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$Rh_2(OAc)_4$-Catalyzed Reaction of 2-(2-Carbonylvinyl)-3-phenyl-2*H*-azirines with Diazo Esters

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Abstract—$Rh_2(OAc)_4$-catalyzed reaction of 2-(2-carbonylvinyl)-3-phenyl-2*H*-azirines with diazo esters proceeds through an intermediate generation of azirinium ylide suffering a nonstereoselective ring opening to form (3*Z*)- and (3*E*)-2-azahexa-1,3,5-trienes. The former depending on configuration of the C^5=C^6 bond may undergo cyclization either in derivative of 2,3-dihydropyridine, or in pyrrolium ylide that isomerizes into a derivative of 1*H*-pyrrole. According to DFT calculation, the preferred formation of pyrroles at increasing volume of *Z*-substituent at the atom C^6 and of substituents at the atom C^1 of 2-azahexatriene occurs due to the destabilization of more sterically loaded transition states of 1,6-cyclization.

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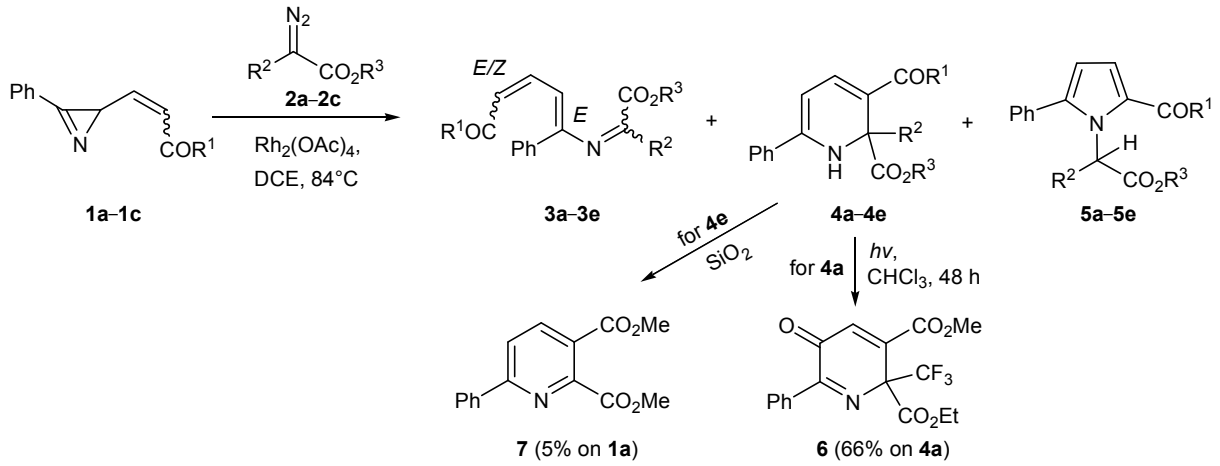
Reactions of rhodium carbenoids generated from diazo carbonyl compounds found a wide application in syntheses of heterocycles [1, 2]. In recent years one of the actively developing strategies for building up 4–6-membered *N*-heterocycles is the carbenoid-mediated transformation of cycles with a weak heteroatom-heteroatom bond [3] or strained heterocycles [4, 5]. As an example of such reactions may serve the synthesis of 2*H*-1,3-oxazines from isoxazoles and diazo carbonyl compounds, allowing performing a recyclization of isoxazole system in one synthetic stage to obtaining final products in high yields [6]. Later it has been demonstrated that in the framework of this approach to 2*H*-1,3-oxazines 2*H*-azirine-2-carbaldehydes may be applied instead of isoxazoles [7–9]. The possibility of application in the synthesis of two synthetically equivalent substrates belonging to different classes of compounds significantly extends the synthetic potential of the preparative method. Examples are also known of successful application of reactions of carbenoids both with isoxazoles and with azirines in the synthesis of pyridines. So, for instance, pyridine-2-carboxylates were synthesized with yields from moderate to good by reactions of isoxazoles with rhodium carbenoids generated from alkenyl diazoacetates [10]. These diazo esters were also applied in the preparation of pyridines with carbenoid-mediated three-atom expansion of the azirine ring [11]. In both methods the construction of pyridine ring was realized with the participation of NCC fragment of the substrate and CCC fragment of the carbenoid. Recently we demonstrated alternative approach to pyridine system by combining fragment NCCCC of substrate, for example, 2-alkenyl-2*H*-azirine, and fragment C of carbenoid [12]. This study consists in a detailed experimental and theoretical investigation of the ways of azirine ring expansion in $Rh_2(OAc)_4$-catalyzed reaction of 2-(2-carbonylvinyl)-3-phenyl-2*H*-azirines **1** with diazo esters **2**.

2-Alkenyl-substituted azirines **1a–1c** were synthesized from 3-phenyl-2*H*-azirine-2-carbaldehyde and the corresponding alkylidenephosphoranes by the method [13]. At a slow addition of diazo compound **2a** solution in 1,2-dichloroethane (DCE) to a mixture of azirine *E*-**1a**, **1b** and $Rh_2(OAc)_4$ (5 mol %) in boiling 1,2-dichloroethane two products were formed: 2-azahexatrienes *E*,*E*-**3a**, **3b** and dihydropyridines **4a**, **4b**. Compounds **3** and **4** were separated by column chromatography, their yields were compiled in the table. In a chloroform solution at room temperature under light a slow oxidation occurs of pyridine **4a** to pyridone **6** (Scheme 1), structure of which was confirmed by X-ray diffraction (XRD) analysis (Fig. 1).

