contained signals from aromatic protons, a singlet at δ 3.88 ppm from protons of the methoxy group, and a singlet at δ 6.14 ppm from the PhCH= proton. In the ^{13}C NMR

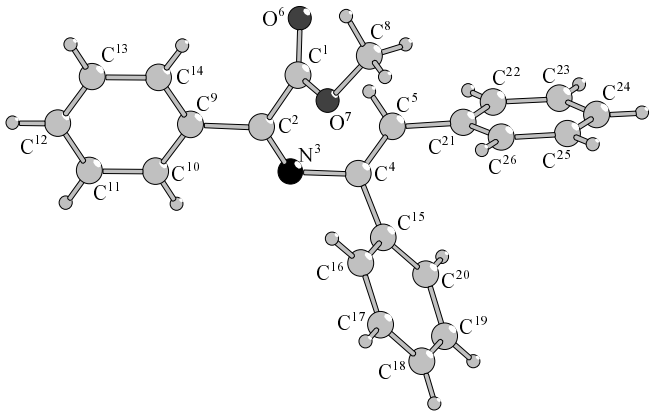
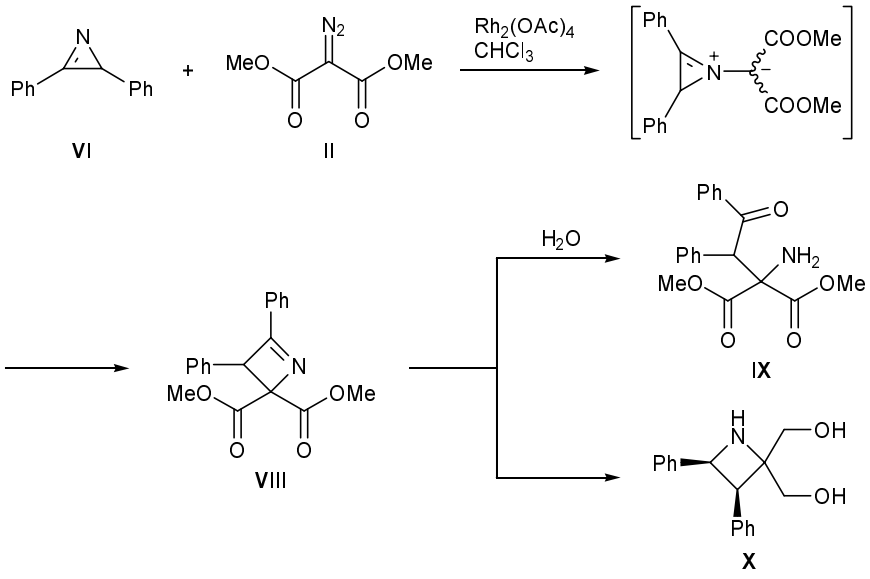


Fig. 2. Structure of the molecule of methyl 2-[(1,2-diphenylethenyl)imino]-2-phenylacetate (**VII**) according to the X-ray diffraction data.

spectrum of **VII**, signals at δ_C 51.6 (MeO), 113.0 (Ph**C**H=), 150.3 (=C–N), 157.6 (C=N), and 165.2 ppm (C=O) were present; also, signals from aromatic carbon atoms were observed. The steric structure of aza diene **VII** was determined by X-ray analysis (Fig. 2). According to the X-ray diffraction data, the phenyl groups at the C=C bond are arranged *cis*, and the aza diene fragment considerably deviates from the planar *s-cis* conformation (the dihedral angle about the C–N bond is 65°).

Surprisingly, the reaction of azirine **VI** with diazomalonate **II** in the presence of a catalytic amount of $Rh_2(OAc)_4$ in boiling chloroform gave 73% of dimethyl 3,4-diphenyl-2,3-dihydroazete-2,2-dicarboxylate (**VIII**) which may be regarded as a product of formal insertion of the rhodium carbenoid into the

Scheme 3.



azirine ring. No expected aza diene was detected in the reaction mixture. Azetine **VIII** dissolved in hexane–ethyl acetate readily undergoes hydrolysis on exposure to atmospheric moisture even at room temperature; the hydrolysis product is dimethyl 2-amino-2-(2-oxo-1,2-diphenylethyl)malonate (**IX**) (Scheme 3).

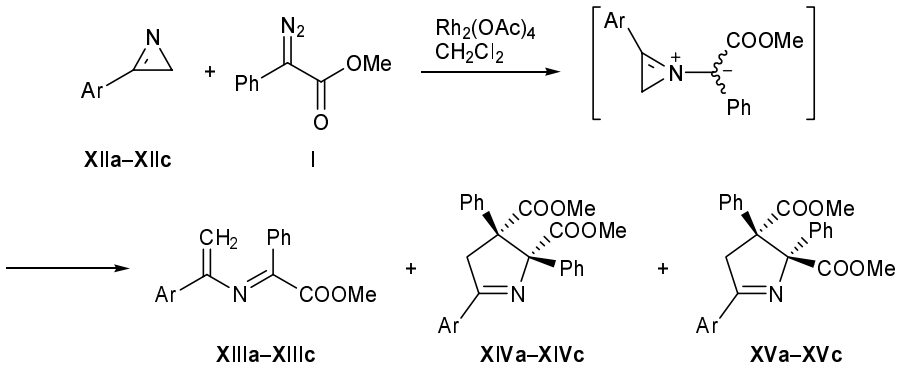
Stretching vibrations of the ester carbonyl groups in **VIII** give rise to absorption at 1750 cm^{-1}. In the ^1H NMR spectrum of **VIII**, protons of the methoxy groups resonated at δ 3.33 and 3.89 ppm, and the 3-H signal appeared as a singlet at δ 5.44 ppm. The ^{13}C NMR spectrum of **VIII** contained signals from carbon atoms in the benzene ring and methoxy groups (δ_C 51.8, 53.0 ppm), signals from carbon atoms in the four-membered ring (δ_C 55.0, 77.0, and 190.4 ppm from C^3, C^2, and C^4, respectively), and two signals at δ_C 166.0 and 167.4 ppm from the carbonyl carbon atoms. Compound **VIII** showed in the mass spectrum the molecular ion peak with *m*/*z* 323 and fragment ion peaks with *m*/*z* 264 $[M - CO_2Me]^+$ and 204 $[M - CO_2Me - HCO_2Me]^+$.

The IR spectrum of **IX** displayed absorption bands due to stretching vibrations of the N–H bonds (3400, 3330 cm^{-1}) and carbonyl groups (1750, 1675 cm^{-1}). Protons of the amino group appeared in the ^1H NMR spectrum of **IX** as a broadened signal at δ 2.62 ppm, ester methoxy groups gave singlets at δ 3.74 and 3.76 ppm, and the singlet at δ 5.72 ppm was assigned to the PhC**H** proton. The ^{13}C NMR spectrum of **IX** contained the following signals (in addition to those belonging to the aromatic carbon atoms), δ_C, ppm: 52.8 and 53.0 (MeO), 56.7 (Ph**C**H), 69.8 (CNH_2), 168.8 and 171.4 (C=O, ester), 198.0 ppm (C=O, ketone).

