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Synthesis of Substituted Methyl Pyridazine-4-carboxylates via Cycloaddition of Diazomethane to 2,3-Disubstituted 2-Cyclopropenecarboxylic Acids

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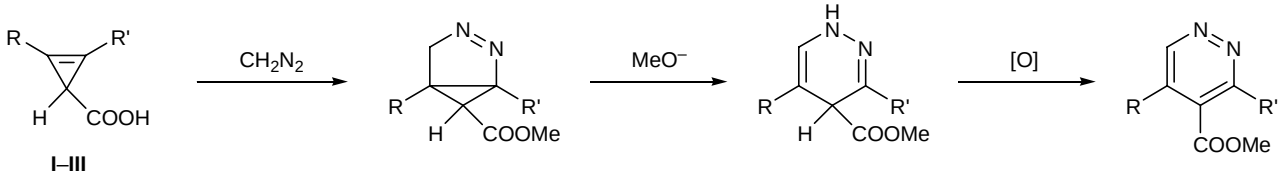
Abstract—A three-step procedure has been developed for the synthesis of 3,5-disubstituted methyl pyridazine-4-carboxylates from accessible 2,3-disubstituted 2-cyclopropenecarboxylates. In the first step, cyclopropene derivatives react with diazomethane to give adducts having 2,3-diazabicyclo[3.1.1]hex-2-ene structure. The regio- and stereoselectivity of the cycloaddition has been determined. The second step is isomerization of the bicyclic adducts into 1,4-dihydropyridazine derivatives by the action of sodium methoxide. Finally, oxidation with potassium permanganate yields the target pyridazine-4-carboxylates.

The double bond in cyclopropene derivatives is much more reactive than in acyclic olefins due to high strain energy [1]. For example, cyclopropenes having no acceptor substituent at the double bond are readily involved in cycloaddition reactions with 1,3-dipoles and conjugated dienes [2], while analogous processes are not typical of nonactivated acyclic olefins. The strained three-membered ring in bicyclic adducts thus formed is capable of undergoing easy cleavage [3]. Therefore, cyclopropene derivatives may be regarded as synthons for introduction of a three-membered carbon fragment into cyclic molecules. In the present work we took advantage of this property of cyclopropene compounds to develop a new three-step procedure for the synthesis of substituted pyridazine-4-carboxylates (Scheme 1).

Each particular step of the proposed procedure, i.e., cycloaddition of diazomethane at the cyclopropene double bond [4, 5, 6], isomerization of substituted 2,3-diazabicyclo[3.1.0]hex-2-enes into 1,4-dihydropyridazine derivatives [7, 8], and oxidation of the latter to substituted pyridazines [9], has already been reported in the literature; however, the overall scheme of transition from 2-cyclopropenecarboxylates to pyridazine-4-carboxylates has not been implemented previously.

As initial compounds we used 2,3-disubstituted 2-cyclopropenecarboxylic acids **I**–**III** which are available through carbene reaction of alkyl diazoacetate with the corresponding disubstituted acetylene [10]. The cycloaddition of diazomethane to compounds **I**–**III** occurs at a fairly low rate. In the presence of more than twofold excess of diazomethane, the process takes no less than 15 days in diethyl ether at 0 to –10°C. The progress of the reaction was monitored by TLC. In the reaction with 2,3-dimethyl-2-cyclopropenecarboxylic acid (**I**, R = R' = Me), the only product was diazabicyclohexene **IV**; from cyclopropene **II** (R = R' = Ph) we obtained two stereoisomeric diazabicyclohexenes **Va** and **Vb** at a ratio of 4:1; and unsymmetrically substituted cyclopropene **III** (R = Me, R' = Ph) gave rise to three isomeric diazabicyclohexenes: two stereoisomers **VIa** and **VIb** and regioisomer **VII** at a ratio of

Scheme 1.



I–III

I, R = R' = Me; **II**, R = R' = Ph; **III**, R = Me, R' = Ph.

