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LETTERS TO THE EDITOR

Synthesis of New Unsaturated Amines by The Stevens Rearrangement

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Abstract—Monoalkylation of 1,4-dichlorobut-2-ene with prop-2-yn-1-ol under phase-transfer catalysis conditions led to the formation of 1-(prop-2-yn-1-yloxy)-4-chlorobut-2-ene. The latter reacted with dimethylamine to afford *N*,*N*-dimethyl-4-(prop-2-yn-1-yloxy)but-2-enyl-1-amine. Its quaternization afforded new ammonium salts containing 4-(prop-2-yn-1-yloxy)but-2-enyl group. Unsaturated tertiary amines formed as a result of Stevens 3,2-rearrangement of quaternary salts.

Keywords: 1-(prop-2-yn-1-yloxy)-4-chlorobut-2-ene, *N*,*N*-dimethyl-4-(prop-2-yn-1-yloxy)but-2-enyl-1-amine, Stevens 3,2-rearrangement, unsaturated tertiary amines

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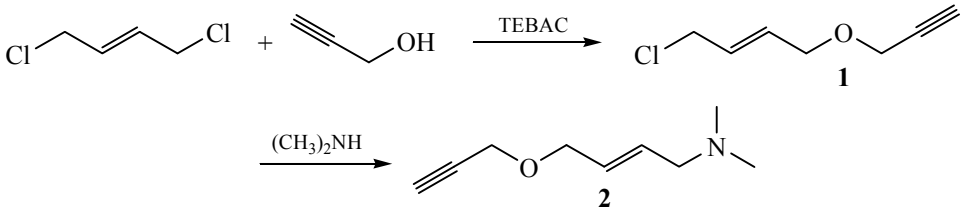
Study of the ylides transformations, including the base-mediated Stevens rearrangement makes it possible to obtain compounds with a new carbon-carbon bond under mild conditions, as well as to clarify the mechanisms of organic reactions and to synthesize compounds with a desired steric configuration [1–5]. In this regard, particular attention is drawn to the Stevens rearrangement of ammonium ylides with allylic type groups, which allow obtaining compounds of different classes, including unsaturated tertiary amines [6–9]. The latter are used for the synthesis of surface-active substances, drugs, biologically active compounds, etc. [10–12].

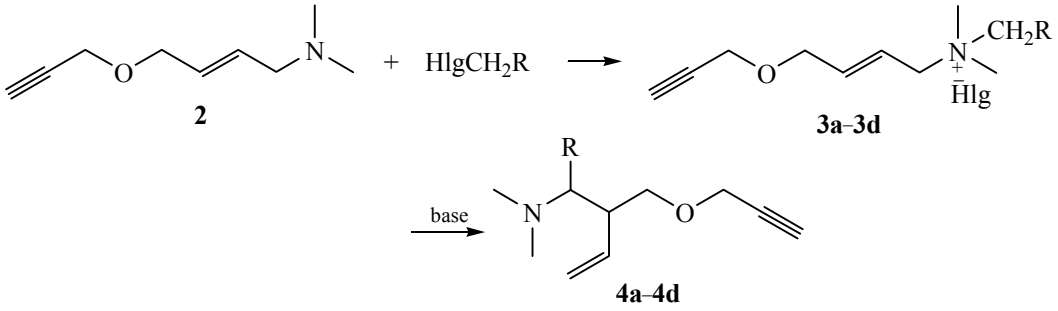
To synthesize new unsaturated amines, we obtained ammonium salts containing 4-(prop-2-yn-1-yloxy)but-2-enyl group (Scheme 1). The reaction of 1,4-dichlorobut-2-ene (*E* : *Z* = 80 : 20) with prop-2-yn-1-ol in the presence of triethylbenzylammonium chloride (TEBAC) as a phase-transfer catalyst afforded 1-(prop-2-yn-1-yloxy)-4-chlorobut-2-ene **1**. The latter reacted with dimethylamine to produce *N*,*N*-dimethyl-4-(prop-2-yn-1-yloxy)but-2-enyl-1-amine **2** as a mixture of *E*,*Z*-isomers in a 60 : 40 ratio (according to GLC and ^{1}H NMR data).