Taking into account that the formation of azetine **VIII** was not expected and that published data for compounds having an analogous skeleton are few in number and sometimes unreliable, we tried to prove the structure of **VIII** via a chemical transformation which would occur with conservation of the four-membered ring. An attempt to reduce compound **VIII** with sodium tetrahydridoborate was unsuccessful: as a result, a complex mixture of unidentifiable products was obtained. However, by treatment of **VIII** with lithium tetrahydridoaluminate in boiling diethyl ether we succeeded in smoothly reducing the ester groups and C=N bond to afford 2-hydroxymethyl-*cis*-3,4-diphenylazetidin-2-ylmethanol (**X**) which was isolated in 77% yield (Scheme 3).

The IR spectrum of **X** contained absorption bands in the region 3450–3250 cm^{-1}, which were attributed to stretching vibrations of the O–H and N–H bonds. The NH and OH protons gave a broadened signal at δ 2.66 ppm in the ^1H NMR spectrum of a solution of **X** in $CDCl_3$; in addition, signals from aromatic protons, two doublets from the OCH_2 protons (δ 3.43 and 3.62 ppm, J = 11.5 Hz, *cis* with respect to 3-Ph; δ 4.12 and 4.19 ppm, J = 11.0 Hz, *trans* with respect to 3-Ph), and two doublets from 3-H and 4-H (δ 3.93 and 5.52 ppm, respectively; J = 9.0 Hz) were present. Signals in the ^{13}C NMR spectrum of **X** were assigned using DEPT sequence, δ_C, ppm: 48.5 (C^3), 57.7 (C^4), 64.2 (C^2), 61.5 and 64.2 (OCH_2). Analysis of the ^1H 2D NOESY spectrum (in $CDCl_3$ containing 5% of DMSO-d_6) allowed us to assign *cis* configuration to compound **X**; the spectrum revealed a strong interaction between 3-H and 4-H, as well as between the OCH_2 protons resonating at δ ~4 ppm and 3-H and 4-H; on the other hand, no interaction was observed between the latter and protons of the OCH_2 group resonating at δ ~3.5 ppm. Protons of the first OCH_2 group (δ ~4 ppm) showed no coupling with the phenyl protons, while protons of the second OCH_2 group displayed such a coupling.

Scheme 4.

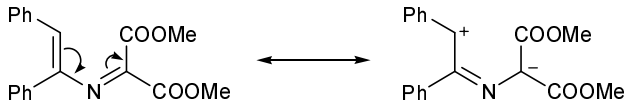


Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-BrC_6H_4 (**c**).

Table 1. Reactions of azirines **XIIa**–**XIIc** with methyl 2-diazo-2-phenylacetate (**I**)

Azirine no.	Reactant ratio **XII**:**I**	Yield of **XIII**, %	Yield of **XIV**/**XV**, %	Isomer ratio **XIV**:**XV**
XIIa	1:2.00	56	10	1.7:1
XIIb	1:1.93	56	20	2.3:1
XIIb	1:3.72	23	45	2.3:1
XIIb	1:6.02	9	60	2.3:1
XIIc	1:2.23	62	18	1.5:1

Azetine **VIII** is most likely to be formed via cyclization of the corresponding aza diene **XI**, though even traces of the latter were not detected in the reaction mixture. Presumably, the cyclization of **XI** to azetine **VIII** is favored by strong polarization of the aza diene molecule due to the presence, on the one hand, of two strong electron-acceptor ester groups (which stabilize negative charge) and, on the other, phenyl substituent (which stabilizes positive charge). The expected *cis* arrangement of the phenyl groups at the C=C bond (taking into account stereoselectivity of the reaction leading to aza diene **VII**) should also favor the above cyclization.



XI

Study of the chemical behavior of 3-aryl-substituted 2*H*-azirines **XIIa**–**XIIc** under conditions of thermocatalytic decomposition of diazo compounds **I** and **II** has shown that intermediate azirinium ylide is stabilized in a more complicated fashion than that observed for their analogs derived from 2-substituted 3-aryl-2*H*-azirines. Heating of a mixture of azirine **XIIa**–**XIIc** and methyl 2-diazo-2-phenylacetate (**I**) in the presence of a catalytic amount of $Rh_2(OAc)_4$ in methylene chloride leads to formation of both aza diene **XIIIa**–**XIIIc** and stereoisomeric dihydropyrroles **XIVa**–**XIVc** and **XVa**–**XVc** which may formally be regarded as products of insertion of two carbenoid molecules into the azirine ring (Scheme 4).

Compounds **XIIIa**–**XIIIc** are yellow substances due to the presence of extended conjugated bond system; the UV spectrum of **XIIIa** contains a long-wave absorption maximum at λ 334 nm (log ε 3.28). Stretching vibrations of the ester carbonyl groups in **XIIIa**–**XIIIc** gave rise to IR absorption at 1750 cm^{-1}. The ^1H NMR spectra of **XIIIa**–**XIIIc** contained signals from aromatic protons, a singlet from the methoxy group (δ ~3.82 ppm), and singlets in the regions δ 4.55–4.61 and 4.97–5.02 ppm, the latter corresponding to protons of the CH_2= group. In the ^{13}C NMR spectra of these compounds, signals from the aromatic carbon atoms and methoxy group and those located at δ_C 94–95 (CH_2=), 154–155 (HC=), 158–159 (N=C), and 164–155 ppm (C=O) were present. Compound **XIIIc** showed in the mass spectrum the molecular ion peak (*m*/*z* 345) with an intensity ratio corresponding to the presence of one bromine atom in the molecule. The most characteristic fragment ion peaks are the following: $[M - MeOH]^+$, $[M - HCO_2Me]^+$, $[M - CO_2Me]^+$, $[M - CO_2Me - HBr]^+$.