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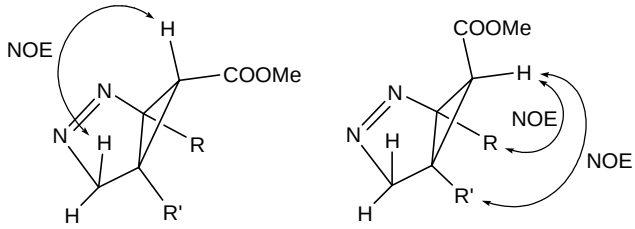
10:1:1. In all cases, the cycloaddition of diazomethane to cyclopropenes **I**–**III** was characterized by *exo*-stereoselectivity which decreased upon replacement of methyl substituents by phenyl groups. The regioselectivity observed in the addition of diazomethane to unsymmetrically substituted cyclopropene **III** is 11:1 in favor of the Auwers adduct.

The assumed diazabicyclohexene structure of compounds **IV**, **Va**, **Vb**, **VIa**, **VIb**, and **VII** satisfactorily agrees with their ^{1}H and ^{13}C NMR spectra (Table 1). In the ^{1}H NMR spectra of these compounds we observed a characteristic two-proton signal at δ 5.0 ppm (*AB* system, CH_2); the ^{13}C NMR spectra contained four signals from carbon atoms of the diazabicyclohexene skeleton, two of which were displaced to the region δ_C 80–90 ppm due to effect of the neighboring azo group. The configuration of C^6 was established using 2D NOESY technique. The 6-H proton in **IV**, **Va**, **VIa**, and **VII** showed NOE with *endo*-4-H (but not with phenyl or methyl protons). By contrast, the corresponding proton in **Vb** and **VIb** showed NOE with protons of the phenyl and methyl groups but not with 4-H. It should be noted that compound **Va** was properly assigned in [4] the *exo* configuration without experimental substantiation. A specific feature of stereoisomers **Va**/**Vb** and **VIa**/**Vb** is difference between the chemical shifts of 6-H: In the spectra of *exo* isomers **Va** and **VIa**, the 6-H signal is displaced upfield by more than 1.2 ppm relative to the position



IV, **Va**, **VIa**, **VII** **Vb**, **VIb**

IV, R = R' = Me; **Va**, **Vb**, R = R' = Ph; **VIa**, **VIb**, R = Ph, R' = Me; **VII**, R = Me, R' = Ph.

of the corresponding signal in the spectra of *endo* isomers **Vb** and **VIb**.

The difference between regioisomers **VIa** and **VII** is seen most clearly by comparing their ^{13}C NMR spectra: In the spectrum of **VII**, the C^1 signal is located 6.2 ppm upfield, while the C^5 signal, 8.2 ppm downfield. This pattern is consistent with the positions of the corresponding signals in the ^{13}C NMR spectra of compounds **IV** and **Va**. The difference in the chemical shifts of the methyl protons in the ^{1}H NMR spectra of regioisomeric adducts **VIa** and **VII** also conforms to the above assignment: in the spectrum of **VII**, the methyl proton signal appears 0.45 ppm downfield due to effect of the neighboring azo group.

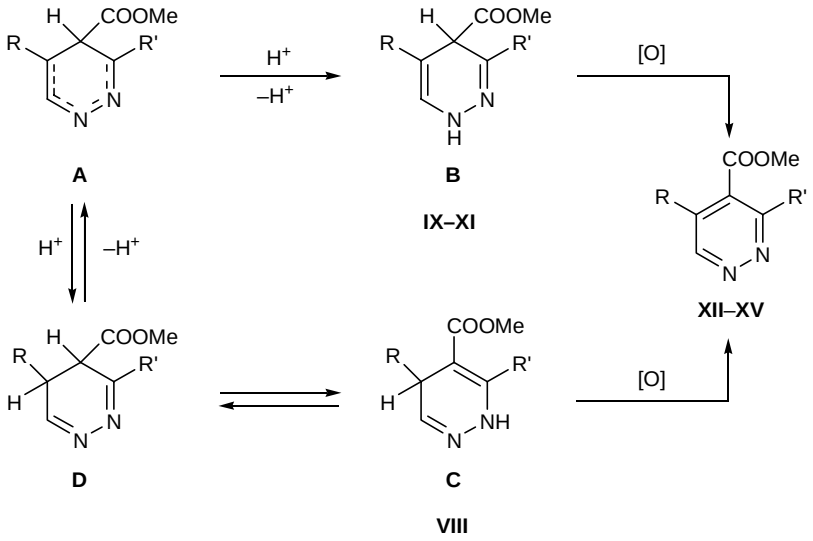
The isomerization of diazabicyclohexenes **IV**–**VII** into substituted 1,4-dihydropyridazines was effected by the action of sodium methoxide in methanol. In all