When amine **2** was reacted with methyl 2-bromoacetate, 2-chloroacetonitrile, 1-bromo-3,3-dimethylbutan-2-one or 2-bromo-1-phenylethanone in an anhydrous diethyl ether medium, the corresponding ammonium salts **3a**–**3d** were obtained as a mixture of *E*,*Z*-isomers in a ratio of 60 : 40 (**3a**–**3c**) and 63 : 35 (**3d**) according to ^{1}H NMR in 91–97% yields.

Scheme 1.



Scheme 2.



R = $COOCH_3$, Hlg = Br (**a**); R = CN, Hlg = Cl (**b**); R = $COC(CH_3)_3$, Hlg = Br (**c**); R = COC_6H_5, Hlg = Br (**d**).

The Stevens rearrangement of ammonium salt **3a** with a methoxycarbonylmethyl group was carried out in anhydrous diethyl ether medium using sodium methoxide as base. The reaction of salts **3b**–**3d** was performed in the presence of powdered potassium hydroxide in anhydrous benzene medium (Scheme 2). The ammonium salts **3a**–**3d** enter exclusively into the Stevens 3,2-rearrangement to form unsaturated amines **4a**–**4d** as a mixture of two diastereomers (according to ^{1}H NMR data). According to IR spectroscopy data, the synthesized ammonium salts **3a**–**3d** and tertiary amines **4a**–**4d** activated in the α-position by electron-withdrawing substituents form intermolecular dimeric associates involving hydrogen at the *sp*-hybridized carbon atom of the terminal acetylene moiety and π-electrons of the triple C≡C bond of another molecule [13].

The structure of all compounds obtained was confirmed by IR and NMR spectroscopy data. The purity of the prepared compounds was monitored by TLC or GLC method.

In summary, a possibility of obtaining new unsaturated tertiary amines by reacting quaternary ammonium salts containing 4-(prop-2-yn-1-yloxy)but-2-enyl group with basic agents under Stevens rearrangement conditions was shown.

1-(Prop-2-yn-1-yloxy)-4-chlorobut-2-ene (1). To a mixture of 0.15 mol of 1,4-dichlorobut-2-ene (mixture of *E*, *Z*-isomers, 80 : 20, according to GLC) and 0.1 g of triethylbenzylammonium chloride were simultaneously added dropwise a 50% aqueous solution of 0.12 mol of sodium hydroxide and 0.051 mol of prop-2-yn-1-ol with cooling and stirring. After the exothermic reaction (~50°C) completed, the mixture was heated for 3 h on a water bath at 50°C. On the next day the mixture was diluted with water (~100 mL) and stirred, then the reaction products were extracted several times with chloroform. The combined extracts were dried with magnesium sulfate. After the solvent removal, the mixture was distilled. Yield 67%, bp 103–105°C (27 mmHg), n_D^{20} 1.4760. IR spectrum, ν, cm^{-1}: 3295 (C≡CH), 2100 (C≡C), 1100 (COC), 630 [δ (C≡CH)]. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): ***trans*-isomer**, 2.39 t (1H, ≡CH, *J* = 2.4), 4.06 d (2H, CH_2Cl, *J* = 5.2), 4.09 d (2H, =CHC$\underline{H_2}$O, *J* = 4.3), 4.15 d (2H, C$\underline{H_2}$C≡CH, *J* = 2.4), 5.81–5.96 m (2H, CH=CH). Found, %: C 58.25; H 6.15; Cl 24.68. C_7H_9ClO. Calculated, %: C 58.13; H 6.23; Cl 24.57.

***N*,*N*-Dimethyl-4-(prop-2-yn-1-yloxy)but-2-enyl-1-amine (2)** was prepared by procedure [14] as a mixture of *E*,*Z*-isomers, 65 : 35. Yield 60% bp 108–110°C (28 mmHg), n_D^{20} 1.4555. IR spectrum, ν, cm^{-1}: 3290 (C≡CH), 2100 (C≡C), 1100 (COC), 630 [δ(C≡CH)]. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.22 s (3.9H) and 2.23 s (2.1H, NCH_3), 2.37 t (0.65H) and 2.39 t (0.35H, ≡CH, *J* = 2.4), 2.92 d (1.3H, *J* = 6.0) and 2.96 d (0.7H, NCH_2, *J* = 5.4), 4.05 br.d (1.3H, *J* = 5.7) and 4.14 br.d (0.7H, =CHC$\underline{H_2}$O, *J* = 5.0), 4.12 d (1.3H, *J* = 2.3) and 4.13 d (0.7H, C$\underline{H_2}$C≡CH, *J* = 2.4), 5.62–5.83 m (2H, CH=CH). Found, %: C 70.69; H 9.75; N 9.21. $C_9H_{15}NO$. Calculated, %: C 70.59; H 9.80; N 9.15.

