Reactions of alkyl diazoacetates with pyridinium ylides[a,b]

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Pyridinium (methoxycarbonyl)methylide generated from (methoxycarbonyl)methylpyridinium halides under the action of K_2CO_3 reacts with alkyl diazoacetates in CH_2Cl_2 at 20 °C, resulting in the successive addition of three CHCOOMe fragments from the ylide to form 3,6-bis(alkoxycarbonyl)-4,5-diazaoctadienoic acid diesters. Heating of the latter in the presence of pyridine leads to their isomerization to give tetraalkyl tetrahydropyridazinetetracarboxylates in high yields. Under more drastic conditions (refluxing xylene in the presence of pyridine), the acyclic tetraesters undergo another transformation to form pyrroletetracarboxylic acid esters in yields of up to 60%.

Key words: alkyl diazoacetates, tetrahydropyridazines, pyridinium ylides, tetra(methoxycarbonyl)pyrrole, functionalized diazadienes and azines.

Earlier,[2] we have found that carbenic decomposition of methyl diazoacetate in refluxing pyridine affords tetramethyl tetrahydropyridazine-3,4,5,6-tetracarboxylate as a mixture of two isomers, whereas the corresponding reaction in refluxing xylene in the presence of pyridine gives rise to tetramethyl pyrroletetracarboxylate. A preliminary study of the mechanism of formation of these compounds demonstrated that the possible pathway of formation of heterocyclic structures can involve the intermediate generation of pyridinium ylides and their reactions with diazo compounds. To validate this assumption, it seemed worthwhile to study the reactions of alkyl diazoacetates with pyridinium ylides generated from other sources. In particular, quaternary pyridinium salts from haloacetic acid esters are convenient precursors of such ylides.[3]

We found that the reaction of (methoxycarbonyl)methylpyridinium iodide (**1**) with K_2CO_3 and methyl diazoacetate in refluxing $CHCl_3$ as well as in pyridine, DMSO, or acetonitrile at 25 °C actually produced tetramethyl tetrahydropyridazine-3,4,5,6-tetracarboxylate (**2**), the latter being formed as a mixture of the same two isomers as those obtained by carbenic decomposition of methyl diazoacetate in refluxing pyridine.[2] The addition of water to the reaction mixture after completion of the reaction followed by extraction with methylene chloride resulted in an increase in the yield of the target compound **2** compared to that achieved by direct extraction of the solid residue, which was obtained after evaporation of the solvents, with ethyl acetate. The yields of tetrahydropyridazines **2** depending on the reaction conditions are given in Table 1. The yields were quantitatively estimated from the ^{1}H NMR spectra of the reaction mixtures and the amounts of the products isolated by column chromatography on silica gel.

Table 1. Yields of 2,3,4,5-tetrahydropyridazine-3,4,5,6-tetracarboxylic acid esters depending on the reaction conditions

Solvent	T/°C	τ/h	Yield (%)
$CHCl_3$	60	7	42
MeCN	25	14	65
Pyridine	22	14	48
DMSO	22	14	37
C_6H_6	80	150	0

Neither salt **1** nor K_2CO_3 are dissolved in benzene, which, apparently, hinders the reaction, whereas prolonged stirring and refluxing leads to resinification of the reaction mixture.

The use of milder conditions (for example, the reaction performed at 20 °C in CH_2Cl_2) allows the identification of a series of intermediates, which are isomeric to tetrahydropyridazines **2** and have (unlike compounds **2**) acyclic structures. The ^{1}H NMR spectrum of the reaction mixture shows signals of two isomeric tetrahydropyridazines **2** along with two sets of signals corresponding to azine **3** and diazadiene **4**. After 5—6 h, the **2** : **3** : **4** ratio was ~1 : 2 : 2, while this ratio changed to ~8 : 1 : 2 after 14 h. Although we can only hypothesize how the formation of azine molecule **3** occurs, it is evident that

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[b] For preliminary communication, see Ref. 1.