In a similar reaction of azirine *E*-**1c** containing a benzoyl substituent at the C=C bond, besides expected products *E*,*E*-**3c** and **4c** one more compound was detected by ^{1}H NMR method in insignificant amount

Scheme 1.



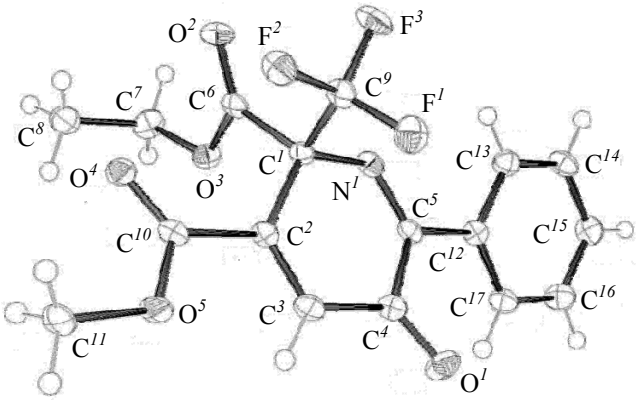


Fig. 1. Structure of 2-ethyl 3-methyl 5-oxo-6-phenyl-2-(trifluoromethyl)-2,5-dihydropyridine-2,3-dicarbo-xylate **6** by XRD data.

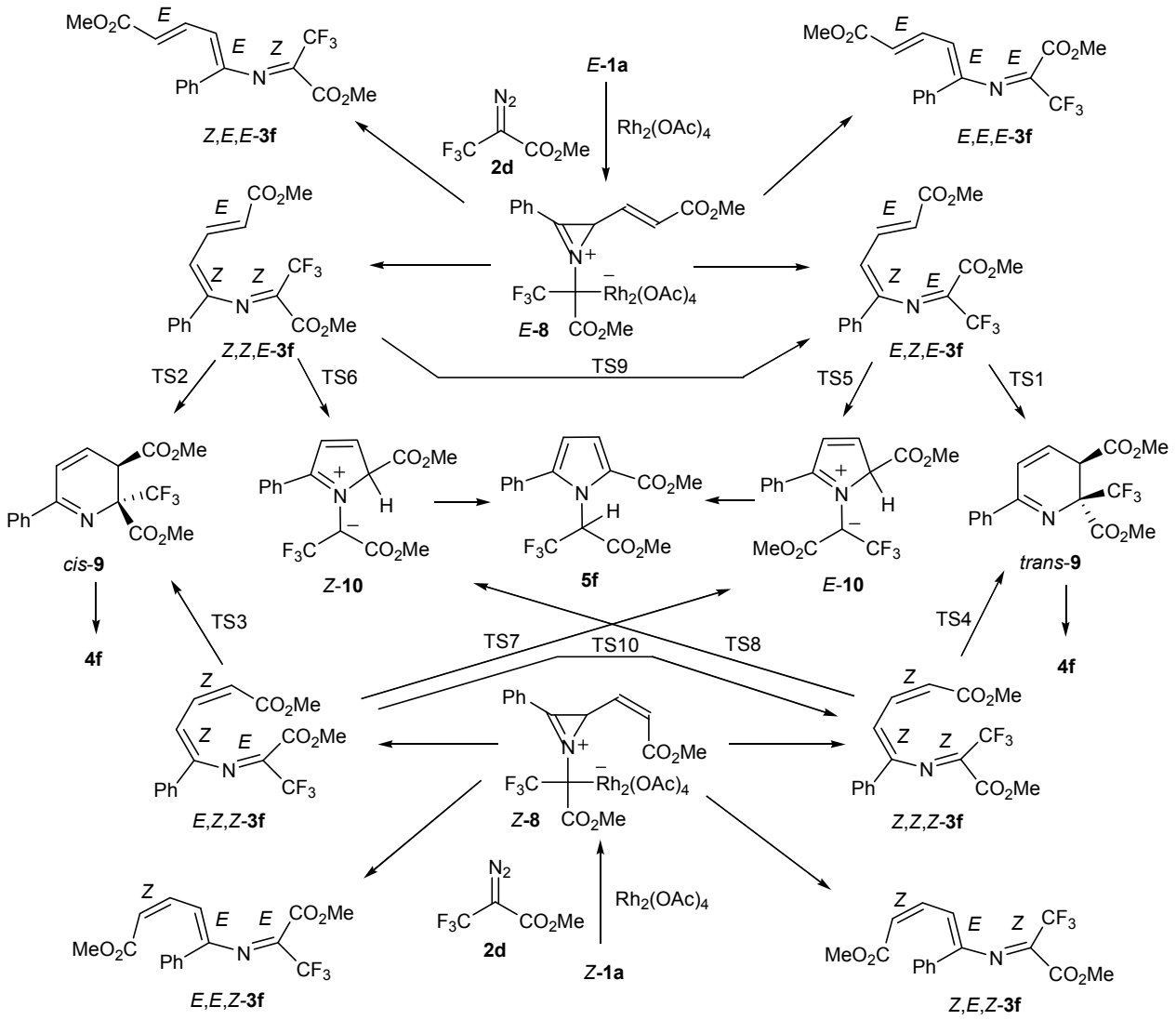
that by typical chemical shifts and signal multiplicity of protons of the pyrrole ring and *N*-substituent [5.13 s (1H), 6.77 d (1H, *J* 4.9 Hz), 7.17 d (1H, *J* 4.9 Hz)] was described as pyrrole structure **5c**. Unfortunately, we failed to isolate it by chromatography due to the instability on silica gel. However pyrrole **5d** that occurred to be more stable was isolated along with compounds *E*,*E*-**3d** and **4d** in reaction of azirine *E*-**1c** with dimethyl diazomalonate **2b**. The reaction of azirine *E*-**1a** with diazo compound **2c**, containing a dimethoxyphosphoryl substituent, proceeds similarly. In this case all three compounds *E*,*E*-**3e**, **4e** and **5e** are formed, however it was possible to isolate in the pure state only the first of them (yield 22%). The formation of pyrrole **5e** was confirmed by ^{1}H NMR data of the reaction mixture that contained typical signals of protons of pyrrole ring and *N*-substituent: 5.49 d (1H, *J* 17.1 Hz), 6.54–6.56 m (1H), 6.96–6.97 m (1H). In dihydropyridine **4e** already in the course of the reaction the elimination of dimethylphosphonate occurred with the formation of pyridine **7** that was isolated in a 5% yield. Ratio of compounds *E*,*E*-**3e**–**7**–**5e** in reaction mixture according to ^{1}H NMR data was 1.5 : 1 : 1.

