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LETTERS TO THE EDITOR

Synthesis of Allenic Diamines via The Stevens Rearrangement of Ammonium Salts

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Due to high reactivity allenes are widely used for the synthesis of compounds of various types [1–3].

According to the literature data, 3,3-dimethylbutan-2-onyl-substituted dimethylammonium salts containing prop-2-ynyl, but-2-ynyl or 3-phenylprop-2-ynyl group underwent 3,2-Stevens rearrangement by the action of basic agents to form allenic aminoketones [4]. In the case of the salts containing ethyl, propyl or butyl group instead of methyl moiety the products of both 3,2- and 1,2-Stevens rearrangement were obtained. The 3,2-rearrangement product converted partially into the hydrogenated analogs due to hydride transfer [5].

In order to obtain new allenic aliphatic and heterocyclic diamines, which have great preparative importance, we synthesized ammonium salts containing 3,3-dimethylbutan-2-onyl and 4-aminobut-2-ynyl groups. The initial salts **IIa**–**IId** were prepared by reacting 1-dimethylamino-4-diethylaminobut-2-yne **Ia**, -4-piperidylbut-2-yne **Ib**, -4-morpholylbut-2-yne **Ic** and -4-pyrazolylbut-2-yne **Id** with bromopinacolone in absolute diethyl ether. The Stevens rearrangement of the synthesized salts **IIa**–**IId** was performed under the action of powdered potassium hydroxide in absolute benzene (Scheme 1).

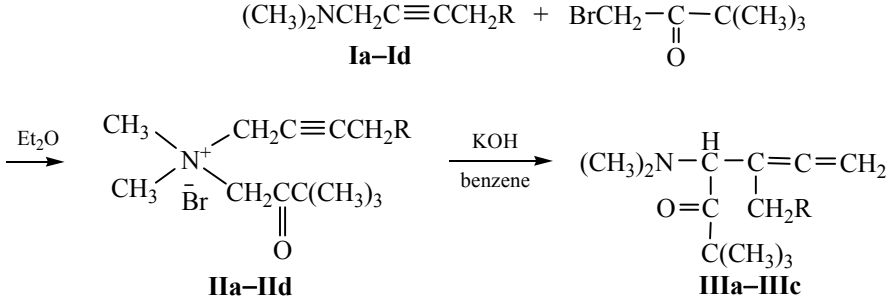
It was found that under these conditions 3,2-Stevens rearrangement occurs exclusively to give the corresponding allenic diamines **IIIa**–**IIIc**. In the case of the salt **IId**, an unseparable mixture of the reaction products formed.

The structures of the synthesized compounds were confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy methods.

Diamines **Ia**–**Id** have been reported in [6].

Synthesis of ammonium salts (IIa–IId). A solution of 0.015 mol of bromopinacolone in 10 mL of absolute diethyl ether was added dropwise to a solution of 0.045 mol of diamines **Ia** or **Ic** in 10 mL of absolute ether. In the case of diamines **IIb** and **IId** a ratio of

Scheme 1.



R = $N(C_2H_5)_2$ (**a**), $N(CH_2)_5$ (**b**), $N(CH_2CH_2)_2O$ (**c**), pyrazolyl (**d**).

diamine–halide was of 5 : 1 and 1 : 1, respectively. The reaction mixture was incubated at room temperature for 2–3 days. The formed salt was washed several times with anhydrous ether, filtered off and dried in a desiccator over $CaCl_2$.

Dimethyl-(4-diethylaminobut-2-yn-1-yl)-(3,3-dimethylbutan-2-on-1-yl)ammonium bromide (IIa). Yield 70%, mp 78–79°C, R_f 0.37. IR spectrum, ν, cm^{-1}: 1720 (CO), 2245 (C≡C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.04 t (6H, $NCH_2C\underline{H}_3$, *J* 7.1), 1.23 s [9H, $C(CH_3)_3$], 2.49 q (4H, $NC\underline{H}_2CH_3$, *J* 7.1), 3.41 s (6H, N^+CH_3), 3.49 t (2H, NCH_2, *J* 1.8), 4.73 t (2H, N^+CH_2, *J* 1.8), 5.30 s (2H, CH_2CO). Found, %: N 8.15; Br^- 23.31. $C_{16}H_{31}BrN_2O$. Calculated, %: N 8.07; Br^- 23.05.