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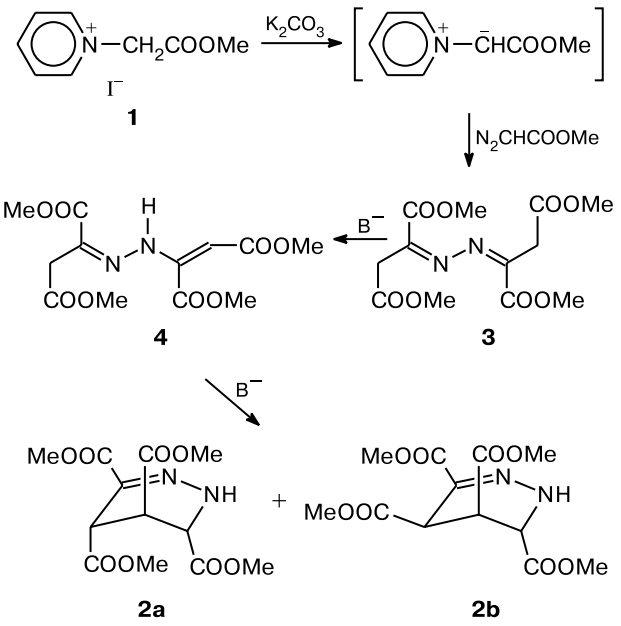
these structures along with diazadiene **4** precede the formation of tetrahydropyridazine derivatives **2**. Actually, heating of diazadiene **4**, which has been isolated in pure form, in pyridine afforded the same two isomeric tetrahydropyridazines **2a,b** in high yield (Scheme 1).

Scheme 1

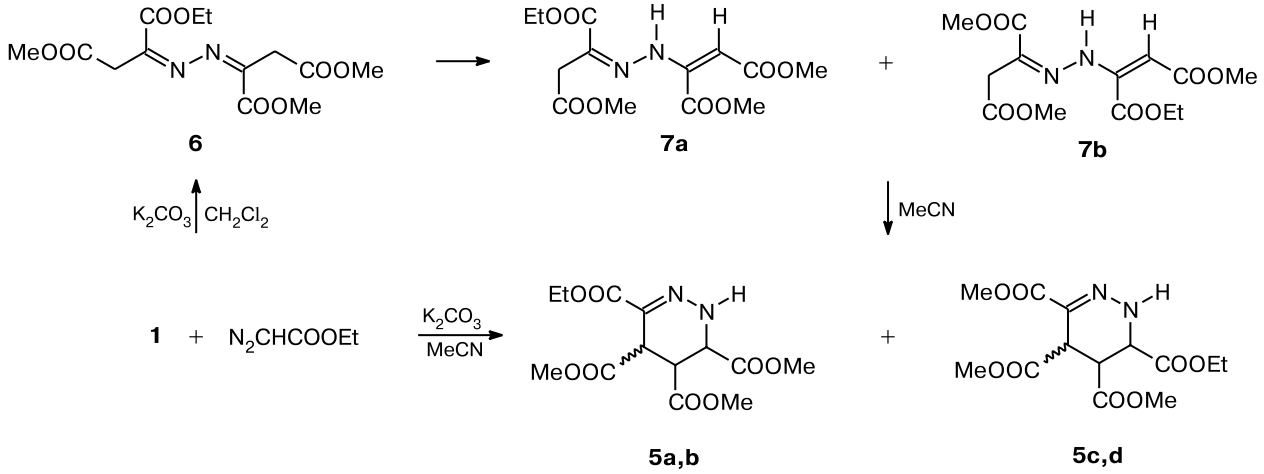


It should be noted that the rearrangement of azine **3** to diazadiene **4** and cyclization of the latter to yield tetrahydropyridazine **2** are accelerated both in the presence of bases and at high temperature. With the aim of increasing the yields of acyclic structures **3** and **4**, we found conditions under which isomerization of azine **3** to diazadiene **4** stopped in the step of formation of diazadiene without subsequent cyclization of the latter to give tetrahydropyridazine. It appeared that the reaction in CH_2Cl_2 at 20 °C in the presence of a small amount of water produced a mixture of azine **3** and diazadiene **4** (~1 : 2.3) in a total yield of up to 60% without an impurity of tetrahydropyridazines **2**. Chromatographic separation of the isomers allowed us to isolate pure diazadiene **4** and azine **3** containing 6—8% of compound **4**.

Azines containing no electron-withdrawing substituents (for example, those formed from aldehydes or ketones and hydrazine) undergo cyclization under the action of alkylating agents and acids to give the corresponding 2-pyrazolines.[4] In the case of azine **3**, the presence of the methoxycarbonyl substituents facilitates the proton abstraction from the methylene fragment, thus promoting the successive transformation of **3** into diazadiene **4** and then into tetrahydropyridazine **2**.