Table 1. ^{1}H and ^{13}C NMR spectra of 2,3-diazabicyclohexenes **IV**, **Va**, **Vb**, **VIa**, **VIb**, and **VII**

Comp. no.	^{1}H NMR spectrum, δ, ppm					^{13}C NMR spectrum, δ_C, ppm							
	4-H[a]	6-H	CH_3	OCH_3	Ph	C^1	C^4	C^5	C^6	CH_3	OCH_3	C=O	Ph
IV	4.57	0.92 s	1.38 s, 1.92 s	3.69 s	–	78.8	87.5	32.1	35.0	8.2, 8.8	51.5	168.7	–
Va	5.09	1.71 s	–	3.53 s	7.19–7.27 (2H), 7.32–7.43 (6H), 7.58–7.67 (2H)	84.3	91.2	42.4	38.0	–	51.6	166.9	127.5, 127.8 (2C), 128.0, 128.2 (2C), 129.9 (2C), 130.0 (2C), 130.5, 132.1
Vb	5.27	3.23 s	–	3.71 s	7.05–7.11 (2H), 7.20–7.35 (8H)	85.1	84.7	44.6	31.1	–	51.9	166.6	127.0 (2C), 127.6, 128.0, 128.3 (2C), 128.5 (2C), 128.6 (2C), 132.3, 134.9
VIa	4.80	1.36 s	1.62 s	3.63 s	7.43 br.s	85.3	88.1	32.9	36.5	10.6	51.6	167.8	128.5 (2C), 128.7, 130.1, 130.3 (2C)
VIb	4.92	2.58 s	1.19 s	3.66 s	7.30–7.39 (2H), 7.39–7.50 (3H)	85.5	82.1	34.6	30.9	15.7	51.7	167.1	128.5 (2C), 128.6, 128.7 (2C), 132.2
VII	4.84	1.33 s	2.07 s	3.63 s	7.03–7.09 (2H), 7.30–7.36 (3H)	79.1	89.8	41.1	35.6	9.9	51.7	167.9	127.7, 128.6 (2C), 129.4 (2C), 133.1

[a] The position of the center of the *AB* quartet is given, J_{AB} = 19.5 Hz (in all cases); $\Delta\delta_{AB}$ = 33, 42, 162, 15, 189, and 60 Hz for compounds **IV**, **Va**, **Vb**, **VIa**, **VIb**, and **VII**, respectively.

Scheme 2.



VIII, **XII,** R = R' = Me; **IX**, **XIII**, R = R' = Ph; **X**, **XIV**, R = Ph, R' = Me; **XI**, **XV**, R = Ph, R' = Me.

cases, the reaction was fast and selective, and the products were formed in high yields. In keeping with published data [7, 8], we believe that the process involves formation of anionic intermediate **A** whose protonation yields substituted 1,4-dihydropyridazine. The latter may be presumed to have structure **B** (as a result of protonation of anion **A** at the nitrogen atom) or **C** (as a result of tautomeric transformation of 4,5-dihydropyridazine **D** arising from protonation of anion **A** at the carbon atom) (Scheme 2).