Dimethylл-(4-piperidylbut-2-yn-1-yl)-(3,3-dimethylbutan-2-on-1-yl)ammonium bromide (IIb). Yield 65%, mp150–151°C, R_f 0.44. IR spectrum, ν, cm^{-1}: 1730 (CO), 2250 (C≡C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.23 s [9H, $C(CH_3)_3$], 1.37–1.46 m [2H, $N(CH_2)_2C\underline{H}_2$], 1.53–1.61 m [4H, $N(CH_2C\underline{H}_2)_2CH_2$], 2.39–2.47 m [4H, $N(C\underline{H}_2CH_2)_2CH_2$], 3.35 t (2H, NCH_2, *J* 1.9), 3.41 s (6H, N^+CH_3), 4.73 t (2H, N^+CH_2, *J* 1.9), 5.27 s (2H, CH_2CO). Found, %: N 7.63; Br^- 22.35. $C_{17}H_{31}BrN_2O$. Calculated, %: N 7.79; Br^- 22.28.

Dimethyl-[4-(*N*-morpholyl)but-2-yn-1-yl]-(3,3-dimethylbutan-2-on-1-yl)ammonium bromide (IIc). Yield 75%, mp172–173°C, R_f 0.38. IR spectrum, ν, cm^{-1}: 1720 (CO), 2250 (C≡C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.23 s [9H, $C(CH_3)_3$], 2.46–2.50 m [4H, $N(C\underline{H}_2CH_2)_2O$], 3.41 s (6H, N^+CH_3), 3.42 t (2H, NCH_2, *J* 1.8), 3.59–2.63 m (4H, OCH_2), 4.75 t (2H, N^+CH_2, *J* 1.8), 5.27 s (2H, CH_2CO). Found, %: N 7.82; Br^- 21.99. $C_{16}H_{29}BrN_2O_2$. Calculated, %: N 7.76; Br^- 22.16.

Dimethyl-(4-pyrazolylbut-2-yn-1-yl)-(3,3-dimethylbutan-2-on-1-yl)ammonium bromide (IId). Yield 80%, mp142–143°C, R_f 0.41. IR spectrum, ν, cm^{-1}: 1720 (CO), 2245 (C≡C), 1520–1530 (pyrazole). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.20 s [9H, $C(CH_3)_3$], 3.44 s (6H, N^+CH_3), 4.79 t (2H, NCH_2, *J* 1.8), 5.20 t (2H, N^+CH_2, *J* 1.8), 5.30 s (2H, CH_2CO), 6.20 d.d (1H, =CH, J^1 2.4, J^2 1.8), 7.38 d.d (1H, =CH, J^1 1.8, J^2 0.6), 7.80 d.d (1H, =CH, J^1 2.4, J^2 0.6). Found, %: N 12.36; Br^- 23.31. $C_{15}H_{24}BrN_3O$. Calculated, %: N 12.28; Br^- 23.39.

4-(Dimethylamino)-2,2-dimethyl-5-(diethylaminomethyl)hepta-5,6-diene-3-one (IIIa). 0.03 mol of powdered potassium hydroxide was added in portions to a suspension of 0.015 mol of salt **IIa** in 10 mL of absolute benzene with vigorous stirring. After the exothermal reaction completed, 2–3 drops of methanol was added and the mixture was heated for 10 min. After cooling, the mixture was treated with water, and the benzene layer was separated. The aqueous layer was extracted twice with diethyl ether. The combined ether extracts were dried with magnesium sulfate. After distilling off the solvent, the residue was distilled in vacuum. Yield 75%, bp 116–119°C (2 mmHg), n_D^{20} 1.4745. IR spectrum, ν, cm^{-1}: 1720 (CO), 1950–1960 (C=C=C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.98 t (6H, $CH_2C\underline{H}_3$, *J* 7.2), 1.09 s [9H, $C(CH_3)_3$], 2.34 s (6H, NCH_3), 2.39 d.q (1H, $C\underline{H}_2CH_3$, J^1 12.8, J^2 7.2), 2.57 d.q (1H, $C\underline{H}_2CH_3$, J^1 12.8, J^2 7.2), 2.78 d.t (1H, NCH_2, J^1 13.3, J^2 1.9), 3.15 d.t (1H, NCH_2, J^1 13.3, J^2 2.9), 4.27 d.d (1H, NCH, J^1 2.9, J^2 1.9), 4.63–4.74 m (2H, $=CH_2$). ^{13}C NMR spectrum, δ_C, ppm: 11.4 ($CH_2\underline{C}H_3$), 25.9 [$C(\underline{C}H_3)_3$], 40.8 (NCH_3), 43.1 [$\underline{C}(CH_3)_3$], 46.1 ($\underline{C}H_2CH_3$), 53.4 (NCH_2), 65.6 (NCH), 75.4 ($=CH_2$), 98.3 ($\underline{C}=C=CH_2$), 207.9 (C=O), 212.3 ($C=\underline{C}=CH_2$). Found, %: C 72.25; H 11.16; N 10.61. $C_{16}H_{30}N_2O$. Calculated, %: C 72.18; H 11.27; N 10.52.

