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# Rearrangements of *N*-Ethoxycarbonylmethyl-1,2,3,4-tetrahydroquinolinium Halogenalkylates Effected by Sodium Hydride. Synthesis of 2,3,4,5-Tetrahydro-1*H*-3-benzazepines

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**Abstract**—Quaternary salts obtained from *N*-alkyl-1,2,3,4-tetrahydroisoquinolines and ethyl haloacetates or diethyl bromomalonate under the action of sodium hydride in boiling 1,4-dioxane were converted into *N*-alkyl-*N*-ethoxycarbonyl-2,3,4,5-tetrahydro-1*H*-3-benzazepines in 49–60% yield. From the reaction mixture by column chromatography products of β-elimination by Hofmann reaction, 2-(*N*-methyl-*N*-ethoxycarbonylmethyl)-aminomethylstyrenes were also isolated (yield 0.6–16%).

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We reported in [1] on rearrangements of N-ylides generated from 1-methyl-4-aryl-1-ethoxycarbonylmethyl-1,2,3,6-tetrahydropyridinium halides. It was established that these anhydrobases at boiling in aprotic solvents underwent recyclization forming 3-aryl-3-vinyl-1-methyl-2-ethoxycarbonylpyrrolidones and/or 2-alkoxycarbonyl-1-methyl-5-aryl-2,3,6,7-tetrahydro-1*H*-azepines. Both at the contraction of initial heterocycle (as a result of [2,3]-sigmatropic rearrangement) and its expansion (due to [1,2]-shift by Stevens rearrangement) the reaction center was the allylamine fragment in the N-ylide. Inasmuch as the quaternary salts of C-unsubstituted tetrahydropyridines suffered only the [2,3]-sigmatropic rearrangement [2] and the introduction of an aryl substituent to $C^4$ position provided a possibility of the [1,2]-shift [1], we decided to investigate the direction of molecular rearrangements in quaternary salts of 1,2,3,4-tetrahydroisoquinolinium.

Only two papers were published on this subject [3, 4]. In [3] it was reported that *N*-(4-nitrobenzyl)-6-hydroxy-1,2,3,4-tetrahydroisoquinolinium bromomethylate under the action of potassium *tert*-butylate in butanol rearranged into tetrahydrobenzazepine, and its 6-methoxy analog suffered Hofmann elimination. On this grounds it was concluded that the benzazepine did not form by Stevens rearrangement but the reaction proceeded through an intermediate quinone methide arising by the cleavage of the allylamine fragment at the C–N bond. In [4] it was stated that an analogous salt, *N*-[(trimethylsilyl)-methyl]tetrahydroisoquinolinium iodomethylate, could in the absence of bases (under the action of cesium fluoride) convert into a tetrahydroazepine system when in the position *1* of the initial salt a phenyl substituent was present.

In the present study we performed quaternization of *N*-methyl- or *N*-ethyl-1,2,3,4-tetrahydroisoquinolines with α-halo derivatives of ethyl acetate at room temperature in ethyl acetate to obtain in high yields (85–98%) quaternary salts **Ia, Ib** and **Va, Vb**. At the use of the 2-bromomalonic acid ester the yield of salt **IX** was considerably lower (to 60%). Further reaction of salts **I, V**, and **IX** with sodium hydride in the boiling 1,4-dioxane under argon atmosphere led to the formation of tetrahydrobenzazepines **II, VI**, and **X** and of aminomethylstyrenes **IV** and **VIII**. The products were isolated by chromatography with the yields 49–60 and 0.6–16% respectively (Scheme 1).