To reveal which starting compounds containing ester groups are involved in the formation of diazadienes **3** and **4** and then of tetrahydropyridazine **2**, we studied the reaction of (methoxycarbonyl)methylpyridinium iodide (**1**) with K_2CO_3 and ethyl diazoacetate in MeCN (25 °C, 14 h), which allowed us to draw a conclusion about the origin of the COOMe and COOEt groups based on the numbers of these groups in the reaction product. As in the case of tetramethyl ester **2**, column chromatography of the reaction mixture on SiO_2 gave two closely-spaced chromatographic bands, each being a mixture of two isomers. Therefore, unlike the reactions of tetramethyl esters **2**, the reaction of ethyl diazoacetate with the ylide generated from compound **1** and K_2CO_3 produced four isomeric tetrahydropyridazines **5a—d** (Scheme 2) in an approximately equimolar ratio (a total yield of 52%). Mass spectrometry and ^{1}H NMR spectroscopy provided evidence that each isomeric tetrahydropyridazine **5a—d** contains only one ethoxycarbonyl group. This result unam-

Scheme 2



biguously indicates that three ylide molecules and only one diazo ester molecule are involved in the reaction.

The same reaction performed in CH_2Cl_2 at 20 °C produced acyclic diazadienes (a total yield of 52—57%) as a mixture (^{1}H NMR spectroscopic data) of unsymmetrical azine **6** and two isomeric diazadienes **7a** and **7b** (see Scheme 2). The latter were formed in an approximately equimolar ratio as a result of proton elimination from a particular methylene group of azine **6** and are virtually unseparable by chromatography on SiO_2. As expected by analogy with tetramethyl ester **3**, azine **6** is slowly isomerized under the reaction conditions in the presence of K_2CO_3 to give diazadienes **7a,b**, which prevents its predominant formation and makes its isolation in pure form difficult.

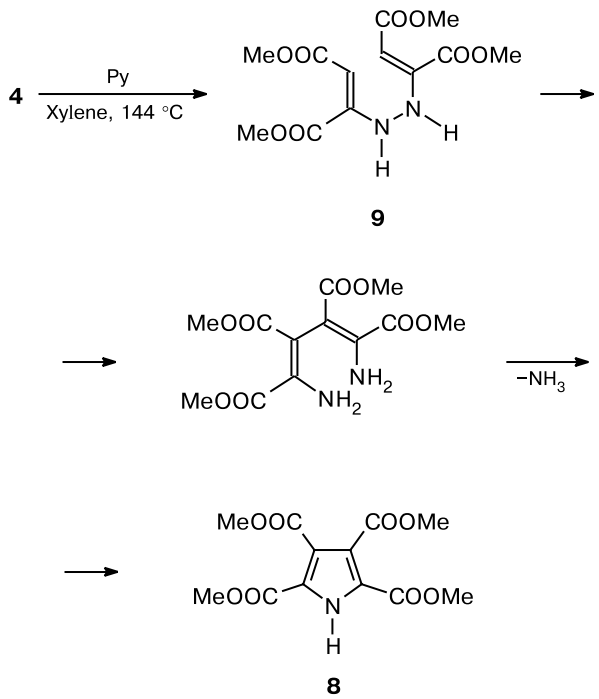
The structures of all the compounds synthesized were established by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of azine **3** shows two signals of the OMe groups and one signal of the CH_2 group. The integral intensity ratio of these signals (3 : 3 : 2) suggests that the molecule of azine **3** is symmetrical and contains two pairs of equivalent ester groups. Isomerization of azine **3** to diazadiene **4** results in violation of the molecular symmetry and the nonequivalence of the ester groups. Although the ^{1}H NMR spectrum in $CDCl_3$ shows only three signals in the region of OMe groups (δ 3.70, 3.78, and 3.87), their integral intensity ratio (1 : 1 : 2) indicates that two methoxycarbonyl groups have equal chemical shifts. Analysis of the ^{1}H and ^{13}C NMR spectra of diazadiene **4** unambiguously indicates that this compound is an individual isomer rather than a mixture of the *E* and *Z* isomers, the low-field position of the signal for the olefinic proton (δ 5.17) being most consistent with an isomer with the cisoid arrangement of the ester groups.