The IR spectra of **XIVa**–**XIVc** and **XVa**–**XVc** revealed ester carbonyl absorption at about 1740 cm^{-1}. Isomers **XIV** and **XV** are characterized by almost similar ^{13}C NMR spectra, which contained a signal at δ_C 48–49 ppm (C^4), two signals at δ_C 48–49 ppm (OCH_3), signals at δ_C 66–68 and 91–92 ppm (C^3 and C^2, respectively), and three signals in the region

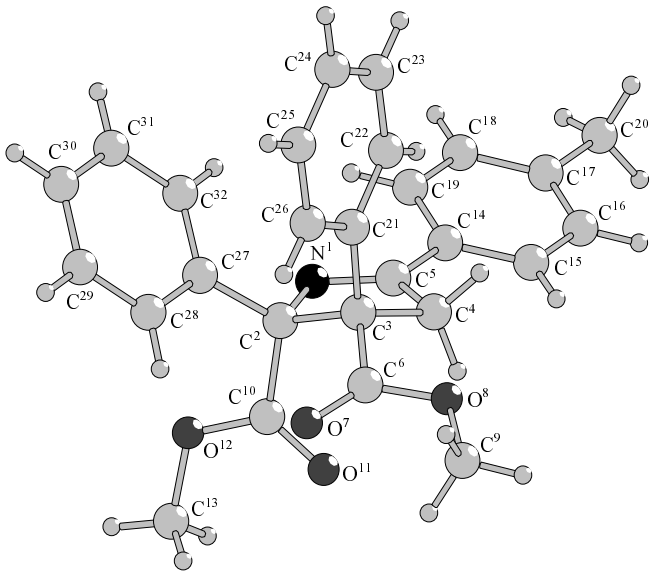
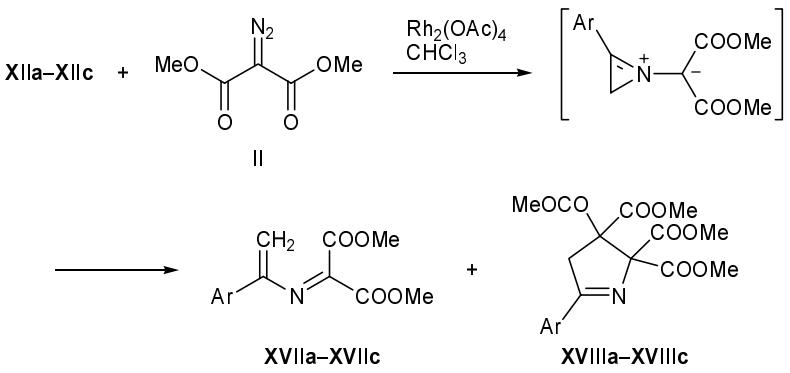


Fig. 3. Structure of the molecule of dimethyl *cis*-5-(4-methylphenyl)-2,3-diphenyl-3,4-dihydro-2*H*-pyrrole-2,3-dicarboxylate (**XIVb**) according to the X-ray diffraction data.

Scheme 5.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-BrC_6H_4 (**c**).

δ_C 170–175 ppm (C=O, C=N); in addition, signals from the aromatic carbon atoms were present. However, isomeric compounds **XIV** and **XV** showed an appreciable difference in the positions of signals from the methoxy protons in the ^{1}H NMR spectra, δ 3.74–3.89 and 3.28–3.55 ppm, respectively. Upfield shift (from an average δ value of ~3.8 ppm) of the methoxycarbonyl group signal in the ^{1}H NMR spectra of dihydropyrrole derivatives is usually observed when that group is located *cis* with respect to the phenyl group at the neighboring carbon atom [15–19]. Therefore, we assigned compounds **XIV** and **XV** the structures of *cis* and *trans* isomers of dimethyl 5-aryl-2,3-diphenyl-3,4-dihydro-2*H*-pyrrole-2,3-dicarboxylates. The structure of **XIVb** was proved by X-ray analysis (Fig. 3).

The product ratio in the reactions of azirines **XIIa**–**XIIc** with diazo ester **I** strongly depended on the initial reactant ratio. The yield of dihydropyrrole derivatives **XIV** and **XV** increased as the diazo compound–azirine molar ratio rose; correspondingly, the fraction of aza diene **XIII** decreased (Table 1). On the other hand, by special experiments we showed that aza dienes **XIII** are not transformed into dihydropyrroles under the given conditions.

Analogous results were obtained in reactions of azirines **XIIa**–**XIIc** with dimethyl diazomalonate (**II**) (Scheme 5, Table 2), where the reactants were taken at a ratio of 1:(1.13–1.24); i.e., excess diazo ester was used. In all cases, the overall yields of aza dienes **XVIIa**–**XVIIc** and dihydropyrroles **XVIIIa**–**XVIIIc** were fairly high.

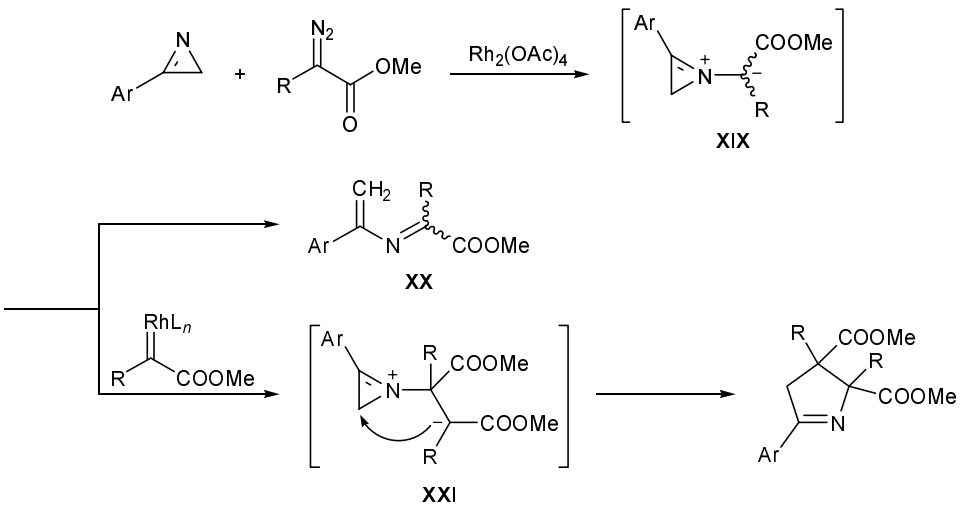
Molecules of aza dienes **XVII** possess an extended conjugated bond system which is responsible for their yellow color. The long-wave absorption maximum in the UV spectrum of **XVIIa** is located at λ 332 nm (logε 3.18). The IR spectra of aza dienes **XVIIa**–**XVIIc** contain an absorption band at 1760 cm^{-1} due to stretching vibrations of the ester carbonyl group. In the ^{1}H spectra of these compounds we observed signals from aromatic protons, singlets from the methoxy protons (δ 3.79 and 3.99 ppm), and singlets from the CH_2= protons at δ 4.56–4.63 and 4.96–5.01 ppm. Compounds **XVIIa**–**XVIIc** showed in the ^{13}C NMR spectra aromatic carbon signals and signals from the methoxy groups, H_2C= fragment (δ_C 96.0–97.3 ppm), N–C= and N=C fragments (δ_C 150.7–153.7 ppm), and two ester carbonyl carbon atoms (δ_C 160.8–161.9 ppm). Aza diene **XVIIa** gave the molecular ion peak with *m*/*z* 247, and the most characteristic ion was $[M - CO_2Me]^+$.