Reactions of azirines **1a–1c** with diazo esters **2a–2c**

Azirine **1**	R^1	Diazo ester **2**	R^2	R^3	Yield **3**, %	Yield **4**, %	Yield **5**, %
E-**1a**	OMe	**2a**	CF_3	Et	45 (*E*,*E*-**3a**)	27 (**4a**)	0 (**5a**)
E-**1b**	H	**2a**	CF_3	Et	19 (*E*,*E*-**3b**)	20 (**4b**)	0 (**5b**)
E-**1c**	Ph	**2a**	CF_3	Et	28 (*E*,*E*-**3c**)	32 (**4c**)	– (**5c**)[a]
E-**1c**	Ph	**2b**	CO_2Me	Me	32 (*E*,*E*-**3d**)	11 (**4d**)	13 (**5d**)
E-**1a**	OMe	**2c**	$P(O)(OMe)_2$	Me	22 (*E*,*E*-**3e**)	– (**4e**)[b]	– (**5e**)[c]
Z-**1a**	OMe	**2a**	CF_3	Et	28 (*E*,*Z*-**3a**)	0 (**4a**)	17 (**5a**)

[a] Decomposed on silica gel. The ratio **4c–5c** in the reaction mixture was 5 : 1 (^{1}H NMR data).
[b] Under the reaction conditions it converted in pyridine **7** (5%), the ratio *E*,*E*-**3e**–**7**–**5e** in the reaction mixture was 1.5 : 1 : 1 (^{1}H NMR data).
[c] Decomposed on silica gel.

Scheme 2.



Unexpectedly in reaction of isomeric azirine *Z*-**1a** with diazo ester **2a** any trace of dihydropyridine **4a** was not discovered. In the reaction mixture with ^{1}H NMR method the presence was observed of only two compounds: azahexatriene *E*,*Z*-**3a** and pyrrol **5a** which were isolated in yields 28 and 17%.

By an example of $Rh_2(OAc)_4$-catalyzed reaction of isomeric azirines *E*- and *Z*-**1a** with methyl 2-diazo-3,3,3-trifluoropropanoate **2d** we demonstrate a general scheme of the mechanism of the investigated process furnishing three main compounds: azahexatriene *E*,*E*- or *E*,*Z*-**3f** (they are shown on Scheme 2 as pairs of invertomeres quickly transforming in each other *E*,*E*,*E*-**3f** ⇄ *Z*,*E*,*E*-**3f** and *E*,*E*,*Z*-**3f** ⇄ *Z*,*E*,*Z*-**3f** respectively), dihydropyridine **4f**, and pyrrole **5f**. This simplified reaction system (methyl ester **2d** instead of ethyl ester **2a**) was chosen for convenient realization of DFT calculations of key stages of the formation of compounds **3**–**5**. Rhodium carbenoid generated from diazo ester reacts with azirines *E*- and *Z*-**1a**, giving rhodium-bound ylides *E*- and *Z*-**8** that undergo opening in 2-azahexatrienes: *E*-**8** in *E*,*E*,*E*-, *Z*,*E*,*E*-, *E*,*Z*,*E*- and *Z*,*Z*,*E*-**3f**, *Z*-**8** in *E*,*E*,*Z*-, *Z*,*E*,*Z*-, *E*,*Z*,*Z*- and *Z*,*Z*,*Z*-**3f**. Azahexatrienes *E*,*E*,*E*-, *Z*,*E*,*E*-**3f**, generated from azirine *E*-**1a**, and azahexatrienes *E*,*E*,*Z*-, *Z*,*E*,*Z*-**3f**, generated from azirine *Z*-**1a**, possess *E*-configuration of the C^3=C^4 bond and are stable compounds to say nothing of the quick inversion with respect to C=N bond. Azahexatrienes with *Z*-configuration of C^3=C^4