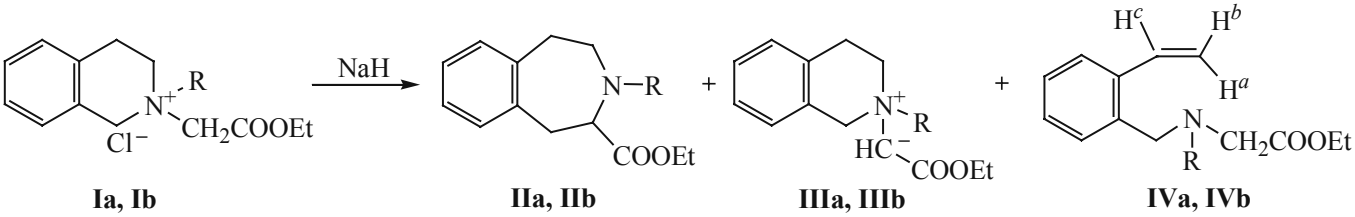
In the mass spectra (LCMS) also the formation was detected of intermediate N-ylides **III** and **VII** that subsequently transformed into the rearrangement products **II** and **VI** and in the products of Hofmann elimination **IV** and **VIII**. In going to 6,7-dimethoxy-

substituted isoquinolinium bromides **Va** and **Vb** the yield of the products of Hofmann elimination sharply decreased. The substitution for two deuterium atoms of two protons attached to $C^4$ did not affect the yields of the rearranged products **VIb** and **VIIIb**. $^1$H NMR and mass spectra of partially deuterated compounds **VIb** and **VIIIb** indicate that in benzazepine **VIb,** the product of [1,2]-shift by Stevens mechanism, both deuterium atoms remained in the previous position at (Scheme 2).

At the same time in the course of formation of the product of Hofmann elimination **VIIIb** one deuterium atom relocated to C-ylide atom (Scheme 3). This is confirmed by $^1$H NMR spectrum where two protons $H^a$ and $H^b$ of the vinyl group $Ar(D)C{=}CH_2^{a,b}$ appeared at 5.15 and 5.65 ppm as two narrow doublets (1H each) with the geminal coupling constant $^2J$ 1.2 Hz, and the methine proton of the =NCH(D)C=O group gave rise to a narrow singlet (1H) at 3.71 ppm (a similar methine proton in the spectrum of benzazepine **VIb** was observed in the region 3.53 ppm as a one-proton doublet of doublets). In the mass spectrum (LCMS) of the elimination product **VIIIb** a peak of molecular ion $[M + 1]^+$ of mass 296 appeared indicating that its structure contained two deuterium atoms. These data suggest that the elimination occurred here through an intramolecular transfer of one axial deuterium atom.

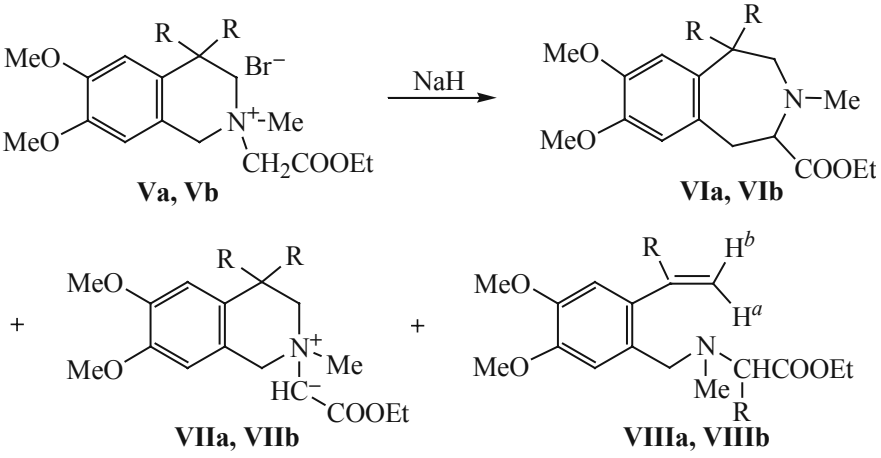
We established by the study of the behavior of the quaternary salt **IX** obtained by quaternization with bromomalonic ester that the existence of steric hindrances to the Stevens rearrangement did not hamper