The ^{1}H and ^{13}C NMR spectra of compounds **6** and **7**, which have a signal of one ethoxy fragment instead of a signal of one of the OMe groups, are similar to the spectra of the corresponding tetramethyl esters **3** and **4**. Since the COOEt fragment can originate only from diazo ester, this group in the resulting diazadienes is, evidently, present at the C atom directly bound to the N atom, which limits the number of possible isomers. Actually, the ^{1}H and ^{13}C NMR spectra of azine **6** show that this compound in $CDCl_3$ exists as one isomer, for which the chemical shifts of the protons of two nonequivalent methylene fragments differ by only 0.02 ppm. Diazadienes **7a,b** are characterized by the formation of two isomers possessing very similar properties, which is manifested in their ^{1}H and ^{13}C NMR spectra (see the Experimental section).

Analysis of the NMR spectra of tetrahydropyridazines **5** was complicated due to formation of four isomers, which were separated only in pairs with different degrees of enrichment. Each pair of isomers is characterized by slightly different shifts of the analogous signals and virtually equal multiplicities of these signals, which indicates that these isomers have similar heterocyclic structures and stereochemistry of the substituents (Table 2). The unambiguous assignment of the signals was made using the double-resonance technique (in particular, spin-spin decoupling of the proton of the NH group) and {C,H} correlations. In our opinion, the observed differences in the pairs of isomers are associated with the position (3 or 6) of the heterocycle occupied by the only ethoxycarbonyl group (isomers **5a,c** and **5b,d**). The most substantial differences in both the physicochemical properties and the NMR spectra are, apparently, attributed to the stereochemistry of the substituent at the C(4) atom. This interpretation of the results agrees well with the earlier data[2] for tetramethyl esters **2a,b** (see Table 2).

We also found that diazadiene **4** is formed as an intermediate in the synthesis of tetramethyl pyrroletetracarboxylate (**8**).[2] Direct heating of ylide **1**, methyl diazoacetate, and K_2CO_3 in xylene (unlike heating in polar solvents) afforded unidentifiable resinous products, whereas refluxing of diazadiene **4**, isolated in pure form, in xylene gave rise to pyrroletetracarboxylate **8** (Scheme 3). This reaction is sensitive to bases. In pure xylene (after 8 h), the ratio of the starting diazadiene **4** to cyclization product **8** was ~20 : 1, whereas the complete conversion of diazadiene **4** in the presence of pyridine (5—10 vol. % with respect to xylene) was achieved within 4 h, and the yield of pyrroletetracarboxylate **8** was as high as 92%.

Scheme 3



Therefore, the direction of cyclization of diazadiene **4** depends substantially on the reaction conditions. In polar

Table 2. ^{1}H and ^{13}C NMR spectra of tetrahydropyridazinetetracarboxylates ($CDCl_3$)