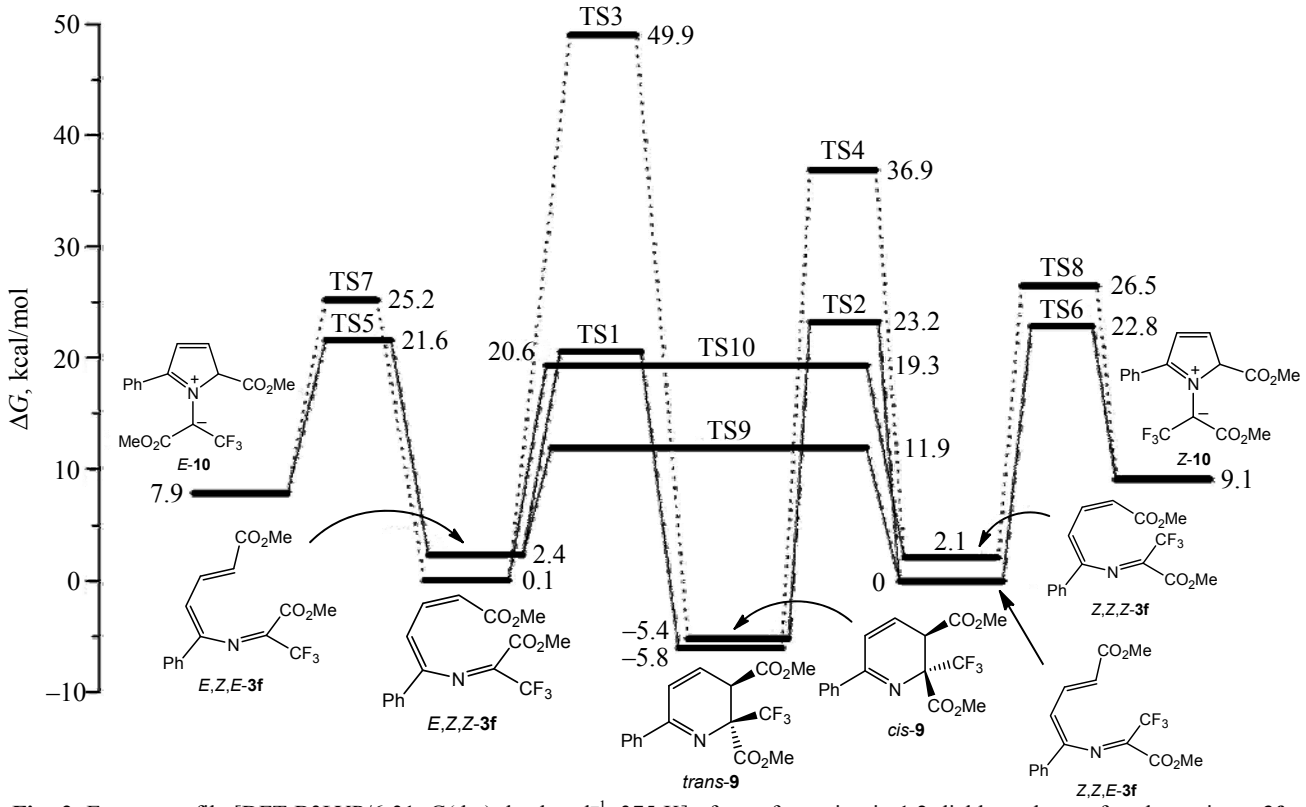


Fig. 2. Energy profile [DFT B3LYP/6-31+G(d,p), kcal mol^{-1}, 375 K] of transformation in 1,2-dichloroethane of azahexatrienes **3f** into dihydropyridines **9** and pyrrolium ylides **10**.

bond in conditions of reaction are unstable and, as the experiment has demonstrated, depending on the configuration of C^5=C^6 bond may undergo 1,6-cyclization into 2,3-dihydropyridines *cis*- and *trans*-**9**, isomerizing into final 1,2-dihydropyridine **4f**, or suffer cyclization into pyrrolium ylides *Z*- and *E*-**10**, isomerizing into final pyrrole **5f**. The described mechanism of the formation of 2-azahexatrienes may include an additional stage of the formation of free azirinium ylide (not shown on Scheme 2), however in general it fully corresponds to experimental and calculated results that we have obtained for reactions of carbenoids with 2-aryl- [14], 2,2-diaryl- [15], 2,2-dialkyl- [16], 2-formyl- [7–9], and 2-bromo-2-methoxycarbonyl-substituted [17, 18], and also with 2-nonsubstituted azirines [15]. However an important stereochemical difference of ring opening should be mentioned in 2-formyl-substituted azirinium ylides and in 2-(2-carbonylvinyl)-substituted ylides of type **8**. In the first case the opening of azirine cycle goes with full 3*Z*-stereoselectivity [7–9], while 2-alkenyl analogs **8** give both geometric isomers of azahexatriene.

To find out the reasons of strong influence of geometry of C=C bond of alkenyl substituent at C^2 in azirine on the ratio of final cyclic products **4** and **5** quantum-chemical calculations of transformation paths of isomeric azahexatrienes *E*,*Z*,*E*-, *Z*,*Z*,*E*-, *E*,*Z*,*Z*-, and *Z*,*Z*,*Z*-**3f** in dihydropyridines *cis*- and *trans*-**9** and in pyrrolium ylides *Z*- and *E*-**10** were performed.

By the method of DFT B3LYP/6-31+G(d,p) accounting for solvation (PCM) with 1,2-dichloroethane free energies were calculated of the most stable conformations of geometric isomers of azahexatriene **3f**, dihydropyridines *cis*- and *trans*-**9**, pyrrolium ylides *Z*- and *E*-**10**, and also of transition states of 1,6-cyclization of azatrienes into dihydropyridines (TS1–TS4), their 1,5-cyclization into pyrrolium ylides (TS5–TS8), and *Z*,*E*-isomerization with respect to C=N bond (TS9, TS10). The correspondence of transition states to saddle point, connecting the initial compounds with the reaction products, was checked by the method of internal reaction coordinate (IRC). Transformations of (5*E*)-azahexatrienes, obtained from azirine *E*-**1a**, are drawn by solid line, and of (5*Z*)-azahexatrienes obtained from azirine *Z*-**1a**, with dotted line (Fig. 2). The inversion of nitrogen atom is also drawn on the diagram with solid line.