Analysis of the ^{1}H and ^{13}C NMR spectra of 1,4-dihydropyridazines **VIII**–**XI** (Table 2) showed that only isomerization of diazabicyclohexene **IV** leads to formation of structure **C**. In all other cases, isomer **B** is formed. The **C** structure of compound **VIII** follows from the presence in the ^{1}H NMR spectrum of a doublet signal (J = 7 Hz) from protons of one methyl group. The spectrum of **X** contained a singlet from the methyl protons, indicating that this compound has structure **B**. Structure **B** of **IX**–**XI** is also confirmed by the presence of a one-proton singlet from 4-H. The other spectral parameters of compounds **VIII**–**XI** do not contradict the assumed structures. We believe that the isomerization of diazabicyclohexenes **IV**–**VII** by

Table 2. ^{1}H and ^{13}C NMR spectra of 1,4-dihydropyridazines **VIII**–**XI**

Comp. no.	^{1}H NMR spectrum, δ, ppm (J, Hz)						^{13}C NMR spectrum, δ_C, ppm					
	4-H	6-H	CH_3	OCH_3	NH	Ph	C^4	C^5	CH_3	OCH_3	C=O	Ph, C^3, C^6
VIII	3.33 d.q (4.8, 7.1)	6.77 d [a] (4.8)	0.94 d (7.1), 2.23 s	3.68 s	7.80 br.s	–	27.3	94.9	17.7, 18.1	50.6	167.6	143.6, 147.0
IX	5.08 s	7.14 d (4.2)	–	3.69 s	8.11 br.s	7.23–7.30 (1H), 7.35–7.49 (5H), 7.51–7.57 (2H), 7.92–7.98 (2H)	41.4	103.1	–	52.4	171.2	124.4 (2C), 124.6, 126.0 (2C), 126.2, 128.3 (2C), 128.5 (2C), 128.7, 135.4, 136.0, 136.7
X	4.40 s	6.47 br.s	1.87 s	3.70 s	[b]	7.32–7.42 (3H), 7.72–7.80 (2H)	44.4	101.4	18.2	52.3	170.9	123.4, 125.4 (2C), 128.2 (2C), 128.9, 134.3, 136.5
XI	4.36 s	7.06 br.s	2.17 s	3.73 s	[b]	7.18–7.25 (1H), 7.32–7.37 (4H)	45.1	102.1	22.4	52.4	170.4	124.0 (2C), 124.9, 126.0, 128.5 (2C), 136.8, 137.9

[a] 3-H.

[b] No NH signal was observed in the spectrum recorded in $CDCl_3$; in DMSO-d_6, a one-proton broadened singlet appeared at δ 9.60 ppm in both cases.

Table 3. ^{1}H and ^{13}C NMR spectra of pyridazine-4-carboxylates **XII**–**XV**

Comp. no.	^{1}H NMR spectrum, δ, ppm				^{13}C NMR spectrum, δ_C, ppm					
	6-H	CH_3	OCH_3	Ph	C^3	C^6	CH_3	OCH_3	C=O	Ph, C^4, C^5
XII	8.95 s	2.30 s, 2.66 s	3.94 s	–	155.1	151.7	16.3, 20.4	52.5	166.3	131.0, 133.8
XIII	9.31 s	–	3.59 s	7.43–7.58 (8H), 7.68–7.78 (2H)	157.0	150.1	–	52.5	166.5	128.0 (2C), 128.4 (2C), 128.45 (2C), 128.5, 129.0 (2C), 129.55, 129.6, 133.8, 136.1, 136.7
XIV	9.12 s	2.41 s	3.71 s	7.42–7.51 (3H), 7.65–7.72 (2H)	156.6	151.8	16.3	52.6	166.7	128.3 (2C), 128.5 (2C), 129.4, 130.9, 134.5, 136.3
XV	9.18 s	2.79 s	3.75 s	7.37–7.45 (2H), 7.45–7.55 (3H)	155.5	149.8	20.3	52.6	166.6	127.9 (2C), 129.0 (2C), 129.6, 129.8, 134.0, 136.0