The IR spectra of **XVIIIa**–**XVIIIc** contained an absorption band in the region 1740–1760 cm^{-1} due to stretching vibrations of the ester carbonyl groups. The four methoxy groups in molecules **XVIIIa**–**XVIIIc** are equivalent in pairs, and they appeared as two singlets at δ 3.76 and 3.83 ppm in the ^{1}H NMR spectra; the spectra also contained a singlet from the methylene

Table 2. Reactions of azirines **XIIa**–**XIIc** with dimethyl 2-diazomalonate (**II**)

Azirine no.	Reactant ratio **XII**:**II**	Yield of **XVII**, %	Yield of **XVIII**, %
XIIa	1:1.13	51	17
XIIb	1:1.21	52	19
XIIc	1:1.24	43	31

Scheme 6.

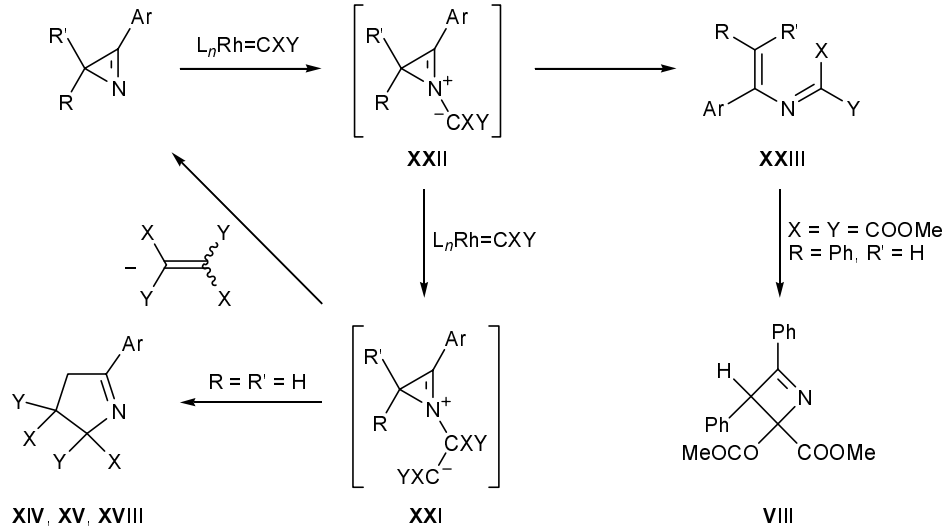


R = Ph, CO_2Me.

group (C^4H_2) in the region δ 3.83–3.87 ppm and signals from aromatic protons. The following signals were present in the ^{13}C NMR spectra of **XVIIIa**–**XVIIIc**, δ_C, ppm: 46.0 (C^4), 65.6–66.6 (C^3), 91.8 (C^2), 167.7–168.0 (C^5), 169.3–174.8 (C=O).

Taking into account that the product ratio **XIII**:(**XIV**/**XV**) in the reactions of 3-aryl-substituted azirines **XIIa**–**XIIc** with diazo ester **II** strongly depends on the initial reactant ratio and that aza diene **XIII** failed to undergo transformation into dihydropyrrole under these conditions, we propose Scheme 6 to rationalize the formation of dihydropyrrole derivatives **XIV**/**XV** and **XVIII**. Carbenoid species generated from the diazo compound and rhodium catalyst reacts with azirine **XII** to give ylide **XIX**. Opening of the three-membered ring in **XIX** leads to aza diene **XX**. Reaction of ylide **XIX** with the second molecule of electrophilic rhodium carbenoid gives zwitterionic intermediate **XXI**. Intermediate **XXI** derived from 2*H*-azirines having no substituent in position *2* undergoes intramolecular nucleophilic substitution to produce dihydropyrrole derivative. The presence of a substituent in the 2-position of 2*H*-azirine hampers such recyclization, so that intermediate **XXI** decomposes into the initial azirine and carbene dimer; therefore, the transformation of ylide **XIX** into aza diene **XX** in

Scheme 7.



X = CO_2Me, Y = Ph, CO_2Me.

reactions with 2-substituted 2*H*-azirines **III** and **VI** is the predominant reaction path (Scheme 6).

It should be noted that no azetine derivatives like **VIII** were detected in reactions of azirines **XII** with diazo esters; this means that the presence of a phenyl group in position *2* of the azirine ring is an important factor favoring formation of azetine **VIII**. Unlike fluorinated azirinium ylides [10, 11], ylides **XIX** generated from 3-aryl-2*H*-azirines and metal carbenoids cannot be trapped via 1,3-dipolar cycloaddition; presumably, bulky phenyl and methoxycarbonyl groups (as compared to fluorine atom) hamper this process.

Thus our study on the reactions of 2*H*-azirines with bis(methoxycarbonyl)carbenoid and methoxycarbonyl(phenyl)carbenoid revealed a number of general relations which can be illustrated by Scheme 7. Addition of carbenoid species to azirines gives azirinium ylides **XXII**. The main transformation pathway of sterically loaded azirinium ylides generated from 2-mono- and 2,2-disubstituted 3-aryl-2*H*-azirines is their isomerization into 2-aza-1,3-dienes **XXIII**. If a substituent favoring polarization of the aza diene is present, e.g., as in the ylide derived from 2,3-diphenyl-2*H*-azirine and dimethyl diazomalonate, recyclization of the aza diene into azetine **VIII** occurs. Difluoro-substituted azirinium ylides generated from 3-aryl-2*H*-azirines lack steric hindrances, and they can be trapped by active dipolarophiles or undergo isomerization into 1,1-difluoro-2-aza-1,3-dienes [11, 12]; analogous adducts with ylides **XXII** could not be obtained. Apart from the isomerization to aza dienes, azirinium ylides generated from 3-aryl-2*H*-azirines and carbenoids are capable of reacting with fairly electrophilic and reactive rhodium carbenoids to give zwitterionic intermediates **XXI** which undergo intramolecular ring closure to dihydropyrrole derivatives **XIV**/**XV** or **XVIII**.

EXPERIMENTAL

The IR spectra were recorded from solutions in chloroform or carbon tetrachloride on a UR-20 spectrometer using 400-μm cells. The NMR spectra were measured on a Bruker DPX-300 spectrometer at 300 and 75 MHz for ^{1}H and ^{13}C, respectively. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1303 instrument. The UV spectra were recorded on a Specord M-40 spectrophotometer. The elemental compositions were determined on an Hewlett–Packard HP-185B CHN analyzer. The progress of reactions was monitored by TLC using Silufol UV-254 plates. Silica gel LS 5/40 μm (Chemapol) was used for chromatographic separation of reaction mixtures.