From calculation results follows that dihydropyridine **9** should be formed preferably as *trans*-isomer by 1,6-cyclization of azahexatriene *E*,*Z*,*E*-**3f**, whose C^5=C^6 bond possesses *E*-configuration (TS1, $\Delta G^{\neq}$ 18.2 kcal mol^{-1}). Into the same dihydropyridine the second 5*E*-isomer (*Z*,*Z*,*E*-**3f**) can transfrom after preliminary overcoming a low barrier inversion of nitrogen atom (TS9, $\Delta G^{\neq}$ 11.9 kcal mol^{-1}) into azahexatriene *E*,*Z*,*E*-**3f** (solid lines). On the contrary, azahexatrienes with *Z*-configuration of the C^5=C^6 bond (*E*,*Z*,*Z*- and *Z*,*Z*,*Z*-**3f**) possess very high activation barriers of 1,6-cyclization (TS3, $\Delta G^{\neq}$ 49.8 kcal mol^{-1}; TS4, $\Delta G^{\neq}$ 34.8 kcal mol^{-1}) (dotted lines) and should undergo 1,5-cyclization into ylides *E*- and *Z*-**10** respectively with significantly lower barriers (TS7, $\Delta G^{\neq}$ 25.1 kcal mol^{-1}; TS8, 24.4 kcal mol^{-1}). Analysis of geometries of transition states of 1,6-cyclizations of azatrienes with *E*-bond C^5=C^6 (TS1 and TS2), on the one hand, and azatrienes with *Z*-bond C^5=C^6 (TS3 and TS4), on the other, demonstrates significantly higher deviations from planarity of dihedral angle HC^5C^6H (43–44 against 16–21 deg), and also noticeable increase in the length of the formed C^1–C^6 bond (2.47–2.52 against 2.34–2.37 Å) in the transition state for 5*Z*-isomers that indicates high steric hindrances created by CO_2Me group and the substituent at the atom C^1 in the transition states TS3 and TS4. Hence, the calculated data for model azatriene system **3f** correlate with experimental results of competition of 1,6- and 1,5-cyclization of thermally unstable (3*Z*)-azahexatrienes, generated from isomeric azirines *Z*- and *E*-**1**. Note that the changes in geometry of C^5=C^6 bond of azahexatriene have much more effect on 1,6-, than on 1,5-cyclization. We attributed this fact to a higher steric load of the transition state on the path to the 6-membered cycle: the binding of two trigonal carbon reaction centers at 1,6-cyclization comparing to binding a trigonal carbon center to digonal nitrogen center at 1,5-cyclization. It follows that increasing volume of substituents at the atom C^1 of azahexatriene which has acquired them from diazo ester also should change the ratio of products of 1,6-/1,5-cyclization in favor of the latter. Indeed, this assumption is confirmed by results of $Rh_2(OAc)_4$-catalyzed reaction of azirine *E*-**1a** with diazo ester **2c** containing a bulky dimethoxyphosphoryl group that, unlike the similar reaction of trifluoromethyl-substituted diazo ester **2a**, gave products of 1,6- and 1,5-cyclization in equal amounts (see the table).

Hence, an important feature of reactions of rhodium carbenoids generated from diazo esters with 2-(2-carbonylvinyl)-3-phenyl-2*H*-azirines **1**, distinguishing them from reactions with 2-formylazirines [7–9], consists in the fact that ylide intermediates generated in first stage open nonselectively, giving mixtures of isomeric azahexatrienes **3**: isolated from reaction mixture stable (3*E*)-isomer and thermally unstable (3*Z*)-isomer. The latter in conditions of reaction may undergo either 1,6-cyclization into 2,3-dihydropyridine isomerizing into more stable 1,2-dihydropyridine form **4**, or suffer 1,5-cyclization into pyrrolium ylide which isomerizes into final pyrrole **5**. The lack of selectivity of ylide intermediate opening in this reaction limits its application as a method of synthesis of pyridine derivatives. One more synthetic limitation is the presence of competitive 1,5-cyclization of (3*Z*)-2-azahexatriene intermediate, giving finally an isomer of pyrrole series. According to DFT calculations, the formation of pyrroles is preferable at increasing the volume of *Z*-substituent at the atom C^6 and substituents at the atom C^1 of 2-azahexatriene due to the destabilization of sterically more loaded transition states of 1,6-cyclization.

EXPERIMENTAL

Melting points of all substances were determined on Boetius heating block equipped with a microscope; uncorrected values were reported. NMR spectra were recorded on spectrometers Bruker DPX-300 [working frequencies 300 (^{1}H), 75 (^{13}C) MHz] or Bruker DPX-400 [working frequencies 400 (^{1}H), 100 (^{13}C) MHz]. Mass spectra were obtained on mass spectrometer Bruker micrOTOF. Data of single crystal XRD analysis were obtained on diffractometer Agilent Technologies Xcalibur Eos (MoK_α-radiation, 100 K). Reactions progress was monitored by TLC on ALUGRAM SIL G/UV_{254} plates. To separate reaction mixtures silica gel Merck 60 was used. Azirines **1a–1c** were synthesized by method [13]. Quantum-chemical calculations were realized using software package GAUSSIAN 09 Rev. C.01 [19].