the action of sodium methoxide is a thermodynamically controlled process. In the case of dimethyl-substituted diazabicyclohexene **IV**, structure **C** of the isomerization product is thermodynamically more favorable, as compared to **B**, for the ester group in the former is attached to sp^2-carbon atom and hence is conjugated with the endocyclic double bond. By contrast, diazabicyclohexenes **VIa** and **VIb** give rise to structure **B**, 1,4-dihydropiridazine **X**; in this case, structure **B** becomes thermodynamically more favorable due to stabilizing effect of the phenyl group in the imine fragment. Alternative structure **C** with the same substitution pattern should be destabilized for steric reasons (conjugation in the *cis*-cinnamate fragment is hindered). Structure **B** is also more favorable for isomerization products **IX** and **XI** (obtained from diazabicyclohexenes **Va**, **Vb**, **VIa**, and **VIb**), for it ensures conjugation between the phenyl substituent and endocyclic double bond; in the respective structure **C**, the phenyl group is forced out of conjugation with the dihydropyridazine ring.

1,4-Dihydropyridazines **VIII**–**XI** were oxidized with potassium permanganate in acetone. As a result, the corresponding pyridazine-4-carboxylates **XII**–**XV** were obtained in high yields. Their structure is convincingly confirmed by the ^{1}H and ^{13}C NMR spectra (Table 3). Pyridazines **XII**–**XV** characteristically showed in the ^{1}H NMR spectra a singlet from the 6-H proton at δ 9.0 ppm. Regioisomeric compounds **XIV** and **XV** can be distinguished by the position of the methyl group signals in the ^{1}H and ^{13}C NMR spectra: in the spectra of 3-methylpyridazine **XV**, these signals are displaced downfield by 0.38 and 4.0 ppm, respectively, relative to the corresponding signals of 5-methylpyridazine **XIV** (cf. [11]). Analogous differences in the positions of the methyl group signals were observed for compounds **X** and **XI** which are precursors of **XIV** and **XV**.

We conclude that the proposed three-step procedure for the synthesis of substituted pyridazine-4-carboxylates via cycloaddition of diazomethane to 2,3-disubstituted 2-cyclopropenecarboxylic acids is advantageous due to high yield in each step and accessibility of initial cyclopropene derivatives. Unfortunately, the first step in the procedure takes a long time, and it seems improbable to eliminate this drawback.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C) using $CDCl_3$ as solvent. 2D NOESY experiments were performed using the same instrument. The elemental compositions were determined on an HP-185B CHN-analyzer. Analytical thin-layer chromatography was performed on Silufol UV-254 plates. The products were separated and purified by column chromatography on silica gel L 40/100 μm (Chemapol). 2,3-Disubstituted 2-cyclopropenecarboxylic acids **I** [12], **II** [13], and **III** [14] were synthesized by known methods. A solution of diazomethane in ether was distilled prior to use.

Methyl 1,5-dimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene-*exo*-6-carboxylate (IV). To a solution of 0.56 g (5 mmol) of acid **I** in 10 ml of diethyl ether we added at 0°C 52 ml of a 0.58 M solution of diazomethane (30 mmol) in diethyl ether, and the mixture was kept for 14 days at 0°C in the dark. The solvent was removed under reduced pressure, and the residue was recrystallized from hexane. Yield 0.75 g (89%),

mp 31°C, R_f 0.25 (hexane–diethyl ether, 1:1). Found, %: C 57.07; H 7.18; N 16.58. $C_8H_{12}N_2O_2$. Calculated, %: C 57.13; H 7.19; N 16.66. The ^{1}H NMR spectrum of the residue obtained by evaporation of the mother liquor contained no signals assignable to the *endo* isomer of **IV**, which indicated strict *exo*-stereoselectivity of the cycloaddition of diazomethane to 2,3-dimethyl-2-cyclopropenecarboxylic acid (**I**).