**Scheme 1.**



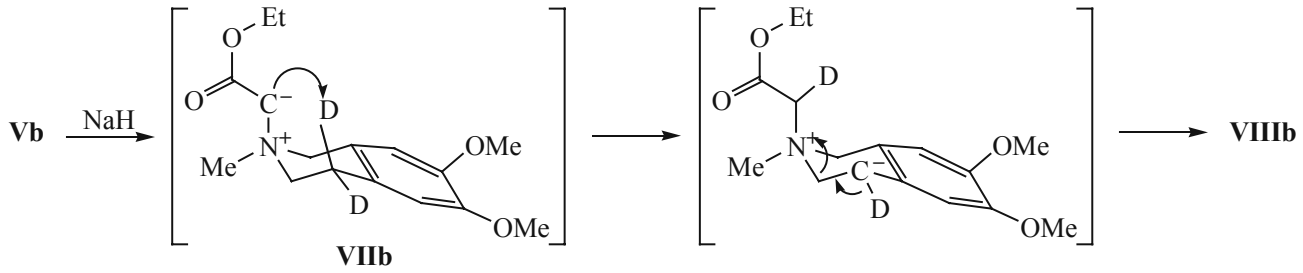

R = Me (**a**), Et (**b**).

**Scheme 2.**

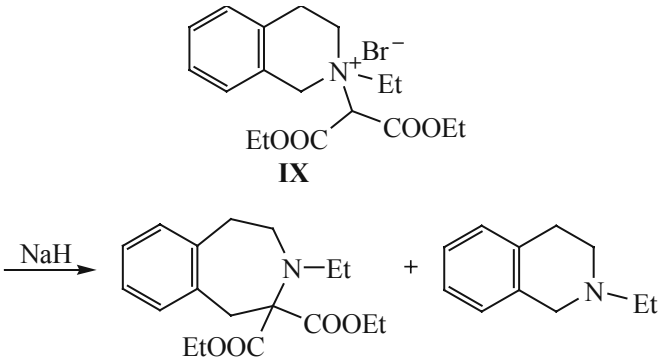



R = H (**a**), D (**b**).

**Scheme 3.**



**Scheme 4.**




the formation of the tetrahydrobenzazepine ring (Scheme 4). In this case tetrahydrobenzazepine **X** was isolated in 60% yield.

At the same time the expected β-elimination side product of the type **IV** or **VIII** was not detected even by the LCMS method apparently because of the easy cleavage of the large substituent at nitrogen resulting in the fast formation of the initial base, 2-ethyltetrahydroisoquinoline, isolated in 30% yield.

## EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord 75IR from pellets with KBr or mulls in mineral oil. $^1$H NMR spectra were registered on spectrometers Varian DPX-300 (operating frequency 300 MHz) and Bruker WM-400 (operating frequency 400 MHz) from solutions in DMSO-$d_6$ (compounds **Ia, Ib, Va, Vb**, and **IX**) and in $CDCl_3$ (compounds **IIa, IIb, IVa, IVb, VIa, VIb, VIIIa, VIIIb**, and **X**). the designation of vinyl group protons in styrenes **IVa, IVb** and **VIIIa, VIIIb** are given on the schemes of reactions of their syntheses. Electron-impact mass spectra were obtained on a chromato-mass-spectrometer Finnigan MAT 95XL, ionizing electrons energy 70 eV. Mass spectra in the LCMS mode (ionization with $H^+$) were taken on a chromato-mass-spectrometer PE SCIEX API 165(150) (Shimadzu HPLC SCL10Avp, autosampler Gilson 215, ELSD Sedex 75). The preparative column chromatography was performed on silica gel L60 (40/100). The reaction progress was monitored and the purity of compounds synthesized was checked by TLC on Silufol UV-254 plates. Initial *N*-methyl- and *N*-ethyl-1,2,3,4-tetrahydroisoquinolines were preaped by N-alkylation of commercial 1,2,3,4-tetrahydroisoquinoline (Aldrich). *N*-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline and 4,4-dideutero-*N*-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline were obtained from the corresponding 3,4-dimethoxyphenylacetonitriles as described in [5].