Analysis of synthesized compounds was carried out on equipment of resource centers of Saint-Petersburg State University "Magnetic Resonance Research Centre", "Centre for X-ray Diffraction Studies" and "Cgemical Analysis and Materials Research Centre". Quantum-chemical calculations were performed in the resource center of St. Petersburg State University "Computing Centre."

Catalytic reactions of azirines (1) with diazo esters (2). General methods. *a*. A mixture of azirine

and diazo compound in 5 mL of anhydrous 1,2-dichloroethane at stirring in an argon atmosphere was heated till boiling (84°C), 5 mol % $Rh_2(OAc)_4$ was added (with respect to diazo ester), the mixture was refluxed till nitrogen evolution ended (10–15 min). The solvent was removed in a vacuum, reaction products were isolated by column chromatography on silica gel eluting with a mixture of petroleum ether–EtOAc.

b. To a refluxing 0.5 M solution of azirine and $Rh_2(OAc)_4$ (5 mol % with respect to diazo ester) in anhydrous 1,2-dichloroethane at stirring in an argon atmosphere was added dropwise at a rate 3.0 mL/h 0.2 M solution of diazo compound in anhydrous 1,2-dichloroethane. The reaction progress was monitored by TLC (eluent petroleum ether–EtOAc). The solvent was removed in a vacuum, reaction products were isolated by column chromatography on silica gel, eluting with a mixture of petroleum ether–EtOAc.

Methyl (2*E*,4*E*)-5-(3-ethoxy-1,1,1-trifluoro-3-oxopropan-2-ylidenamino)-5-phenylpenta-2,4-dienoate (*E*,*E*-3a) and **2-ethyl 3-methyl 6-phenyl-2-(trifluoromethyl)-1,2-dihydropyridine-2,3-dicarboxylate (4a)** were obtained by method *b* from 100 mg (0.50 mmol) of azirine *E*-**1a** and 136 mg (0.75 mmol) of diazo ester **2a** in yields of 79 mg (45%) and 48 mg (27%) respectively. Spectral data of compounds *E*,*E*-**3a** and **4a** are described in [12].

Methyl (2*Z*,4*E*)-5-(3-ethoxy-1,1,1-trifluoro-3-oxopropan-2-ylidenamino)-5-phenylpenta-2,4-dienoate (*E*,*Z*-3a) and **methyl 1-(3-ethoxy-1,1,1-trifluoro-3-oxopropan-2-yl)-5-phenyl-1*H*-pyrrole-2-carboxylate (5a)** were obtained by method *b* from 30 mg (0.15 mmol) of azirine *Z*-**1a** and 40 mg (0.22 mmol) of diazo ester **2a** in yields of 15 mg (28%) and 9 mg (17%) respectively. Spectral data of compounds *E*,*Z*-**3a** and **5a** are described in [12].

Ethyl 3,3,3-trifluoro-2-[(1*E*,3*E*)-5-oxo-1-phenylpenta-1,3-dien-1-ylimino]propanoate (*E*,*E*-3b) and **ethyl 3-formyl-6-phenyl-2-(trifluoromethyl)-1,2-dihydropyridine-2-carboxylate (4b)** were obtained by method *b* from 150 mg (0.88 mmol) of azirine *E*-**1b** and 160 mg (0.88 mmol) of diazo ester **2a** in yields of 55 mg (19%) and 58 mg (20%) respectively.

Compound *E*,*E*-**3b**. Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz), δ, ppm: 1.32 t (3H, CH_3, *J* 7.0 Hz), 4.34 q (2H, CH_2, *J* 7.0 Hz), 5.91 d (1H, C^2H, *J* 11.3 Hz), 6.26 d.d (1H, C^4H, *J* 15.3, 7.9 Hz), 7.23 d.d (1H, C^3H, *J* 15.3, 11.3 Hz), 7.45–7.55 m (5H, H_{arom}), 9.52 d [1H, CH(O), *J* 7.9 Hz]. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz), δ, ppm: 13.9 (CH_3), 63.1 (CH_2), 111.5 (C^2), 117.9 q (CF_3, *J* 278.8 Hz), 125.2 (C^4), 128.9, 129.0, 130.3, 132.6 (C_{arom}), 146.9 q ($\underline{C}CF_3$, *J* 36.0 Hz), 147.3 (C^3), 155.6, 158.0 (C^1, $\underline{C}O_2Et$), 193.1 [CH(O)]. Found $[M + Na]^+$ 348.0823. $C_{16}H_{14}F_3NNaO_3$. Calculated $[M + Na]^+$ 348.0818.

Compound **4b**. Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz), δ, ppm: 1.32 t (3H, CH_3, *J* 7.0 Hz), 4.28–4.40 m (2H, CH_2), 5.55 br.s (1H, NH), 5.59 d.d (1H, C^5H, *J* 7.0, 1.8 Hz), 7.29 d (1H, C^4H, *J* 7.0 Hz), 7.44–7.57 m (5H, H_{arom}), 9.36 s [1H, CH(O)]. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz), δ, ppm: 13.7 (CH_3), 63.2 (CH_2), 65.4 q (C^2, *J* 30.1 Hz), 94.9 (C^5), 116.2 (C^3), 124.2 q (CF_3, *J* 290.5 Hz), 126.7, 129.2, 131.2, 133.9 (C_{arom}), 147.3 (C^4), 151.3 (C^6), 166.7 ($\underline{C}O_2Et$), 187.6 [CH(O)]. Found $[M + Na]^+$ 348.0821. $C_{16}H_{14}F_3NNaO_3$. Calculated $[M + Na]^+$ 348.0818.