Azirine **III** was synthesized by the procedure described in [20], azirine **VI** was prepared as reported in [21], and 3-aryl-2*H*-azirines **XIIa**–**XIIc** were obtained as described in [22].

Reaction of azirines with methyl 2-diazo-2-phenylacetate (*general procedure***).** *a*. A 25-ml two-necked flask equipped with a reflux condenser and a drying tube was purged with argon and charged with 1 mmol of the corresponding azirine, 4.4 mg (1.1 mol %) of $Rh_2(OAc)_4$, and 3.5 ml of methylene chloride. The mixture was heated to the boiling point under stirring, and a solution of 1.3–6.0 mmol of methyl 2-diazo-2-phenylacetate in 6.5 ml of methylene chloride was added at a rate of 1/6 mmol/h (0.01–0.05 mmol each 2–5 min) through a syringe. The progress of the reaction was monitored by TLC (hexane–ethyl acetate, 10:1). The products were isolated by column chromatography on silica gel; solid substances were purified by recrystallization.

Reaction of azirines with dimethyl 2-diazomalonate (*general procedure***).** *b*. A mixture of 2.5 mmol of the corresponding azirine, 13.2 mg (3.3 mol %) of $Rh_2(OAc)_4$, and 2.8–3.1 mmol of dimethyl 2-diazomalonate in 10 ml of anhydrous chloroform was refluxed under vigorous stirring, the progress of the reaction being monitored by TLC. The products were isolated by column chromatography on silica gel; solid substances were purified by recrystallization.

Methyl 2-phenyl-2-[phenyl(fluoren-9-ylidene)methylimino]acetate (IV) was obtained from 0.25 g (0.95 mmol) of azirine **III** and 0.215 g (1.22 mmol) of methyl 2-diazo-2-phenylacetate according to method *a* (reaction time 3 h); the product was isolated by chromatography using hexane–ethyl acetate (20:1) as eluent. Yield 0.333 g (86%). The physical constants and spectral parameters of compound **IV** were reported in [23]. X-Ray diffraction data: $C_{29}H_{21}NO_2$; M 415.47; unit cell parameters: a = 11.1569(5), b = 12.4256(7), c = 31.0580(13) Å; β = 90.992(4)°; V = 4305.0(4) Å^3; Z = 8; d = 1.282 mg/mm^3; monoclinic crystals; space group $P2_1/c$ (no. 14); MoK_α irradiation; λ = 0.71073 Å; temperature 133 K; R_{All} = 0.0604, wR_2 = 0.1156; total of 19887 reflections were measured, 7080 of which were independent (R_{int} = 0.0396).

Dimethyl 2-[phenyl(fluoren-9-ylidene)methylimino]malonate (V) was obtained from 0.250 g (0.95 mmol) of azirine **III** and 0.174 g (1.1 mmol) of diazo ester **II** according to method *b* (reaction time

9 h); the product was isolated by chromatography using hexane–ethyl acetate (5:2) as eluent. Yield 0.301 g (80%), orange crystals, mp 126–128°C (from hexane–ethyl acetate). IR spectrum ($CHCl_3$): ν(C=O) 1750 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.37 s (3H, MeO), 4.02 s (3H, MeO), 6.21–6.24 m (1H, H_{arom}), 6.83–6.88 m (1H, H_{arom}), 7.21–7.28 m (1H, H_{arom}), 7.35–7.45 m (4H, H_{arom}), 7.51–7.54 m (3H, H_{arom}), 7.63–7.70 m (2H, H_{arom}), 8.43–8.45 m (1H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 52.0 br (MeO), 53.0 br (MeO), 118.9, 119.2, 124.9, 126.3, 127.3, 128.4 (2C), 128.5, 129.1, 129.2, 130.3 (2C), 134.2, 135.2, 136.7, 137.3, 140.2, 141.4, 143.5 (C_{arom}, =C), 147.0 (C=N), 162.1, 162.4 br (C=O). Found, %: C 75.40; H 4.85; N 3.36. $C_{25}H_{19}NO_4$. Calculated, %: C 75.55; H 4.82; N 3.52.

A solution of 0.1 g (0.25 mmol) of compound **V** and 5 mg of $Rh_2(OAc)_4$ in 5 ml of anhydrous chloroform or benzene was refluxed for 4 h under stirring. According to the TLC data, the initial compound remained unchanged.

Methyl 2-[(1,2-diphenylethenyl)imino]-2-phenylacetate (VII) was obtained from 0.2 g (1.04 mmol) of azirine **VI** and 0.23 g (1.3 mmol) of methyl 2-diazo-2-phenylacetate according to method *a* (reaction time 3 h); the product was isolated by chromatography using hexane–ethyl acetate (10:1) as eluent. Yield 0.24 g (68%); the physical constants and spectral parameters of compound **VII** were reported in [23]. X-Ray diffraction data: $C_{23}H_{19}NO_2$; *M* 341.39; unit cell parameters: *a* = 8.6073(6), *b* = 11.4414(12), *c* = 18.6707(13) Å; β = 90.650(5)°; *V* = 1838.6(3) $Å^3$; *Z* = 4; *d* = 1.233 mg/mm^3; monoclinic crystals; space group $P2_1/c$ (no. 14); MoK_α irradiation, λ = 0.71073 Å; temperature 133 K; R_{All} = 0.0423, wR_2 = 0.0889; total of 10550 reflections were measured, 3133 of which were independent (R_{int} = 0.0495).

A solution of 0.1 g (0.29 mmol) of compound **VII** in 5 ml of anhydrous methylene chloride was stirred for 4 h under reflux. According to the TLC data, the initial compound remained unchanged. The same result was obtained when the mixture was stirred for 4 h under reflux in the presence of 5 mg of $Rh_2(OAc)_4$.

Dimethyl 3,4-diphenyl-2,3-dihydroazete-2,2-dicarboxylate (VIII) and dimethyl 2-amino-2-(2-oxo-1,2-diphenylethyl)malonate (IX). The reaction was performed using 0.5 g (2.59 mmol) of azirine **VI** and 0.51 g (3.23 mmol) of dimethyl 2-diazomalonate according to method *b* (reaction time 17 h); by column chromatography (hexane–ethyl acetate, 6:1) we isolated 0.61 g (73%) of compound **VIII**. When a solution of **VIII** in hexane–ethyl acetate was stored at room temperature on exposure to air, compound **VIII** underwent hydrolysis to ester **IX**. The physical constants and spectral parameters of compounds **VIII** and **IX** were reported in [23].