Compound	δ (*J*/Hz)														
	H(4)	H(5)	H(6)	OMe (s)	OCH_2	Me (t)	NH	C(3)	C(4)	C(5)	C(6)	OMe	OCH_2	Me	COO
2a [2]	4.36 (t, $J_{4,5} \approx J_{4,6}$ = = 1.8)	3.74 (dt, $J_{5,6}$ = 3.6, $J_{4,5} \approx J_{1,5}$ = = 1.8)	4.12 (dt, $J_{5,6}$ = 3.6, $J_{4,6} \approx J_{1,6}$ = = 1.8)	3.68, 3.76, 3.84, 3.85	—	—	7.21	126.3	39.4	37.8	51.5	52.9, 53.0, 52.3, 52.8	—	—	164.5, 168.6, 168.9, 170.9
2b	4.18 (dd, ($J_{4,5}$ = 2.6, $J_{4,6}$ = 1.7)	3.86 (ddd, $J_{5,6}$ = 3.2, $J_{4,5}$ = 2.6, $J_{1,5}$ = 1.6)	4.50 (dt, $J_{5,6}$ = 3.2, $J_{4,6} \approx J_{1,6}$ = = 1.5)	3.69, 3.72, 3.76, 3.83	—	—	7.16	128.1	37.3	38.7	52.9	52.3, 52.8, 53.0, 53.2	—	—	164.5, 169.5, 170.2, 170.4
5a	4.36 (t, $J_{4,5} \approx J_{4,6}$ = = 1.7)	3.75 (dt, $J_{5,6}$ = 4.0, $J_{4,5} \approx J_{1,5}$ = = 1.8)	4.09 (dt, $J_{5,6}$ = 4.0, $J_{4,6} \approx J_{1,6}$ = = 1.6)	3.67, 3.78, 3.85	4.30, 4.34 (both dq, ^2J = 10.7, ^3J = 7.1)	1.32 (^3J = = 7.1)	7.21	126.4	39.6	37.8	51.6	52.8, 53.1, 52.4	62.2	14.1	164.6, 168.1, 169.0, 171.1
5b	4.16 (dd, $J_{4,5}$ = 2.6, $J_{4,6}$ = 1.6)	3.81 (ddd, $J_{5,6}$ = 3.4, $J_{4,5}$ = 2.6, $J_{1,5}$ = 1.5)	4.47 (dt, $J_{5,6}$ = 3.4, $J_{4,6} \approx J_{1,6}$ = = 1.6)	3.69, 3.72, 3.76	4.29, 4.31 (both dq, ^2J = 10.7, ^3J = 7.0)	1.35 (^3J = = 7.0)	7.06	128.7	37.4	38.9	52.8	52.8, 53.1, 53.2	61.4	14.2	164.0, 169.5, 170.3, 170.5
5c	4.37 (t, $J_{4,5} \approx J_{4,6}$ = = 1.7)	3.74 (dt, $J_{5,6} \approx$ 4.0, $J_{4,5} \approx J_{1,5}$ = = 1.7)	4.11 (dt, $J_{5,6} \approx$ 4.0, $J_{4,6} \approx J_{1,6}$ = = 1.6)	3.68, 3.77, 3.85	4.31 (q, ^3J = 7.1)	1.35 (^3J = = 7.1)	7.19	126.9	39.3	38.0	51.6	52.9, 53.0, 52.5	61.4	14.3	164.1, 168.7, 169.1, 171.1
5d	4.19 (dd, $J_{4,5}$ = 2.6, $J_{4,6}$ = 1.6)	3.80 (m)	4.45 (dt, $J_{5,6}$ = 3.5, $J_{4,6} \approx J_{1,6}$ = = 1.7)	3.69, 3.76, 3.83	4.16, 4.18 (both dq, ^2J = 10.7, ^3J = 7.1)	1.35 (^3J = = 7.1)	7.05	128.3	37.5	38.8	52.4	52.9, 53.0, 53.1	62.5	13.9	164.5, 170.2, 170.4, 171.2

solvents in the presence of bases, the easy deprotonation of diazadiene **4** (in the presence of electron-withdrawing substituents) and cyclization of the resulting anion to give the six-membered heterocycle occur. In less polar solvents (for example, in xylene) and at high temperature, isomerization of diazadiene **4** to disubstituted hydrazine **9** is, apparently, the main process, and compound **9**, by analogy with the formation of indoles,[5] undergoes cyclization to give pyrrole derivative **8** with elimination of NH_3.

The above-described procedure provides a route to diazadienes and tetrahydropyridazines containing a large number of electron-withdrawing substituents, which cannot be synthesized according to procedures described in the literature.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-300 (300.13 and 75.5 MHz) and Bruker DRX-500 (500.13 MHz) spectrometers in $CDCl_3$ containing 0.05% of Me_4Si as the internal standard. The mass spectra were obtained on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct inlet). Chemically pure solvents and freshly distilled pyridine were used in reactions. Column chromatography was carried out on silica gel 60 (0.040—0.063 mm; Merck). (Methoxycarbonyl)methylpyridinium iodide (**1**) was synthesized according to a procedure described earlier.[6] Methyl and ethyl diazoacetates were prepared by diazotization of hydrochlorides of the corresponding aminoacetic acid esters.[7]

3,4,5,6-Tetra(methoxycarbonyl)-1,4,5,6-tetrahydropyridazine (2). ***A.*** A mixture of pyridinium iodide **1** (17.9 g, 64 mmol), methyl diazoacetate (1.6 g, 16 mmol), and K_2CO_3 (22.0 g, 0.16 mol) in acetonitrile (100 mL) was stirred at 25 °C for 14 h. The reaction mixture was concentrated *in vacuo*, treated with H_2O (200 mL), and extracted with methylene chloride (3×50 mL). The organic fractions were combined and dried with anhydrous $MgSO_4$, and the solvent was removed *in vacuo*. The residue was eluted with ethyl acetate through a layer of silica gel (~10 cm). After removal of the solvent, tetrahydropyridazines **2** were obtained in a yield of 3.25 g (65%) as a mixture of two isomers (~1 : 1) identical to those prepared earlier[2] (^{1}H and ^{13}C NMR spectroscopic data are given in Table 2).