**Quaternary salts Ia, Ib, Va, Vb**, **and IX.** *General procedure.* A solution of 100 mmol of *N*-alkyl-1,2,3,4-tetrahydroisoquinoline and 120 mmol of an ester of haloacetic or bromomalonic acid in 50 ml of anhydrous ethyl acetate was maintained for 5–12 h at 20°C. The reaction mixture was filtered, the isolated precipitate was washed with ethyl acetate. The reaction product was obtained in the form of colorless crystals.

**2-Methyl-2-(2-ethoxy-2-oxoethyl)-1,2,3,4-tetrahydroisoquinolinium chloride (Ia).** Yield 2.42 g (90%), mp 165–167°C. IR spectrum, ν, cm$^{-1}$: 1748 (C=O). $^1$H NMR spectrum, δ, ppm: 1.23 t (3H, $CH_2CH_3$, $J$ 7.3 Hz), 3.36 s (3H, $NCH_3$), 3.44 s (2H, $NCH_2CO$), 3.99 m (2H, $H^4$), 4.22 q (2H, $CH_2CH_3$, $^3J$ 7.3 Hz), 4.65 m (2H, $H^3$), 4.80 d, 4.87 d (1H each, $H^1$, $^2J$ 15.0 Hz), 7.05–7.55 m ($4H_{arom}$). Found, %: C 62.30; H 7.45; Cl 13.10; N 5.16. $C_{14}H_{20}ClNO_2$. Calculated, %: C 62.33; H 7.47; Cl 13.14; N 5.19.

**2-Ethyl-2-(2-ethoxy-2-oxoethyl)-1,2,3,4-tetrahydroisoquinolinium chloride (Ib).** Yield 2.46 g (87%), mp 178–180°C. IR spectrum, ν, cm$^{-1}$: 1740 (C=O). $^1$H NMR spectrum, δ, ppm: 1.15 t (3H, $NCH_2CH_3$, $^3J$ 7.1 Hz), 1.25 t (3H, $OCH_2CH_3$, $^3J$ 7.0 Hz), 3.40 s (2H, $NCH_2CO$), 3.86–4.20 m (4H, $H^4$, $NCH_2CH_3$), 4.22 q (2H, $OCH_2CH_3$, $^3J$ 7.00 Hz), 4.49 m (2H, $H^3$), 4.90 d, 4.95 d (пО 1H, $H^1$, $^2J$ 15.0 Hz), 7.07–7.44 m ($4H_{arom}$). Found, %: C 63.35; H 7.89; Cl 12.45; N 4.93. $C_{15}H_{22}ClNO_2$. Calculated, %: C 63.48; H 7.81; Cl 12.49; N 4.94.

**2-Methyl-6,7-dimethoxy-2-(2-ethoxy-2-oxoethyl)-1,2,3,4-tetrahydroisoquinolinium bromide (Va).** Yield 3.67 g (98%), mp 163–165°C. IR spectrum, ν, cm$^{-1}$: 1738 (C=O). $^1$H NMR spectrum, δ, ppm: 1.25 t (3H, $OCH_2CH_3$, $^3J$ 7.0Hz ), 3.10 br.s (2H, $H^4$), 3.29 s (3H, $NCH_3$), 3.73 s, 3.76 s (3H each, $OCH_3$), 3.88 m (2H, $H^3$), 4.25 q (2H, $OCH_2CH_3$, $^3J$ 7.0 Hz), 4.53 d, 4.57 d (1H each, $H^1$, $^2J$ 16.4 Hz), 4.70 d, 4.78 d (пО 1H, $NCH_2CO$, $^2J$ 16.8 Hz), 6.80 C, 6.90 C (пО 1H, $H^{5,8}$). Found, %: C 51.19; H 6.50; Br 21.29; N 3.75. $C_{16}H_{24}BrNO_4$. Calculated, %: C 51.35; H 6.46; Br 21.35; N 3.74.