Reduction of dimethyl 3,4-diphenyl-2,3-dihydroazete-2,2-dicarboxylate (VIII). A solution of 0.8 g (2.48 mmol) of compound **VIII** in 10 ml of anhydrous diethyl ether was added dropwise to a mixture of 0.16 g (4.22 mmol) of $LiAlH_4$ and 40 ml of anhydrous diethyl ether in an argon atmosphere under stirring and cooling with cold water. The mixture was heated for 3 h under reflux, cooled, and treated in succession with 0.16 ml of water, 0.16 ml of 15% aqueous NaOH, and 0.48 ml of water. The organic phase was filtered and evaporated, and the residue was recrystallized from ethyl acetate to obtain 0.511 g (77%) of compound **X**.

2-Hydroxymethyl-3,4-diphenylazetidin-2-ylmethanol (X). mp 161–162°C (from ethyl acetate). IR spectrum (KBr), ν, cm^{-1}: 3450, 3265 (OH, NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.66 br.s (3H, OH, NH), 3.43 d (1H, OCH_2, *J* = 11.5 Hz), 3.62 d (1H, OCH_2, *J* = 11.5 Hz), 3.93 d (1H, 3-H, *J* = 9.0 Hz), 4.12 d (1H, OCH_2, *J* = 11.0 Hz), 4.19 d (1H, OCH_2, *J* = 11.0 Hz), 5.52 d (1H, 4-H, *J* = 9.0 Hz), 6.97–7.00 m (2H, H_{arom}), 7.06–7.16 m (6H, H_{arom}), 7.20–7.25 m (2H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 48.5 (C^3), 57.7 (C^4), 61.5 (CH_2), 64.2 (CH_2, C^2), 125.4, 125.6, 126.1 (2C), 126.8 (2C), 127.5 (2C), 130.6 (2C), 137.3, 142.4 (C_{arom}). Found, %: C 75.82; H 7.20; N 5.24. $C_{17}H_{19}NO_2$. Calculated, %: C 75.81; H 7.11; N 5.20.

Methyl 2-phenyl-2-(1-phenylethenylimino)-acetate (XIIIa), dimethyl *cis*-2,3,5-triphenyl-3,4-dihydro-2*H*-pyrrole-2,3-dicarboxylate (XIVa), and dimethyl *trans*-2,3,5-triphenyl-3,4-dihydro-2*H*-pyrrole-2,3-dicarboxylate (XVa). The reaction was performed using 0.5 g (4.27 mmol) of azirine **XIIa** and 1.5 g (8.52 mmol) of methyl 2-diazo-2-phenylacetate according to method *a* (reaction time 9 h); by column chromatography (hexane–ethyl acetate, 10:1) we isolated 0.61 g (56%) of aza diene **XIIIa** and 0.18 g (10%) of a mixture of stereoisomeric dihydropyrroles **XIVa** and **XVa** at a ratio of 3:1.8.

Compound **XIIIa**. Yellow viscous liquid. UV spectrum (hexane): λ_{max} 334 nm (log ε 3.28). IR spectrum ($CHCl_3$): ν(C=O) 1750 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.82 s (3H, MeO), 4.60 s (1H, CH_2=), 5.02 s (1H, CH_2=), 7.36–7.59 m (8H, H_{arom}),

7.92–7.94 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 51.5 (MeO), 95.3 (CH_2=), 125.5, 127.8, 128.0, 128.2, 128.4, 131.5, 133.1, 135.9 (C_{arom}), 155.0 (C=), 158.6 (C=N), 164.8 (C=O). Found, %: C 76.65; H 5.92; N 4.98. $C_{17}H_{15}NO_2$. Calculated, %: C 76.96; H 5.70; N 5.28.

Compounds **XIVa** and **XVa** (mixture of diastereoisomers). mp 145–157°C (from hexane–CH_2Cl_2). IR spectrum ($CHCl_3$): ν(C=O) 1740 cm^{-1}. Found, %: C 75.53; H 5.83; N 3.28. $C_{26}H_{23}NO_4$. Calculated, %: C 75.53; H 5.61; N 3.39.

Compound **XIVa**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.74 s (3H, MeO), 3.89 s (3H, MeO), 3.93 d (1H, 4-H, J = 17.7 Hz), 4.43 d (1H, 4-H, J = 17.7 Hz), 6.76–6.79 m (2H, H_{arom}), 6.91–6.98 m (3H, H_{arom}), 7.02–7.08 m (3H, H_{arom}), 7.34–7.42 m (2H, H_{arom}) 7.52–7.62 m (3H, H_{arom}) 8.12–8.15 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 48.2 (C^4), 52.3 (MeO), 52.6 (MeO), 66.1 (C^3), 91.1 (C^2), 126.4 (2C), 126.5 (3C), 126.6, 127.4 (2C), 127.9 (2C), 128.1 (2C), 128.4 (2C), 131.4, 132.9, 137.1, 138.8 (C_{arom}), 172.3, 173.7, 175.6 (C=O, C=N).

Compound **XVa**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.29 s (3H, MeO), 3.55 s (3H, MeO), 3.60 d (1H, 4-H, J = 16.7 Hz), 4.30 d (1H, 4-H, J = 16.7 Hz), 7.25–7.40 m (8H, H_{arom}), 7.46–7.51 m (5H, H_{arom}), 8.07–8.09 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 49.0 (C^4), 51.7 (MeO), 52.0 (MeO), 67.7 (C^3), 91.4 (C^2), 125.9 (2C), 126.5, 126.7, 127.2 (2C), 127.7 (2C), 128.0 (2C), 128.1 (2C), 128.3 (2C), 131.2, 131.4, 136.8, 142.1 (C_{arom}), 170.0, 171.9, 174.0 (C=O, C=N).

A solution of 0.1 g (0.38 mmol) of compound **XIVa** in 5 ml of anhydrous methylene chloride was refluxed for 4 h under stirring. According to the TLC data, the initial compound remained unchanged. The same result was obtained when the mixture was stirred for 4 h under reflux in the presence of 5 mg of $Rh_2(OAc)_4$.

Methyl 2-phenyl-2-[1-(4-methylphenyl)ethenylimino]acetate (XIIIb), dimethyl *cis*-5-(4-methylphenyl)-2,3-diphenyl-3,4-dihydro-2*H*-pyrrole-2,3-dicarboxylate (XIVb), and dimethyl *trans*-5-(4-methylphenyl)-2,3-diphenyl-3,4-dihydro-2*H*-pyrrole-2,3-dicarboxylate (XVb). The reaction was performed with 0.5 g (3.82 mmol) of azirine **XIIb** and 1.3 g (7.39 mmol) of methyl 2-diazo-2-phenylacetate according to method *a* (reaction time 7 h); by column chromatography (hexane–ethyl acetate, 10:1) we isolated 0.596 g (56%) of aza diene **XIIIb** and 0.32 g (20%) of a mixture of stereoisomeric pyrroles **XIVb** and **XVb** at a ratio of 7:3. The stereoisomers were separated by fractional crystallization from hexane–methylene chloride.