4-(Dimethylamino)-2,2-dimethyl-5-(piperidin-1-ylmethyl)hepta-5,6-diene-3-one (IIIb) was prepared similarly. Yield 87%, bp 131–133°C (2 mmHg), n_D^{20} 1.4920. IR spectrum, ν, cm^{-1}: 1720 (CO), 1955–1960 (C=C=C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.10 s [9H, $C(CH_3)_3$], 1.37–1.58 m [6H, $N(CH_2C\underline{H}_2)_2C\underline{H}_2$], 2.26–2.43 m [4H, $N(C\underline{H}_2CH_2)_2CH_2$], 2.32 s (6H, NCH_3), 2.69 d.t (1H, NCH_2, J^1 12.8, J^2 1.7), 2.94 d.t (1H, NCH_2, J^1 12.8, J^2 2.7), 4.27 d.d (1H, NCH, J^1 2.7, J^2 1.7), 4.65–4.75 m (2H, $=CH_2$). Found, %: C 73.55; H 10.69; N 10.15. $C_{17}H_{30}N_2O$. Calculated, %: C 73.38; H 10.79; N 10.07.

4-(Dimethylamino)-2,2-dimethyl-5-(*N*-morpholinomethyl)hepta-5,6-diene-3-one (IIIc) was prepared similarly. Yield 79%, bp 143–144°C (2 mmHg), n_D^{20} 1.4940. IR spectrum, ν, cm^{-1}: 1720 (CO), 1960 (C=C=C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.10 s [9H, $C(CH_3)_3$], 2.31 s (6H, NCH_3), 2.31–2.47 m [4H, $N(C\underline{H}_2CH_2)_2O$], 2.76 d.t (1H, NCH_2, J^1 12.9, J^2 1.8), 2.99 d.t (1H, NCH_2, J^1 12.9, J^2 2.7), 3.50–3.62 m (4H, OCH_2), 4.23 d.d (1H, NCH, J^1 2.7, J^2 1.8), 4.68–4.79 m (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 26.0 [$C(\underline{C}H_3)_3$], 41.1 (NCH_3), 43.2 [$\underline{C}(CH_3)_3$], 53.2 [$N(\underline{C}H_2CH_2)_2O$], 58.1 ($NCH_2$), 65.9 ($OCH_2$), 66.5 (NCH), 75.6 ($=CH_2$), 96.6 ($\underline{C}=C=CH_2$), 208.5 (C=O), 211.3 ($C=\underline{C}=CH_2$). Found, %: C 68.64; H 10.06; N 10.04. $C_{16}H_{28}N_2O_2$. Calculated, %: C 68.57; H 10.00; N 10.00.

IR spectra were recorded on a Specord IR 75 instrument in mineral oil or in a thin layer. NMR spectra of the solutions of DMSO-d_6–CCl_4 were obtained on a Varian Mercury-300 [300.075 (^{1}H), 75.46 MHz (^{13}C)] spectrometer at 303 K relative to internal TMS. GLC analysis was done on a LHM-80 instrument equipped with a thermal conductivity detector [column temperature 50–220°C, 16 deg/min, 2000 × 3 mm, 10% Apiezon-L on Inerton-AW carrier (0.2–0.25 mm), the rate of carrier gas (helium) 60 mL/min]. TLC analysis was carried out on Silufol UV-254 plates eluting with *n*-butanol–ethanol–water–acetic acid mixture (10 : 7 : 6 : 4) and developing with iodine vapor.

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REFERENCES

1. Krause, N., and Hashmi, A.S.K., *Modern Allene Chemistry*, Weinheim: Wiley-VSH, 2004, vols. 1–2.
2. Tang, Y., Shen, L., Dellaria, B.J., and Hsang, R.P., *Tetrahedron Lett*., 2008, vol. 49, p. 6404. DOI: 10.1016/j.tetlet.2008.08.089.
3. Harrington, P.E., Murai, T., Chu, C., and Tius, M.A., *J. Am. Chem. Soc*., 2002, vol. 124, no. 34, p. 10091. DOI: 10.1021/jaO20591o.
4. Kocharyan, S.T., Karapetyan, V.E., Churkina, N.P., and Osyan, A.M., *Khim. Zh. Armenii*, 2002, vol. 54, no. 3, p. 134.
5. Ovsepyan, V.S., *Khim. Zh. Armenii*, 2004, vol. 57, nos. 1–2, p. 78.
6. Sahakyan, T.A., Gyul'nazaryan, A.Kh., and Manukyan, M.O., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 10, p. 1952. DOI: 10.1134/S1070363213100265.