**4,4-Dideutero-2-methyl-6,7-dimethoxy-2-(2-ethoxy-2-oxoethyl)-1,2,3,4-tetrahydroisoquinolinium bromide (Vb).** Yield 3.2 g (85%), mp 162–164°C. IR spectrum, ν, cm$^{-1}$: 1738 (C=O). $^1$H NMR spectrum, δ, ppm: 1.25 t (3H, $OCH_2CH_3$, $^3J$ 7.0 Hz), 3.29 s (3H, $NCH_3$), 3.73 s, 3.76 s (3H each, $OCH_3$), 3.86 d, 3.92 d

(1H each, $H^3$, $^2J$ 12.1 Hz), 4.25 q (2H, $OCH_2CH_3$, $^3J$ 7.0 Hz), 4.53 d, 4.57 d (1H each, $H^1$, $^2J$ 16.4 Hz), 4.70 d, 4.78 d (1H each, $NCH_2CO$, $^2J$ 16.8 Hz), 6.80 s, 6.90 s (1H each, $H^{5,8}$). Found, %: Br 21.25; N 3.71. $C_{16}H_{22}BrD_2NO_4$. Calculated, %: Br 21.23; N 3.72.

**2-Ethyl-2-[di(ethoxycarbonyl)methyl]-1,2,3,4-tetrahydroisoquinolinium bromide (IX).** Yield 2.6 g (65%), mp 177–179°C. IR spectrum, ν, $cm^{-1}$: 1743 br (C=O). $^1H$ NMR spectrum, δ, ppm: 1.30 t (6H, $OCH_2CH_3$, $^3J$ 7.2 Hz), 1.51 t (3H, $NCH_2CH_3$, $^3J$ 7.1 Hz), 3.25 m (2H, $H^4$), 3.84 m (4H, $H^3$ and $NCH_2CH_3$), 4.38 m (4H, $OCH_2CH_3$), 4.90 d, 4.94 d (1H each, $H^1$, $^2J$ 16.8 Hz), 6.07 s (1H, CHCOO), 7.08–7.27 m ($4H_{arom}$). Found, %: C 54.0; H 6.52; Br 19.94; N 3.2. $C_{18}H_{26}BrNO_4$. Calculated, %: C 54.01; H 6.55; Br 19.96; N 3.5.

**Benzazepines IIa, IIb, VIa, VIb, and X and aminomethylstyrenes IVa, IVb and VIIIa, VIIIb.** *General procedure.* To a dispersion of 1 mmol of tetrahydroisoquinolinium quaternary salts **Ia, Ib, Va, Vb**, and **IX** in 30 ml of anhydrous dioxane was added at 20°C 0.28 g (1.2 mmol) of sodium hydride under an argon atmosphere. The mixture was boiled for 7 h, then the reaction mixture was cooled, excess NaH was decomposed by ethanol, and the solvents were removed in a vacuum. The residue was treated with water, the organic compounds were extracted into $CH_2Cl_2$. The extract was twice washed with water, dried by anhydrous $MgSO_4$, and the solvent was evaporated in a vacuum. The oily residue was subjected to column chromatography on silica gel. At elution with hexane–ethyl acetate, 10:1, were isolated aminomethylstyrenes **IVa, IVb** and **VIIIa, VIIIb**; at elution with hexane–ethyl acetate, 2:1, were isolated benzazepines **IIa, IIb, VIa, VIb,** and **X**.

**3-Methyl-2-ethoxycarbonyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine (IIa).** Yield 0.11 g (49%), colorless thick oily substance. IR spectrum, ν, $cm^{-1}$: 1730 (C=O). $^1H$ NMR spectrum, δ, ppm: 1.40 t (3H, $CH_2CH_3$, *J* 7.2 Hz), 2.50 s (3H, $NCH_3$), 2.67 m (1H, $H^4$), 2.91–3.05 m (2H, $H^1$), 3.17 m (2H, $H^5$), 3.26 t (1H, $H^4$, *J* 14.1 Hz), 3.47 d.d (1H, $H^2$, *J* 7.0, 3.4 Hz), 4.08 q (2H, $CH_2CH_3$, *J* 7.2 Hz), 7.05–7.18 m (4H, $H^C$ and $H_{arom}$). Mass spectrum, *m/z* ($I_{rel}$, %): 233 $[M]^+$ (3), 218 (4), 146 (100), 144 (100), 144 (7), 131 (5), 115 (4), 94 (3). Found, %: C 72.00; H 8.18; N 6.0. $C_{14}H_{19}NO_2$. Calculated, %: C 72.07; H 8.21; N 6.0.