The physical constants and spectral parameters of compounds **XIIb**, **XIVb**, and **XVb** were reported in [23]. X-Ray diffraction data for compound **XIVb**: $C_{27}H_{25}NO_4$; M 427.48; a = 8.6917(8), b = 11.9194(10), c = 12.4069(10) Å; α = 67.39(1), β = 73.14(1), γ = 80.43(1)°; V = 1133.44(17) $Å^3$; Z = 2; d_{calc} = 1.252 mg × mm^{-3}; triclinic crystals, space group P-1 (no. 2); MoK_α irradiation, λ = 0.71073 Å; temperature 133 K; R_{All} = 0.0504, wR_2 = 0.1192; total of 12071 reflections were measured, 3875 of which were independent (R_{int} = 0.0622).

The reaction of 0.5 g (3.82 mmol) of azirine **XIIb** with 2.5 g (14.2 mmol) of methyl 2-diazo-2-phenylacetate according to method *a* (reaction time 12 h), followed by chromatographic separation using hexane–ethyl acetate (10:1) as eluent, gave 0.245 g (23%) of aza diene **XIIIb** and 0.72 g (45%) of diastereoisomer mixture **XIVb**/**XVb**. Likewise, the reaction of 0.5 g (3.82 mmol) of azirine **XIIb** with 4 g (23 mmol) of methyl 2-diazo-2-phenylacetate according to method *a* (reaction time 17 h), followed by chromatographic separation using hexane–ethyl acetate (10:1) as eluent, gave 0.098 g (9%) of aza diene **XIIIb** and 0.982 g (60%) of mixture **XIVb**/**XVb**. The same result was obtained in the reaction of azirine **XIIb** with methyl 2-diazo-2-phenylacetate in the presence of dimethyl acetylenedicarboxylate.

The reaction of 0.15 g (0.87 mmol) of methyl 2-diazo-2-phenylacetate with 0.2 g (0.72 mmol) of aza diene **XIIIb** according to method *a* (reaction time 5 h) was accompanied by decomposition of compound **XIIIb**, and no products were identified.

A solution of 0.1 g (0.36 mmol) of compound **XIIIb** in 5 ml of anhydrous $CHCl_3$ was refluxed for 4 h under stirring. According to the TLC data, the initial compound remained unchanged. The same result was obtained when the mixture was stirred for 4 h under reflux in the presence of 5 mg of $Rh_2(OAc)_4$.

Methyl 2-phenyl-2-[1-(4-bromophenyl)ethenylimino]acetate (XIIIc), dimethyl *cis*-5-(4-bromophenyl)-2,3-diphenyl-3,4-dihydro-2*H*-pyrrole-2,3-dicarboxylate (XIVc), and dimethyl *trans*-5-(4-bromophenyl)-2,3-diphenyl-3,4-dihydro-2*H*-pyrrole-2,3-dicarboxylate (XVc). The reaction of 0.5 g (2.55 mmol) of azirine **XIIc** with 1 g (5.68 mmol) of

methyl 2-diazo-2-phenylacetate according to method *a* (reaction time 5 h), followed by chromatographic separation of the product mixture using hexane–ethyl acetate (8:1) as eluent, gave 0.54 g (62%) of aza diene **XIIIc** and 0.22 g (18%) of a mixture of stereoisomeric pyrroles **XIVc** and **XVc** at a ratio of 3:2.

Compound **XIIIc**. Yellow viscous liquid. IR spectrum ($CHCl_3$): ν(C=O) 1750 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.82 s (3H, MeO), 4.61 s (1H, CH_2=), 5.00 s (1H, CH_2=), 7.42–7.57 m (7H, H_{arom}), 7.82–7.91 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 51.5 (MeO), 95.7 (=CH_2), 122.3, 127.1 (2C), 127.8 (2C), 128.4 (2C), 131.1 (2C), 131.6, 132.9, 134.9 (C_{arom}), 154.0 (=C), 159.0 (C=N), 164.6 (C=O). Found, %: C 59.30; H 4.49; N 4.51. $C_{17}H_{14}BrNO_2$. Calculated, %: C 59.32; H 4.10; N 4.07.

Compounds **XIVc** and **XVc** (mixture of diastereoisomers). mp 162–175°C (from hexane–CH_2Cl_2). IR spectrum ($CHCl_3$): ν(C=O) 1740 cm^{-1}. Found, %: C 63.39; H 4.62; N 2.60. $C_{26}H_{22}BrNO_4$. Calculated, %: C 63.43; H 4.50; N 2.84.

Compound **XIVc**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.74 s (3H, MeO), 3.87 d (1H, 4-H, J = 17.4 Hz), 3.88 s (3H, MeO), 4.41 d (1H, 4-H, J = 17.4 Hz), 6.71–6.75 m (2H, H_{arom}), 6.91–6.99 m (2H, H_{arom}), 7.02–7.06 m (3H, H_{arom}), 7.30–7.45 m (2H, H_{arom}), 7.67–7.70 m (2H, H_{arom}), 7.97–8.00 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 48.2 (C^4), 52.3 (MeO), 52.7 (MeO), 66.3 (C^3), 91.3 (C^2), 126.0, 126.4 (2C), 126.5 (2C), 126.8, 127.5 (2C), 128.1 (2C), 129.4 (2C), 131.7 (2C), 131.8, 136.9, 132.7, 141.8 (C_{arom}), 172.2, 173.6, 173.6 (C=O, C=N).

Compound **XVc**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.28 s (3H, MeO), 3.54 s (3H, MeO), 3.56 d (1H, 4-H, J = 17.4 Hz), 4.28 d (1H, 4-H, J = 17.4 Hz), 7.02–7.05 m (2H, H_{arom}), 7.25–7.48 m (8H, H_{arom}), 7.63–7.67 m (2H, H_{arom}), 7.92–7.96 m (8H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 49.0 (C^4), 51.8 (MeO), 52.0 (MeO), 67.2 (C^3), 91.5 (C^2), 126.2, 126.6 (2C), 126.7 (2C), 127.2 (2C), 127.7 (2C), 127.9, 128.1 (2C), 129.5 (2C), 131.6, 136.7, 138.7, 142.7 (C_{arom}), 169.8, 171.8, 173.1 (C=O, C=N).

Dimethyl 2-(1-phenylethenylimino)malonate (XVIIa) and tetramethyl 5-phenyl-3,4-dihydro-2*H*-pyrrole-2,2,3,3-tetracarboxylate (XVIIIa) were obtained from 0.5 g (4.27 mmol) of azirine **XIIa** and 0.76 g (4.81 mmol) of dimethyl 2-diazomalonate according to method *b* (reaction time 18 h); by column chromatography using hexane–ethyl acetate (10:1) as eluent we isolated 0.54 g (51%) of aza diene **XVIIa** and 0.27 g (17%) of pyrrole **XVIIIa**.