Ethyl 3,3,3-trifluoro-2-[(1*E*,3*E*)-5-oxo-1,5-diphenylpenta-1,3-dien-1-ylimino]propanoate (*E*,*E*-3c) and **ethyl 3-benzoyl-6-phenyl-2-(trifluoromethyl)-1,2-dihydropyridine-2-carboxylate (4c)** were obtained by method *a* from 200 mg (0.81 mmol) of azirine *E*-**1c** and 295 mg (1.62 mmol) of diazo ester **2a** in yields of 91 mg (28%) and 104 mg (32%) respectively.

Compound *E*,*E*-**3c**. Orange crystals, mp 61–63°C (hexane–Et_2O). ^{1}H NMR spectrum ($CDCl_3$, 400 MHz), δ, ppm: 1.29 t (3H, CH_3, *J* 7.0 Hz), 4.30 q (2H, CH_2, *J* 7.0 Hz), 5.97 d (1H, C^2H, *J* 11.9 Hz), 7.13 d (1H, C^4H, *J* 15.0 Hz), 7.45–7.64 m (9H, H_{arom}, C^3H), 7.92–7.96 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) δ, ppm: 13.9 (CH_3), 63.1 (CH_2), 113.2 (C^2), 118.0 q (CF_3, *J* 278.8 Hz), 127.2 (C^4), 128.3, 128.6, 128.7, 129.0, 130.0, 132.79, 132.81, 137.9 (C_{arom}), 140.1 (C^3), 146.8 q ($\underline{C}CF_3$, *J* 36.0 Hz), 155.1, 158.5 (C^1, $\underline{C}O_2Et$), 189.7 ($\underline{C}OPh$). Found $[M + H]^+$ 402.1311. $C_{22}H_{19}F_3NO_3$. Calculated $[M + H]^+$ 402.1312.

Compound **4c**. Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz), δ, ppm: 1.37 t (3H, CH_3, *J* 7.0 Hz), 4.35–4.55 m (2H, CH_2), 5.11 br.s (1H, NH), 5.54 d.d (1H, C^5H, *J* 7.0, 1.5 Hz), 7.15 d (1H, C^4H, *J* 7.0 Hz), 7.43–7.59 m (8H, H_{arom}), 7.67–7.71 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$, 100 MHz), δ, ppm: 13.7 (CH_3), 63.2 (CH_2), 66.4 q (C^2, *J* 30.1 Hz), 94.9 (C^5), 114.8 (C^3), 124.9 q (CF_3, *J* 289.0 Hz), 126.8, 128.2, 128.8, 129.0, 130.9, 131.3, 134.1, 138.9 (C_{arom}), 142.7 (C^4), 149.1 (C^6), 168.0 ($\underline{C}O_2Et$), 193.9 ($\underline{C}OPh$). Found $[M + H]^+$ 402.1313. $C_{22}H_{19}F_3NO_3$. Calculated $[M + H]^+$ 402.1312.

Dimethyl 2-[(1*E*,3*E*)-5-oxo-1,5-diphenylpenta-1,3-dien-1-ylimino]malonate (*E*,*E*-3d), dimethyl 3-benzoyl-6-phenyl-1,2-dihydropyridine-2,2-dicarboxylate (4d), and **dimethyl 2-(2-benzoyl-5-phenyl-1*H*-pyrrol-1-yl)malonate (5d)** were obtained by method *a* from 50 mg (0.20 mmol) of azirine *E*-**1c** and 64 mg (0.40 mmol) of diazo ester **2b** in yields of 24 mg (32%), 8 mg (11%) and 10 mg (13%) respectively.

Compound *E*,*E*-**3d**. Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 3.76 br.s (3H, OCH_3), 3.96 br.s (3H, OCH_3), 6.09 d (1H, C^2H, *J* 11.5 Hz), 7.13 d (1H, C^4H, *J* 14.8 Hz), 7.35–7.60 m (9H, H_{arom}, C^3H), 7.92–7.96 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 52.8 (OCH_3), 53.6 (OCH_3), 114.8 (C^2), 127.2 (C^4), 128.3, 128.5, 128.6, 129.2, 129.8, 132.7, 133.0, 137.9 (C_{arom}), 140.3 (C^3), 149.7, 156.4 (C^1, C=N), 161.2 ($\underline{C}O_2Me$), 161.8 ($\underline{C}O_2Me$), 189.7 ($\underline{C}OPh$). Found $[M + H]^+$ 378.1341. $C_{22}H_{20}NO_5$. Calculated $[M + H]^+$ 378.1336.

Compound **4d**. Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 3.89 s (6H, OCH_3), 5.56 d.d (1H, C^5H, *J* 6.7, 1.8 Hz), 5.76 br.s (1H, NH), 7.03 d (1H, C^4H, *J* 6.7 Hz), 7.43–7.56 m (6H, H_{arom}), 7.62–7.67 m (2H, H_{arom}), 7.74–7.78 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 53.6 (OCH_3), 67.5 (C^2), 95.8 (C^5), 118.4 (C^3), 127.2, 128.1, 128.97, 129.04, 130.7, 131.1, 134.3, 139.18, 139.21 (C^4, C_{arom}), 148.5 (C^6), 171.1 ($\underline{C}O_2Me$), 193.8 ($\underline{C}OPh$). Found $[M + H]^+$ 378.1341. $C_{22}H_{20}NO_5$. Calculated $[M + H]^+$ 378.1336.