**2-Methyl-1,2,3,4-tetrahydroisoquinolinium 2-ethoxycarbonylmethylide (IIIa).** Characterized by chromato-mass-spectrometry. Yield 13%. Mass spectrum, *m/z* ($I_{rel}$, %): 233 (3) $[M]^+$, 160 (100), 158 (3), 145 (7), 117 (9), 91 (4).

**Ethyl N-(2-vinylbenzyl)-N-methylglycinate (IVa).** Yield 0.03 g (16%), thick oily substance. IR spectrum, ν, $cm^{-1}$: 1740 (C=O). $^1H$ NMR spectrum, δ, ppm: 1.30 t (3H, $OCH_2CH_3$, $^3J$ 7.1 Hz), 2.40 s (3H, $NCH_3$), 3.30 s (2H, $NCH_2Ar$), 3.75 m (2H, $NCH_2CO$), 4.20 q (2H, $OCH_2CH_3$, $^3J$ 7.1 Hz), 5.32 d.d (1H, $H^b$, $^2J$ 1.0, $^3J$ 11.0 Hz), 5.68 d.d (1H, $H^a$, $^2J$ 1.0, $^3J$ 15.0 Hz), 7.20–7.70 m (4H, $H^C$ and $H_{arom}$), 7.56 d.d ($1H_{arom}$, *J* 7.6 1.1 Hz). Mass spectrum, *m/z* ($I_{rel}$, %): 233 (19) $[M]^+$, 218 (2), 204 (3), 160 (74), 146 (4), 117 (100), 116 (10), 115 (25), 91 (9). Found, %: C 72.04; H 8.19; N 5.96. $C_{14}H_{19}NO_2$. Calculated, %: C 72.07; H 8.21; N 6.0.

**3-Ethyl-2-ethoxycarbonyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine (IIb).** Yield 0.13 g (55%), thick oily substance. IR spectrum, ν, $cm^{-1}$: 1730 (C=O). $^1H$ NMR spectrum, δ, ppm: 1.19 t (3H, $NCH_2CH_3$, $^3J$ 7.00 Hz), 1.24 t (3H, $OCH_2CH_3$, $^3J$ 7.2 Hz), 2.66–2.98 m (4H, $H^1$ and $H^5$), 3.11 t (1H, $H^4$, *J* 13.5 Hz), 3.22–3.37 m (4H, $H^4$ and $NCH_2CH_3$), 3.81 d.d (1H, $H^2$, *J* 6.8, 7.2 Hz), 4.04 q (2H, $OCH_2CH_3$, $^3J$ 7.2 Hz), 7.03–7.26 m ($4H_{arom}$). Mass spectrum, *m/z* ($I_{rel}$, %): 247 (3) $[M]^+$, 174 (100), 145 (7), 117 (8), 115 (6). Found, %: C 72.79; H 8.54; N 5.62. $C_{15}H_{21}NO_2$. Calculated, %: C 72.84; H 8.56; N 5.66.

**2-Ethyl-1,2,3,4-tetrahydroisoquinolinium 2-ethoxycarbonylmethylide (IIIb).** Characterized by chromato-mass-spectrometry. Yield 14%. Mass spectrum, *m/z* ($I_{rel}$, %): 247 (2) $[M]^+$, 218 (5), 160 (100), 158 (4), 130 (4).