Ammonium salts (3a–3d). To a solution of 0.01 mol of amine **2** in 5 mL of anhydrous ether was added dropwise a solution of 0.01 mol of halide in 5 mL of anhydrous ether. The reaction mixture was kept at room temperature for 2–3 days. The formed salt was washed several times with anhydrous ether and dried in a desiccator over $CaCl_2$.

(*E*,*Z*)-*N*,*N*-Dimethyl-*N*-(2-methoxy-2-oxoethyl)-4-(prop-2-yn-1-yloxy)but-2-enyl-1-aminium bromide (3a). Yield 92% (60:40), mp 51–52°C, R_f 0.41. IR spectrum, ν, cm^{-1}: 1730 (COO), 640, 3180 (C≡CH),

2100 (C≡C), 1080 (COC), 890, 920, 990, 1640, 3025, 3090 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.04 t (1H, ≡CH, *J* = 2.4), 3.37 s (3.6H) and 3.40 s (2.4H, NCH_3), 3.82 s (1.8H) and 3.83 s (1.2H, OCH_3), 4.14 d.d (1.2H, *J* = 5.0, *J* = 1.4) and 4.26 d.d (0.8H, =CHC$\underline{H}_2$O, *J* = 6.3, *J* = 1.3), 4.17 d (1.2H) and 4.19 d (0.8H, C$\underline{H}_2$C≡CH, *J* = 2.4), 4.43 d (1.2H, *J* = 7.5) and 4.49 d (0.8H, *J* = 7.8, NC$\underline{H}_2$CH=), 4.69 s (1.2H) and 4.77 s (0.8H, CH_2C=O), 5.84–6.03 m (1H) and 6.10–6.28 m (1H, CH=CH). Found, %: N 4.51; Br^- 26.25. $C_{12}H_{20}BrNO_3$. Calculated, %: N 4.57; Br^- 26.14.

(*E*,*Z*)-*N*,*N*-Dimethyl-*N*-(cyanomethyl)-4-(prop-2-yn-1-yloxy)but-2-enyl-1-aminium chloride (3b). Yield 96.5% (60:40), R_f 0.43. IR spectrum, ν, cm^{-1}: 2230 (C≡N), 2095 (C≡C), 640, 3170 (C≡CH), 1080 (COC), 890, 920, 990, 1640, 3025, 3090 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.05 t (0.4H) and 3.06 t (0.6H, ≡CH, *J* = 2.4), 3.36 s (3.6H) and 3.39 s (2.4H, NCH_3), 4.16 d.d (1.2H, *J* = 4.9, *J* = 1.6) and 4.32 d.d (0.8H, =CHC$\underline{H}_2$O, *J* = 6.2, *J* = 1.5), 4.18 d (1.2H) and 4.20 d (0.8H, C$\underline{H}_2$C≡CH, *J* = 2.4), 4.44 d (1.2H, *J* = 7.5) and 4.52 d (0.8H, NC$\underline{H}_2$CH=, *J* = 7.9), 5.39 s (1.2H) and 5.47 s (0.8H, CH_2C≡N), 5.85–6.03 m (1H, =CH), 6.18 d. t (0.4H, *J* = 11.1, *J* = 6.2) and 6.31 d. t (0.6H, =CH, *J* = 15.3, *J* = 4.9). Found, %: N 12.30; Cl 16.02. $C_{11}H_{17}ClN_2O$. Calculated, %: N 12.25; Cl 15.54.