Reaction of diazomethane with 2,3-diphenyl-2-cyclopropenecarboxylic acid (II). To a suspension of 0.95 g (4 mmol) of acid **II** in 25 ml of diethyl ether we added at 0°C 50 ml of a 0.55 M solution of diazomethane (27.5 mmol) in diethyl ether. The resulting solution was kept for 20 days at –10°C in the dark. The solvent was removed under reduced pressure to obtain 1.21 g of a substance which, according to the ^{1}H NMR data, was a mixture of compounds **Va** and **Vb** at a ratio of ~4:1. Crystallization from 15 ml of hexane–diethyl ether (1:1) (after prolonged cooling at –20°C) gave 0.86 g (73%) of methyl 1,5-diphenyl-2,3-diazabicyclo-[3.1.0]hex-2-ene-*exo*-6-carboxylate (**Va**), mp 121°C [4], R_f 0.29 (hexane–diethyl ether, 1:1). The mother liquor was evaporated under reduced pressure, and the viscous oily residue, 0.32 g, was dissolved in warm hexane. The solution was cooled, and a portion of crystals (a mixture of compounds **Va** and **Vb**) was separated. The solvent was removed from the mother liquor to obtain 0.17 g (14%) of methyl 1,5-diphenyl-2,3-diazabicyclo[3.1.0]hex-2-ene-*endo*-6-carboxylate (**Vb**) as a light yellow viscous oily substance, R_f 0.28. According to the ^{1}H NMR data, product **Vb** contained ~15% of *exo* isomer **Va**. Found, %: C 72.62; H 5.53; N 9.48. $C_{18}H_{16}N_2O_2$. Calculated, %: C 73.95; H 5.52; N 9.58.

Reaction of diazomethane with 2-methyl-3-phenyl-2-cyclopropenecarboxylic acid (III). To a suspension of 0.8 g (4.6 mmol) of acid **III** in 15 ml of diethyl ether we added 52 ml of a 0.55 M solution of diazomethane (28.6 mmol) in diethyl ether. The mixture was kept for 15 days at –10°C in the dark. The solvent was removed under reduced pressure to obtain 1.03 g of a colorless solid which, according to the ^{1}H NMR data, was a mixture of compounds **VIa**, **VIb**, and **VII** at a ratio of 10:1:1. This mixture was dissolved in 10 ml of hexane–diethyl ether (1:1), the solution was kept for 3 h at –20°C, and the precipitate was filtered off. We thus isolated 0.72 g (68%) of methyl 5-methyl-1-phenyl-2,3-diazabicyclo[3.1.0]hex-2-ene-*exo*-6-carboxylate (**VIa**). mp 107°C. Found, %: C 67.99; H 6.17; N 12.17. $C_{13}H_{14}N_2O_2$. Calculated, %: C 67.81; H 6.13; N 12.17. Removal of the solvent from the filtrate gave 0.31 g of a substance which contained compounds **VIa**, **VIb**, and **VII** (according to the ^{1}H NMR data). It was subjected to column chromatography on silica gel. We isolated (in the order of elution) 59 mg (5.6%) of compound **VII**, R_f 0.28 (hexane–diethyl ether, 1:1); an additional portion of **VIa**, 73 mg (6.9%), R_f 0.20; and compound **VIb**, 64 mg (6.1%), R_f 0.18.

Methyl 1-methyl-5-phenyl-2,3-diazabicyclo-[3.1.0]hex-2-ene-*exo*-6-carboxylate (VII). mp 65°C. Found, %: C 67.56; H 6.26; N 11.94. $C_{13}H_{14}N_2O_2$. Calculated, %: C 67.81; H 6.13; N 12.17.

Methyl 5-methyl-1-phenyl-2,3-diazabicyclo-[3.1.0]hex-2-ene-*endo*-6-carboxylate (VIb). mp 62°C. Found, %: C 67.79; H 6.11; N 12.13. $C_{13}H_{14}N_2O_2$. Calculated, %: C 67.81; H 6.13; N 12.17.

Isomerization of diazabicyclohexenes IV–VII to 1,4-dihydropyridazines VIII–XI (*general procedure*). To a solution of 1.0 mmol of diazabicyclohexene **IV–VII** in 3 ml of methanol we added 1 ml of a 0.2 M solution of sodium methoxide (0.2 mmol) in methanol. The mixture was stirred for 5 min at 20°C, diluted with 40 ml of diethyl ether, washed with water, dried over magnesium sulfate, and evaporated under reduced pressure.