**Ethyl N-(2-vinylbenzyl)-N-ethylglycinate (IVb).** Yield 0.03 g (14%), yellowish thick oily substance. IR spectrum, ν, $cm^{-1}$: 1740 (C=O). $^1H$ NMR spectrum, δ, ppm: 1.18 t (3H, $NCH_2CH_3$, $^3J$ 7.1 Hz), 1.24 t (3H, $OCH_2CH_3$, $^3J$ 7.2 Hz), 3.30 s (3H, $ArCH_2N$), 3.38 q (2H, $NCH_2CH_3$, $^3J$ 7.1 Hz), 3.60 s (2H, $NCH_2CO$), 4.06 q (2H, $OCH_2CH_3$, $^3J$ 7.2 Hz), 5.28 d.d (1H, $H^b$, $^2J$ 1.0, $^3J$ 10.9 Hz), 5.72 d.d (1H, $H^a$, $^2J$ 1.0, $^3J$ 14.8 Hz), 7.15–7.30 m (4H, $H^C$ and $H_{arom}$), 7.58 d ($1H_{arom}$, *J* 7.2 Hz). Mass spectrum, *m/z* ($I_{rel}$, %): 247 (35) $[M]^+$, 218 (5), 174 (100), 117 (95), 115 (28), 91 (10). Found, %: C 72.80; H 8.53; N 5.64. $C_{15}H_{21}NO_2$. Calculated, %: C 72.84; H 8.56; N 5.66.

**3-Methyl-7,8-dimethoxy-2-ethoxycarbonyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine (VIa).** Yield 0.16 g (56%), yellow thick oily substance. IR spectrum, ν, $cm^{-1}$: 1727 (C=O). $^1H$ NMR spectrum, δ, ppm: 1.16 t (3H, $OCH_2CH_3$, $^3J$ 7.1 Hz), 2.40 s (3H, $NCH_3$), 3.10–3.16 m (4H, $H^1$ and $H^5$), 3.24 m (2H, $H^4$), 3.51 d.d (1H, $H^2$, *J* 6.9 and 3.2 Hz), 3.70 s (3H, $OCH_3$), 3.75 m (3H,

$OCH_3$), 3.90 q (2H, $OCH_2CH_3$, $^3J$ 7.1 Hz), 6.48 s, 6.62 s (1H each, $H^6$ and $H^9$). Mass spectrum, *m/z*: 294 [$M$ + 1]$^+$. Found, %: C 65.49; H 7.87; N 4.75. $C_{16}H_{23}NO_4$. Calculated, %: C 65.51; H 7.90; N 4.77.

**2-Methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium 2-ethoxycarbonylmethylide (VIIa).** Characterized by chromato-mass-spectrometry. Yield 12%. Mass spectrum, *m/z* ($I_{rel}$, %): 294 [$M$ + 1]$^+$.

**Ethyl *N*-(2-vinyl-4,5-dimethoxybenzyl)-*N*-methylglycinate (VIIIa).** Yield 0.007 g (0.6%), thick oily substance. IR spectrum, ν, cm$^{-1}$: 1737 (C=O). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (3H, $CH_2CH_3$, $^3J$ 7.2 Hz), 2.42 s (3H, $NCH_3$), 3.25 s (2H, $NCH_2Ar$), 3.70 s (2H, $NCH_2CO$), 3.90 s, 3.94 s (3H each, $OCH_3$), 4.21 q (2H, $OCH_2$, $^3J$ 7.2 Hz), 5.23 d.d (1H, $H^b$, $^2J$ 1.2, $^3J$ 11.0 Hz), 5.58 d.d (1H, $H^a$, $J$ 1.2 and 15.0 Hz), 6.9 d.d, 7.06 d.d (1H each, $H^{3,6}$, $^5J$ 0.8 Hz), 7.17 q (1H, $H^C$, $J$ 15.0 and 11.0 Hz). Mass spectrum, *m/z*: 294 [$M$ + 1]$^+$. Found, %: C 65.49; H 7.89; N 4.75. $C_{16}H_{23}NO_4$. Calculated, %: C 65.51; H 7.90; N 4.77.