Compound **XVIIa**. Yellow viscous oily liquid. UV spectrum (hexane): λ_{max} 332 nm (logε 3.18). IR spectrum ($CHCl_3$): ν(C=O) 1760 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.79 s (3H, MeO), 3.99 s (3H, MeO), 4.62 s (1H, =CH_2), 5.01 s (1H, =CH_2), 7.36–7.38 m (3H, H_{arom}), 7.47–7.55 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 52.1 (MeO), 53.2 (MeO), 96.9 (=CH_2), 125.5 (2C), 128.1 (2C), 128.7, 134.4 (C_{arom}), 150.9 (NC=), 153.7 (C=N), 161.0 (C=O), 161.9 (C=O). Mass spectrum (70 eV), m/z (I_{rel}, %): 247 $[M]^+$ (13), 188 $[M - CO_2Me]^+$ (5), 103 (100), 77 (33).

Compound **XVIIIa**. mp 183°C (from hexane–ethyl acetate). IR spectrum ($CHCl_3$): ν(C=O) 1755 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.76 s (6H, MeO), 3.83 s (6H, MeO), 3.87 s (2H, 4-H), 7.41–7.52 m (3H, H_{arom}), 7.91–7.94 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 46.0 (C^4), 52.9 (MeO), 53.1 (MeO), 65.6 (C^3), 91.8 (C^2), 128.0 (2C), 128.2 (2C), 131.6, 132.2 (C_{arom}), 167.9, 169.4, 174.8 (C=O, C=N). Found, %: C 57.47; H 5.06; N 3.68. $C_{18}H_{19}NO_8$. Calculated, %: C 57.29; H 5.07; N 3.71.

Dimethyl 2-[1-(4-methylphenyl)ethenylimino]-malonate (XVIIb) and tetramethyl 5-(4-methylphenyl)-3,4-dihydro-2*H*-pyrrole-2,2,3,3-tetracarboxylate (XVIIIb) were obtained from 0.5 g (3.82 mmol) of azirine **XIIb** and 0.73 g (4.62 mmol) of dimethyl 2-diazomalonate according to method *b* (reaction time 16 h); by column chromatography using hexane–ethyl acetate (10:1) as eluent we isolated 0.52 g (52%) of aza diene **XVIIb** and 0.282 g (19%) of pyrrole **XVIIIb**.

Compound **XVIIb**. Yellow crystals, mp 38–40°C (from hexane). UV spectrum (hexane): λ_{max} 347 nm (logε 3.13). IR spectrum ($CHCl_3$): ν(C=O) 1760 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.37 s (3H, Me), 3.79 s (3H, MeO), 3.99 s (3H, MeO), 4.56 s (1H, =CH_2), 4.96 s (1H, =CH_2), 7.16–7.19 m (2H, H_{arom}), 7.35–7.38 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.9 (Me), 52.1 (MeO), 53.2 (MeO), 96.0 (=CH_2), 125.4 (2C), 128.8 (2C), 131.5, 138.7 (C_{arom}), 150.7 (N–C=), 153.6 (C=N), 161.1 (C=O), 161.9 (C=O). Found, %: C 64.21; H 5.85; N 5.33. $C_{14}H_{15}NO_4$. Calculated, %: C 64.36; H 5.79; N 5.36.

Compound **XVIIIb**. mp 169°C (from hexane–ethyl acetate). IR spectrum ($CHCl_3$): ν(C=O) 1760 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.41 s (3H, Me), 3.76 s (6H, MeO), 3.82 s (6H, MeO), 3.85 s (2H, 4-H), 7.23–7.26 m (2H, H_{arom}), 7.80–7.83 m (2H, H_{arom}).

^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 21.2 (Me), 46.0 (C^4), 52.9 (MeO), 53.0 (MeO), 66.6 (C^3), 91.8 (C^2), 128.1 (2C), 128.9 (2C), 129.6, 142.2 (C_{arom}), 168.0, 169.5, 174.6 (C=O, C=N). Found, %: C 58.57; H 5.34; N 3.43. $C_{19}H_{21}NO_8$. Calculated, %: C 58.31; H 5.41; N 3.58.

Dimethyl 2-[1-(4-bromophenyl)ethenylimino]-malonate (XVIIc) and tetramethyl 5-(4-bromophenyl)-3,4-dihydro-2*H*-pyrrole-2,2,3,3-tetracarboxylate (XVIIIc) were obtained from 0.5 g (2.55 mmol) of azirine **XIIc** and 0.5 g (3.16 mmol) of dimethyl 2-diazomalonate according to method *b* (reaction time 14 h); by column chromatography using hexane–ethyl acetate (10:1) as eluent we isolated 0.357 g (43%) of aza diene **XVIIc** and 0.36 g (31%) of pyrrole **XVIIIc**.

Compound **XVIIc**. Yellow viscous liquid. IR spectrum ($CHCl_3$): ν(C=O) 1760 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.79 s (3H, MeO), 3.99 s (3H, MeO), 4.63 s (1H, CH_2=), 5.00 s (1H, CH_2=), 7.33–7.36 m (2H, H_{arom}), 7.48–7.51 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 52.2 (MeO), 53.3 (MeO), 97.3 (=CH_2), 122.9, 127.0 (2C), 131.3 (2C), 133.2 (C_{arom}), 151.3 (NC=), 152.6 (C=N), 160.8 (C=O), 161.7 (C=O). Found, %: C 47.79; H 3.91; N 4.03. $C_{13}H_{12}BrNO_4$. Calculated, %: C 47.88; H 3.71; N 4.29.

Compound **XVIIIc**. mp 195°C (from hexane–ethyl acetate). IR spectrum ($CHCl_3$): ν(C=O) 1740 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.76 s (6H, MeO), 3.83 s (8H, MeO, CH_2), 7.56–7.60 m (2H, H_{arom}), 7.77–7.80 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 45.9 (C^4), 53.0 (MeO), 53.2 (MeO), 65.7 (C^3), 91.8 (C^2), 126.4, 129.5 (2C), 131.1, 131.5 (2C) (C_{arom}), 167.7, 169.3, 173.8 (C=O, C=N). Found, %: C 47.31; H 4.21; N 2.90. $C_{18}H_{18}BrNO_8$. Calculated, %: C 47.39; H 3.98; N 3.07.

A solution of 0.2 g (0.58 mmol) of compound **XVIIc** in 5 ml of anhydrous benzene was refluxed for 4 h under stirring. According to the TLC data, the initial compound remained unchanged. The same result was obtained when the mixture was stirred for 4 h under reflux in the presence of 5 mg of $Rh_2(OAc)_4$.

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