(*E*,*Z*)-*N*,*N*-Dimethyl-*N*-(3,3-dimethyl-2-oxobutyl)-4-(prop-2-yn-1-yloxy)but-2-enyl-1-aminium bromide (3c). Yield 97% (60:40), R_f 0.49. IR spectrum, ν, cm^{-1}: 1700 (CO), 2095 (C≡C), 640, 3160(C≡CH), 1060 (COC), 890, 920, 990, 1640, 3025, 3090 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.20 s (5.4H) and 1.21 s (3.6H, CH_3, *t*-Bu), 2.98 t (0.4H) and 2.99 t (0.6H, ≡CH, *J* = 2.4), 3.31 s (3.6H) and 3.33 s (2.4H, NCH_3), 4.12 d.d (1.2H, *J* = 4.9, *J* = 1.3) and 4.24 d.d (0.8H, =CHC$\underline{H}_2$O, *J* = 6.4, *J* = 1.4), 4.16 d (1.2H) and 4.19 d (0.8H, C$\underline{H}_2$C≡CH, *J* = 2.4), 4.36 d (1.2H, *J* = 7.4) and 4.44 d (0.8H, NC$\underline{H}_2$CH=, *J* = 7.8), 5.10 s (1.2H) and 5.19 s (0.8H, CH_2C=O), 5.81–6.00 m (1H) and 6.07–6.18 m (1H, CH=CH). Found, %: N 4.28; Br^- 24.16. $C_{15}H_{26}BrNO_2$. Calculated, %: N 4.22; Br^- 24.19.

(*E*,*Z*)-*N*,*N*-Dimethyl-*N*-(2-oxo-2-phenylethyl)-4-(prop-2-yn-1-yloxy)but-2-enyl-1-aminium bromide (3d). Yield 91% (65:35), hygroscopic, R_f 0.44. IR spectrum, ν, cm^{-1}: 1670 (CO), 2090 (C≡C), 640, 3180 (C≡CH), 1070 (COC), 890, 920, 990, 1640, 3025, 3090 (C=C), 700, 775, 980, 1490, 1600, 3035, 3080 (C_6H_5). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.94 t (0.65H) and 2.98 t (0.35H, ≡CH, *J* = 2.4), 3.42 s (3.9H) and 3.45 s (2.1H, NCH_3), 4.12 d.d (1.3H, *J* = 4.9, *J* = 1.3) and 4.27 d.d (0.7H, =CHC$\underline{H}_2$O, *J* = 6.4, *J* = 1.3), 4.14 d (1.3H) and 4.19 d (0.7H, C$\underline{H}_2$C≡CH, *J* = 2.4), 4.47 d (1.3H, *J* = 7.4) and 4.55 d (0.7H, NC$\underline{H}_2$CH=, *J* = 7.8), 5.55 s (1.3H) and 5.63 s (0.7H, CH_2C=O), 5.88–6.26 m (2H, CH=CH), 7.53–7.60 m (2H, $H^{3,5}$ Ph), 7.66–7.72 m (1H, H^4 Ph), 8.06–8.11 m (2H, $H^{2,6}$ Ph). Found, %: N 3.91; Br^- 22.77. $C_{17}H_{22}BrNO_2$. Calculated, %: N 3.98; Br^- 22.73.

Methyl 2-(dimethylamino)-3-[(prop-2-yn-1-yloxy)-methyl]pent-4-enoate (4a). A mixture of 0.01 mol of salt **3a** and 0.02 mol of NaOMe in 15 mL of anhydrous diethyl ether was well triturated. After the exothermic reaction completed, 2–3 drops of methanol were added, and the mixture was triturated again and then refluxed for 15 min. After cooling, water and diethyl ether were added. The ether layer was separated, and the reaction products were twice extracted from the aqueous layer with ether. The combined extracts were dried with magnesium sulfate. After distilling off the solvent the mixture was distilled in a vacuum. Yield 45%, a mixture of diastereomers in a 1 : 1 ratio, bp 114–115 °C (3 mmHg), n_D^{20} 1.4640. IR spectrum, ν, cm^{-1}: 1730 (COO), 2100 (C≡C), 630, 3295 (C≡CH), 1100 (COC), 900, 930, 990, 1635, 3020, 3090 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.28 s (3H) and 2.31 s (3H, NCH_3), 2.33 t (0.5H) and 2.33 t (0.5H, ≡CH, *J* = 2.4), 2.70–2.84 m (1H, C$\underline{H}$–CH=), 3.22 d (0.5H) and 3.29 d (0.5H, NCH, *J* = 10.6), 3.46 d.d (0.5H, *J* = 9.5, *J* = 5.1) and 3.50 d.d (0.5H, OC$\underline{H}_2$CH, *J* = 9.5, *J* = 4.8), 3.58 d.d (0.5H, *J* = 9.0, *J* = 6.1) and 3.65 d.d (0.5H, OC$\underline{H}_2$CH, *J* = 9.0, *J* = 3.6), 3.64 s (1.5H) and 3.70 s (1.5H, OCH_3), 4.06 d (1H, C$\underline{H}_2$C≡CH, *J* = 2.4), 4.11 d.d (0.5H) and 4.12 d.d (0.5H, C$\underline{H}_2$C≡CH, *J* = 15.9, *J* = 2.4), 5.08 d.d.d (0.5H) and 5.12 d.d.d (0.5H, $=CH_2$, *J* = 10.3, *J* = 1.8, *J* = 0.6), 5.11 d.d.d (0.5H) and 5.15 d.d.d (0.5H, $=CH_2$, *J* = 17.2, *J* = 1.8, *J* = 0.9), 5.72 d.d.d (0.5H, *J* = 17.2, *J* = 10.3, *J* = 8.8) and 5.78 d.d.d (0.5H, =CH, *J* = 17.2, *J* = 10.3, *J* = 8.6). Found, %: C 64.16; H 8.49; N 6.09. $C_{12}H_{19}NO_3$. Calculated, %: C 64.00; H 8.44; N 6.22.