**5,5-Dideutero-3-methyl-7,8-dimethoxy-2-ethoxycarbonyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine (VIb).** Yield 0.16 g (56%). Yellowish thick oily substance. IR spectrum, ν, cm$^{-1}$: 1727 (C=O). $^1$H NMR spectrum, δ, ppm: 1.16 t (3H, $OCH_2CH_3$, $^3J$ 7.1 Hz), 2.40 s (3H, $NCH_3$), 2.61 d (1H, $H^4$, $J$ 16.1 Hz), 2.95–3.16 m (3H, $H^{1,4}$), 3.53 d.d (1H, $H^2$, $J$ 7.0 and 3.3 Hz), 3.68 s (3H, $OCH_3$), 3.72 s (3H, $OCH_3$), 3.93 q (2H, $OCH_2CH_3$, $^3J$ 7.1 Hz), 6.65 s, 6.72 s (1H each, $H^6$ and $H^9$). Mass spectrum: *m/z* 296 [$M$ + 1]$^+$. Found, %: N 4.75. $C_{16}H_{21}D_2NO_4$. Calculated, %: N 4.74.

**4,4-Dideutero-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium 2-ethoxycarbonylmethylide (VIIb).** Characterized by chromato-mass-spectrometry. Yield 6%. Mass spectrum: *m/z* 296 [$M$ + 1]$^+$.

**Ethyl deutero{[2-(1-deuterovinyl)-4,5-dimethoxybenzyl](methyl)amino}acetate (VIIIb).** Yield 0.005 g (2%), yellow oily substance. IR spectrum, ν, cm$^{-1}$: 1739 (C=O). $^1$H NMR spectrum, δ, ppm: 1.13 t (3H, $OCH_2CH_3$, $^3J$ 7.2 Hz), 2.25 s (3H, $NCH_3$), 3.65 s (2H, $ArCH_2N$), 3.71 s (1H, NCHDC=O), 3.75 s (3H, $CH_3O$), 3.82 s (3H, $CH_3O$), 4.01 q (2H, $OCH_2CH_3$, $^3J$ 7.2 Hz), 5.15 d (1H, $H^b$, $^2J$ 1.2 Hz), 5.65 d (1H, $H^a$, $^2J$ 1.2 Hz), 6.90 s, 7.10 s (1H each, $H^{3,6}$). Mass spectrum: *m/z* 296 [$M$ + 1]$^+$. Found, %: N 4.72. $C_{16}H_{21}D_2NO_4$. Calculated, %: N 4.74.

**3-Ethyl-2,2-di(ethoxycarbonyl)-2,3,4,5-tetrahydro-1*H*-benzazepine (X).** Yield 0.19 g (60%), thick oily substance. IR spectrum, ν, cm$^{-1}$: 1737 (C=O). $^1$H NMR spectrum, δ, ppm: 1.16 t (3H, $NCH_2CH_3$, $^3J$ 7.21 Hz), 1.23 t (6H, $OCH_2CH_3$, $^3J$ 7.1 Hz), 2.87 m (2H, $H^5$, $^3J$ 5.7 Hz), 3.03 t (2H, $H^5$, $J$ 5.7 Hz), 3.93 s (2H, $H^1$), 4.25 m (6H, $CH_2CH_3$), 6.93 d.d (1H, $H^9$, $J$ 7.0 and 3.4 Hz), 7.03 m ($3H_{arom}$). Mass spectrum: *m/z* 320 [$M$ + 1]$^+$. Found, %: C 67.67; H 7.85; N 4.37. $C_{18}H_{25}NO_4$. Calculated, %: C 67.69; H 7.89; N 4.39. From the reaction mixture by chromatography was also isolated 2-ethyl-1,2,3,4-tetrahydroisoquinoline (initial base for the synthesis of quaternary salt **IX**). Thick oily substance. Yield 0.04 g (30%). $^1$H NMR and mass spectra identical to those of the initial 2-ethyltetrahydroisoquinoline.

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