Compound **5d**. Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 3.79 s (6H, OCH_3), 5.87 s [1H, CHC(O)], 6.35 d (1H, C^4H, *J* 4.0 Hz), 6.92 d (1H, C^3H, *J* 4.0 Hz), 7.40–7.60 m (8H, H_{arom}), 7.83–7.87 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 53.2 (OCH_3), 61.8 [$\underline{C}HC(O)$], 110.6 (C^4), 123.2 (C^3), 128.1, 128.9, 129.1, 129.3, 129.6, 130.9, 131.4, 131.5, 139.3 (C^2, C_{arom}), 143.6 (C^5), 165.6 ($\underline{C}O_2Me$), 186.5 ($\underline{C}OPh$). Found $[M + H]^+$ 378.1339. $C_{22}H_{20}NO_5$. Calculated $[M + H]^+$ 378.1336.

2-Ethyl 3-methyl 5-oxo-6-phenyl-2-(trifluoromethyl)-2,5-dihydropyridine-2,3-dicarboxylate (6) was obtained at holding of 48 mg of pyridine **4a** under light in solution of chloroform (2 mL) for 2 days. After purification by column chromatography on silica gel with eluent petroleum ether–EtOAc yield was 33 mg (66%). Yellow crystals, mp 63–65°C (hexane–Et_2O). ^{1}H NMR spectrum ($CDCl_3$, 400 MHz), δ, ppm: 1.31 t (3H, $C\underline{H}_3CH_2$, *J* 7.0 Hz), 3.94 s (3H, OCH_3), 4.28–4.41 m (2H, $CH_3C\underline{H}_2$), 7.36 s (1H, C^4H), 7.46–7.51 m (2H, H_{arom}), 7.53–7.59 m (1H, H_{arom}), 7.98–8.02 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$, 100 MHz), δ, ppm: 13.8 ($\underline{C}H_3CH_2$), 53.4 (OCH_3), 63.4 ($CH_3\underline{C}H_2$), 71.2 q (C^2, *J* 27.3 Hz), 121.5 q (CF_3, *J* 286.1 Hz), 128.3, 129.8, 131.9, 132.7, 135.7 (C^4, C_{arom}), 143.9 (C^3), 162.1, 163.4, 165.5 (C^6, $\underline{C}O_2Me$, $\underline{C}O_2Et$), 175.7 (C^5). Found $[M + H]^+$ 370.0913. $C_{17}H_{15}F_3NO_5$. Calculated $[M + H]^+$ 370.0897.

XRD analysis (CCDC 1542058). $C_{17}H_{14}F_3NO_5$, *m* 369.29, *T* 100 K, monoclinic crystal system, space group $P2_1/c$, *a* 10.3152(7), *b* 9.6779(4), *c* 16.5819(6) Å; β 90.288(4)°, *V* 1655.34(14) Å^3, *Z* 4, *d* 1.482 mg/mm^3, μ (MoK_α) 0.131, *R* 0.0863, wR_2 0.1080, 6698 reflections, of them 3255 independent (R_{int} 0.0382).

Methyl (2*E*,4*E*)-5-[1-(dimethoxyphosphoryl)-2-methoxy-2-oxoethylidenamino]-5-phenylpenta-2,4-dienoate (*E*,*E*-3e) and **dimethyl 6-phenylpyridine-2,3-dicarboxylate (7)** were obtained by method *b* from 100 mg (0.50 mmol) of azirine *E*-**1a** and 207 mg (1.00 mmol) of diazo ester **2c** in yields 41 mg (22%) and 7 mg (5%) respectively.

Compound *E*,*E*-**3e**. Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz), δ, ppm: 3.72 s [3H, C(O)OCH_3], 3.78 br.s [3H, C(O)OCH_3], 3.91 br.d [6H, P(O)OCH_3, *J* 10.7 Hz], 5.82 d (1H, C^4H, *J* 11.9 Hz), 6.00 d (1H, C^2H, *J* 15.3 Hz), 7.34–7.48 m (6H, H_{arom}, C^3H). ^{13}C NMR spectrum ($CDCl_3$, 100 MHz), δ, ppm: 51.5 [C(O)O$\underline{C}H_3$], 52.9 [C(O)O$\underline{C}H_3$], 54.5 [P(O)OCH_3], 112.5 (C^4), 122.7 (C^2), 128.6, 129.0, 129.7, 133.2 (C_{arom}), 140.4 (C^3), 167.2 ($\underline{C}O_2Me$). Signals of carbon atoms of fragment C–N=C overlapped. Found $[M + Na]^+$ 404.0872. $C_{17}H_{20}NNaO_7P$. Calculated $[M + Na]^+$ 404.0870.

Compound **7**. Colorless crystals, mp 93–94°C (mp 95–96°C [20]). ^{1}H NMR spectrum ($CDCl_3$, 400 MHz), δ, ppm: 3.97 s (3H, OCH_3), 4.05 s (3H, OCH_3), 7.47–7.54 m (3H, H_{arom}), 7.90 d (1H, C^5H, *J* 8.2 Hz), 8.07–8.12 m (2H, H_{arom}), 8.32 d (1H, C^4H, *J* 8.2 Hz). Found $[M + H]^+$ 272.0911. $C_{15}H_{14}NO_4$. Calculated $[M + H]^+$ 272.0917.

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