B. A mixture of pyridinium iodide **1** (17.9 g, 64 mmol), methyl diazoacetate (1.6 g, 16 mmol), and K_2CO_3 (22.0 g, 0.16 mol) in $CHCl_3$ (100 mL) was refluxed with stirring for 6 h. The precipitate that formed was filtered off and the solvent was removed *in vacuo*. The brightly colored residue was dissolved in ethyl acetate, filtered off from the precipitate, concentrated *in vacuo*, passed through a layer of silica gel (~10 cm), and washed with AcOEt (50 mL). After removal of the solvent *in vacuo*, a mixture of the same two isomers of tetrahydropyridazine **2** (~1 : 1) was obtained in a yield of 2.10 g (42%).

C. The synthesis was carried out analogously to the method ***A*** using the same amounts of the reagents in pyridine (80 mL) at 25 °C for 14 h to prepare a mixture of two isomers of tetrahydropyridazine **2** (~1 : 1) in a yield of 2.40 g (48%).

D. The synthesis was carried out analogously to the method ***A*** with the use of DMSO (80 mL) as the solvent (25 °C, 48 h). After treatment of the reaction mixture, a mixture of two isomers of tetrahydropyridazine **2** (~1 : 1) was obtained in a yield of 1.71 g (37%).

Dimethyl 3,6-bis(methoxycarbonyl)-4,5-diazaocta-3,5-diene-1,8-dioate (3) and dimethyl 3,6-bis(methoxycarbonyl)-4,5-diazaocta-2,5-diene-1,8-dioate (4). Water (2—5 mL) was added to a mixture of pyridinium iodide **1** (17.9 g, 64 mmol), methyl diazoacetate (1.60 g, 16 mmol), and K_2CO_3 (22.0 g, 0.16 mol) in CH_2Cl_2 (100 mL), and the reaction mixture was stirred at 20 °C for 8 h. The precipitate that formed was filtered off and the solvent was removed *in vacuo*. The resinous residue was treated with AcOEt without heating. The mixture was filtered, the filtrate was passed through a small layer of silica gel, and the solution was concentrated *in vacuo* without heating. A viscous pale-yellow liquid was obtained in a yield of 3.05 g (~60%). The ^{1}H NMR spectrum showed that the mixture contained compounds **3** and **4** in a ratio of 1 : 2.3. Column chromatography on silica gel (benzene—AcOEt, 1 : 1, as the eluent) afforded pure diazadiene **4** and azine **3** containing 6—8% of compound **4**.

Compound **4**, colorless liquid. Found (%): C, 45.16; H, 4.93; N, 8.94. $C_{12}H_{16}N_2O_8$. Calculated (%): C, 45.57; H, 5.10; N, 8.86. ^{1}H NMR ($CDCl_3$), δ: 3.49 (s, 2 H, CH_2); 3.70 and 3.78 (both s, 3 H each, 2 OMe); 3.87 (s, 6 H, 2 OMe); 5.17 (s, 1 H, =CH); 13.82 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 39.3 (CH_2); 51.7, 52.1, 52.6, and 52.8 (4 OMe); 91.8 (=CH); 129.2 (=C); 149.2 (C=N); 161.7, 163.6, 168.2, and 170.1 (CO). Partial mass spectrum, m/z (I_{rel} (%)): 316 $[M]^+$ (55), 285 (25), 257 (35), 225 (40).

Compound **3** (contains 6—8% of compound **4**), colorless liquid. ^{1}H NMR ($CDCl_3$), δ: 3.62 (s, 4 H, 2 CH_2); 3.69 and 3.91 (both s, 6 H each, 2 OMe). ^{13}C NMR ($CDCl_3$), δ: 34.3 (CH_2); 52.5 and 53.9 (OMe); 145.7 (C=N); 163.0 and 167.9 (CO).