2-(Dimethylamino)-3-[(prop-2-yn-1-yloxy)methyl]pent-4-enenitrile (4b) was obtained similarly. Yield 49%, a mixture of two diastereomers in a 68 : 32 ratio, bp 110–112 °C (3 mmHg), n_D^{20} 1.4690. IR spectrum, ν, cm^{-1}: 2220 (C≡N), 2100 (C≡C), 640, 3290 (C≡CH), 1090 (COC), 890, 920, 990, 1645, 3020, 3090 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.30 s (1.92H) and 2.32 s (4.08H, NCH_3), 2.37 t (0.68H) and 2.41 t (0.32H, ≡CH, *J* = 2.4), 2.50–2.62 m (1H, C$\underline{H}$–CH=), 3.57 d.d (0.64H, *J* = 9.0, *J* = 4.3) and

3.63 d.d (0.64H, OC$\underline{H}_2$CH, J = 9.0, J = 4.8), 3.68 d.d (0.32H, J = 9.2, J = 3.3) and 3.81 d.d (0.32H, OC$\underline{H}_2$CH, J = 9.2, J = 3.7), 3.72 d (0.32H, J = 10.7) and 3.75 d (0.68H, NCH, J = 9.8), 4.10 d.d (0.68H) and 4.13 d.d (0.68H, C$\underline{H}_2$C≡CH, J = 16.0, J = 2.4), 4.15 d (0.64H, C$\underline{H}_2$C≡CH, J = 2.4), 5.17 d.d.d (0.32H, J = 17.5, J = 1.6, J = 0.9) and 5.17 d.d.d (0.32H, =CH_2, J = 10.0, J = 1.6, J = 0.6), 5.29 br.d.d (0.68H, J = 10.2, J = 1.4) and 5.32 d.d.d (0.68H, =CH_2, J = 17.2, J = 1.4, J = 0.9), 5.79 d.d.d (0.32H, J = 17.5, J = 10.0, J = 8.5) and 5.82 d.d.d (0.68H, =CH, J = 17.2, J = 10.2, J = 8.7). Found, %: C 68.67; H 8.39; N 14.49. $C_{11}H_{16}N_2O$. Calculated, %: C 68.75; H 8.33; N 14.58.