Methyl 4,6-dimethyl-1,4-dihydropyridazine-5-carboxylate (VIII) was obtained from diazabicyclohexene **IV**. Colorless oily substance, yield 84%, R_f 0.13 (hexane–diethyl ether, 1:1). Found, %: C 56.81; H 7.38; N 16.38. $C_8H_{12}N_2O_2$. Calculated, %: C 57.13; H 7.19; N 16.65.

Methyl 3,5-diphenyl-1,4-dihydropyridazine-4-carboxylate (IX) was obtained from diazabicyclohexene **Va**. Yield 96%, mp 110–111°C; published data [4]: mp 106–109°C; R_f 0.21 (hexane–diethyl ether, 1:1). Found, %: C 73.90; H 5.52; N 9.32. $C_{18}H_{16}N_2O_2$. Calculated, %: C 75.95; H 5.52; N 9.58. The same product was formed by isomerization of compound **Vb** (according to the TLC data).

Methyl 5-methyl-3-phenyl-1,4-dihydropyridazine-4-carboxylate (X) was obtained from diazabicyclohexene **VIa**. Colorless oily substance, yield 91%, R_f 0.23 (hexane–diethyl ether, 1:1). Found, %: C 67.57; H 6.38; N 12.01. $C_{13}H_{14}N_2O_2$. Calculated, %: C 67.81; H 6.13; N 12.17. The same product was formed by isomerization of compound **VIb** (according to the TLC data).

Methyl 3-methyl-5-phenyl-1,4-dihydropyridazine-4-carboxylate (XI) was obtained from diazabicyclohexene **VII**. Colorless oily substance, yield 78%, R_f 0.20 (hexane–diethyl ether, 1:2). Found, %: C 67.49; H 6.40; N 11.96. $C_{13}H_{14}N_2O_2$. Calculated, %: C 67.81; H 6.13; N 12.17.

Oxidation of 1,4-dihydropyridazines VIII–XI (*general procedure*). To a solution of 1 mmol of 1,4-dihydropyridazine **VIII–XI** in 5 ml of acetone we added a solution of 0.17 g (1.1 mmol) $KMnO_4$ in 2 ml of water. The mixture was stirred for 0.5 h and filtered, the filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel.

Methyl 3,5-dimethylpyridazine-4-carboxylate (XII) was obtained from 1,4-dihydropyridazine **VIII**. Yield 77%, mp 43–44°C, R_f 0.11 (hexane–diethyl ether, 1:3). Found, %: C 57.71; H 6.06; N 16.54. $C_8H_{10}N_2O_2$. Calculated, %: C 57.81; H 6.07; N 16.86.

Methyl 3,5-diphenylpyridazine-4-carboxylate (XIII) was obtained from 1,4-dihydropyridazine **IX**. Yield 95%, mp 124–125°C, R_f 0.22 (hexane–diethyl ether, 1:2). Found, %: C 74.18; H 4.92; N 9.36. $C_{18}H_{14}N_2O_2$. Calculated, %: C 74.47; H 4.86; N 9.65.

Methyl 5-methyl-3-phenylpyridazine-4-carboxylate (XIV) was obtained from 1,4-dihydropyridazine **X**. Yield 86%, mp 47–48°C, R_f 0.15 (hexane–diethyl ether, 1:2). Found, %: C 68.56; H 5.39; N 12.16. $C_{13}H_{12}N_2O_2$. Calculated, %: C 68.40; H 5.30; N 12.28.

Methyl 3-methyl-5-phenylpyridazine-4-carboxylate (XV) was obtained from 1,4-dihydropyridazine **XI**. Yield 74%, mp 60–61°C, R_f 0.17 (hexane–diethyl ether, 1:2). Found, %: C 68.38; H 5.34; N 12.21. $C_{13}H_{12}N_2O_2$. Calculated, %: C 68.40; H 5.30; N 12.28.

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