Dimethyl 6(3)-ethoxycarbonyl-3(6)-methoxycarbonyl-4,5-diazaocta-2,5-diene-1,8-dioate (7a,b). The synthesis was carried out analogously to the synthesis of diazadienes **3** and **4**. A mixture of isomeric diazadienes **6**, **7a**, and **7b** was prepared in a yield of 0.73 g (55%) in a ratio of ~0.4 : 1 : 1 from pyridinium iodide **1** (5.30 g, 19 mmol), ethyl diazoacetate (0.46 g, 4 mmol), and K_2CO_3 (5.52 g, 40 mmol) followed by filtration through a small layer of SiO_2 and removal of the solvents. Azine **6** was identified only by spectroscopy. ^{1}H NMR ($CDCl_3$), δ: 1.38 (t, Me, J = 7.1 Hz); 3.60 and 3.62 (both s, 2 CH_2); 3.68 (s, 2 OMe); 3.91 (s, OMe); 4.36 (q, OCH_2, J = 7.1 Hz). Column chromatography on SiO_2 (benzene—AcOEt, 1 : 1, as the eluent) afforded 4,5-diazaocta-2,5-diene-1,8-dioic acid esters **7a,b** as a mixture of isomers. Found (%): C, 46.92; H, 4.98; N, 8.84. $C_{13}H_{18}N_2O_8$. Calculated (%): C, 47.27; H, 5.49; N, 8.48. ^{1}H NMR ($CDCl_3$), δ, isomer **7a**: 1.33 (t, Me, J = 7.1 Hz); 3.48 (s, CH_2); 3.70, 3.77, and 3.86 (all s, 3 OMe); 4.33 (q, OCH_2, J = 7.1 Hz); 5.18 (s, =CH); 13.80 (s, NH); isomer **7b**: 1.30 (t, Me, J = 7.1 Hz); 3.48 (s, CH_2); 3.69, 3.76, and 3.86 (all s, 3 OMe); 4.34 (q, OCH_2, J = 7.1 Hz); 5.17 (s, =CH); 13.80 (s, NH). ^{13}C NMR ($CDCl_3$), δ, isomer **7a**: 14.05 (Me); 39.26 (CH_2); 51.74, 52.14 и 52.68 (3 OMe); 62.19 (OCH_2); 91.69 (=CH); 129.17 (C=N); 149.56 (=C); 161.80, 163.28, 168.30, and 170.23 (4 COO); isomer **7b**: 14.05 (Me); 39.51 (CH_2); 51.74, 52.15, and 52.87 (3 OMe); 61.86 (OCH_2); 91.68 (=CH); 129.70 (C=N); 149.36 (=C); 161.48, 163.81, 168.03 и 170.23 (4 COO).

Trimethoxycarbonyl(ethoxycarbonyl)-1,4,5,6-tetrahydropyridazines (5). A mixture of pyridinium iodide **1** (3.61 g, 13 mmol), ethyl diazoacetate (0.4 g, 3.5 mmol), and K_2CO_3 (4.83 g, 35 mmol) in MeCN (20 mL) was stirred at 20 °C for 14 h. The precipitate that formed was filtered off and the solvent was removed *in vacuo*. The resinous residue was treated with AcOEt, filtered from the precipitate, and passed through a small layer of silica gel. After removal of the solvents, tetrahydropyridazines **5** were obtained in a yield of 0.52 g (51%) as a mixture of four isomers (~1 : 1 : 1 : 1). Column chromatography on SiO_2 (benzene—AcOEt, 1.5 : 1, as the eluent) afforded two main fractions containing esters **5a** and **5c** in a ratio of 1 : 1.1, esters **5b** and **5d** in a ratio of 1 : 1.4, and two small fractions enriched in isomers **5a** and **5b** (**5a** : **5c** = 5.5 : 1, **5b** : **5d** = 7 : 1). Samples of the two major fractions were characterized by elemental analysis. Found (%): C, 47.01 (47.07); H, 5.28 (5.24); N, 8.64 (8.66). $C_{13}H_{18}N_2O_8$. Calculated (%): C, 47.27; H, 5.49; N, 8.48. The ^{1}H and ^{13}C NMR spectroscopic data are given in Table 2.

2,3,4,5-Tetra(methoxycarbonyl)pyrrole (8). A solution of diazadiene **4** (70 mg, 0.22 mmol) in a mixture of *o*-xylene (3 mL) and pyridine (0.2 mL) was refluxed for 4 h. Then the solvents were removed *in vacuo*. The residue was treated with AcOEt, filtered through a layer of silica gel (~2 cm), and washed additionally with AcOEt (5 mL). The solvent was removed *in vacuo*. Pyrroletetracarboxylate **8** was obtained in a yield of 61 mg (92%). Product **8** was identical to the sample prepared earlier.[2]

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