2,2-Dimethyl-4-(dimethylamino)-5-[(prop-2-yn-1-yloxy)methyl]hept-6-en-3-one (4c) was obtained similarly. Yield 62%, a mixture of two diastereomers in a ratio of 75 : 25, bp 128–130 °C (5 mmHg), n_D^{20} 1.4680. IR spectrum, ν, cm^{-1}: 1700 (C=O), 2095 (C≡C), 610, 3250 (C≡CH), 1080 (COC), 895, 920, 985, 1630, 3025, 3090 (C=C). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.10 s (2.25H) and 1.17 s (6.75H, CH_3, *t*-Bu), 2.33 t (0.75H) and 2.37 t (0.25H, ≡CH, J = 2.4), 2.38 s (4.5H) and 2.42 s (1.5H, NCH_3), 2.85–2.95 m (0.25H) and 2.95–3.06 m (0.75H, C$\underline{H}$–CH=), 3.31 d.d (0.75H, OC$\underline{H}_2$CH, J = 9.1, J = 3.4) and 3.34 d.d (0.75H, J = 9.1, J = 4.0), 3.59 d.d (0.25H, J = 9.0, J = 3.4) and 3.63 d.d (0.25H, OC$\underline{H}_2$CH, J = 9.0, J = 5.0), 3.76 d (0.25H) and 3.87 d (0.75H, NCH, J = 10.5), 4.00 d (1.5H) and 4.13 d (0.5H, C$\underline{H}_2$C≡CH, J = 2.4), 4.99–5.06 m (0.5H, =CH_2), 5.11 d.d (0.75H, J = 10.2, J = 1.9) and 5.22 d.d (0.75H, =CH_2, J = 17.2, J = 1.9), 5.60–5.73 m (0.25H) and 5.99 m (0.75H, =CH). Found, %: C 71.65; H 9.87; N 5.61. $C_{15}H_{25}NO_2$. Calculated, %: C 71.71; H 9.96; N 5.58.

2-(Dimethylamino)-1-phenyl-3-[(prop-2-yn-1-yloxy)-methyl]pent-4-ene-1-one (4d) was prepared similarly. Yield 81%, a mixture of two diastereomers in a 60 : 40 ratio, bp 162–164 °C (3 mmHg), n_D^{20} 1.5032. IR spectrum, ν, cm^{-1}: 2100 (C≡C), 1670 (C=O), 640, 3290 (C≡CH), 1080 (COC), 890, 920, 990, 1640, 3035, 3090 (C=C), 720, 770, 1520, 1610, 3025, 3060 (C_6H_5). ^{1}H NMR spectrum, δ, ppm (J, Hz): 2.23 s (3.6H) and 2.28 s (2.4H, NCH_3), 2.61 t (0.6H) and 2.77 t (0.4H, ≡CH, J = 2.4), 2.86–2.98 m (1H, C$\underline{H}$–CH=), 3.37 d.d (0.6H) and 3.43 d.d (0.6H, OC$\underline{H}_2$CH, J = 9.3, J = 4.2), 3.64 d.d (0.4H, J = 8.9, J = 3.4) and 3.69 d.d (0.4H, OC$\underline{H}_2$CH, J = 8.9, J = 5.6), 3.86 d (1.2H, C$\underline{H}_2$C≡CH, J = 2.4), 4.09 d.d (0.4H) and 4.14 d.d (0.4H, C$\underline{H}_2$C≡CH, J = 16.0, J = 2.4), 4.35 d (0.4H) and 4.42 d (0.6H, NCH, J = 10.6), 4.91 d.d.d (0.4H) and 5.07 d.d.d (0.6H, =CH_2, J = 10.3, J = 1.9, J = 0.7), 5.00 d.d.d (0.4H) and 5.17 d.d.d (0.6H, =CH_2, J = 17.3, J = 1.9, J = 0.9), 5.69 d.d.d (0.4H, J = 17.3, J = 10.3, J = 8.4) and 5.94 d.d.d (0.6H, =CH, J = 17.3, J = 10.3, J = 8.8), 7.42–7.57 m (3H) and 7.85–7.93 m (2H, Ph). Found, %: C 75.33; H 7.68; N 5.21. $C_{17}H_{21}NO_2$. Calculated, %: C 75.27; H 7.75; N 5.17.

IR spectra were recorded on a Specord IR-75 spectrometer in mineral oil or in a thin layer. NMR spectra were registered on a Varian Mercury-300 spectrometer in DMSO-d_6–CCl_4 at 303 K operating at 300 MHz, internal reference TMS. The purity of ammonium salts was monitored by TLC on Silufol UV-254 plates, eluting with a butane-1-ol–ethanol–water–acetic acid system (10 : 7 : 6 : 4) and detecting with iodine vapors. The purity of other compounds was monitored by GLC using an LKhM-80 chromatograph with a thermal conductivity detector, a column temperature of 50–220°C (heating rate 16 deg/min), 2000×3 mm, 10% Apiezon-L on an Inerton-AW carrier (0.2–0.25 mm), the carrier gas (helium) flow was 60 mL/min.

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