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Synthesis of the Unsaturated Diamines by the Stevens Rearrangement of 4-Diethylaminobutyn-2-yl-Containing Ammonium Salts

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Abstract—Ammonium salts containing 4-diethylaminobutyn-2-yl and 2-alkenyl groups undergo the Stevens 3,2-rearrangement under the action of potassium hydroxide in anhydrous benzene to form the unsaturated diamines.

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Under the basic conditions the allyl- and propargylcontaining ammonium salts undergo Stevens 2,3rearrangement to form the corresponding amines [1– 6]. In the case of 4-allyloxy(phenyloxy)butyn-2-ylcontaining salts the unsaturated aminoesters of different structure have been obtained [7].

In order to obtain the unsaturated mixed diamines we studied the Stevens rearrangement of ammonium salts containing 4-diethylaminobutyn-2-yl and allyl groups.

The initial ammonium salts **IIa–IId** were synthesized by the reaction of 1-dimethylamino-4-diethylaminobut-2-yne **I** obtained by the Mannich reaction [8] with a 2-alkenyl halides in a molar ratio of 3:1 in anhydrous diethyl ether (Table 1).

The Stevens rearrangement of the obtained salts **IIa–IId** was carried out under the action of powdered potassium hydroxide in anhydrous benzene.

Under the reaction conditions the salts **Ha–IId** were found to undergo the Stevens 2,3-rearrangement to form the corresponding diamines **IIIa–IIId** (Table 2).

The structure of the obtained compounds was confirmed by IR, ¹H, and ¹³C NMR spectra (Table 3). Their individuality was proved by the GLC and TLC methods.

Comp. no.	Yiels, %	R_{f}	Found, %		Farmenta	Calculated, %	
			Ν	Hlg	Formula	Ν	Hlg
IIa	72	0.4	9.78	27.75	$C_{13}H_{25}N_2Br$	9.69	27.68
IIb	65	0.43	10.69	13.71	$C_{14}H_{27}N_2Cl$	10.83	13.73
IIc	64	0.45	9.31	26.48	$C_{14}H_{27}N_2Br$	9.24	26.40
IId ^a	67	0.38	7.72	21.84	$C_{19}H_{29}N_2Br$	7.67	21.92

Table 1. Yields and elemental analysis data of ammonium salts IIa-IId

^a mp of salt **IId** is 95–97°C.



According to the ¹H NMR spectra, compounds **IIIc** and **IIId** exist as two diastereomers in a ratio of 25:75 and 10:90, respectively.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 instrument from the samples as a slurry in mineral oil or as a thin layer. The NMR spectra were recorded on

a Varian Mercury-300 spectrometer [300.075 MHz (¹H), 75.46 MHz (¹³C] in DMSO- d_6 -CCl₄ (1:3) at 303 K relative to internal TMS.

The GLC analysis was performed on a LKhM-80 instrument [ramp 50–220°C at a rate 16 deg min⁻¹, column 2000×3 mm, 10% Apiezon-L on Inerton-AW (0.2–0.25 mm), the carrier gas helium, flow rate

Table 2. Yields, physicochemical characteristics, and elemental analysis data of compounds I, IIIa–IIId

Comp.	Yield,	bp, °C (mm Hg)	$n_{\rm D}^{20}$	Found, %			Formula	Calculated, %		
no.	%			С	Н	Ν	ronnula	С	Н	Ν
Ι	60	86–87 (7)	1.4540	71.57	11.81	16.60	$C_{10}H_{20}N_2$	71.43	11.90	16.67
IIIa	41	130–131 (24)	1.4670	75.28	11.51	13.61	$C_{13}H_{24}N_2$	75.00	11.54	13.46
IIIb	55	128–129 (13)	1.4680	75.36	11.26	12.54	$C_{14}H_{26}N_2$	75.67	11.71	12.62
IIIc	45	130–132 (18)	1.4730	75.91	11.89	12.78	$C_{14}H_{26}N_2$	75.67	11.71	12.62
IIId	51	142–144 (2)	1.5260	80.55	9.38	9.98	$C_{19}H_{28}N_2$	80.28	9.86	9.86

Table 3. IR, ¹H, and ¹³C NMR spectral parameters of compounds I, IIIa–IIId

Comp. no.	v, cm ⁻¹	δ, ppm (<i>J</i> , Hz)				
I	2240 (C=C)	$\delta_{\text{H}:}$ 1.02 t (6H, CH ₂ C <u>H₃</u> , ³ <i>J</i> 7.1), 2.19 s (6H, NCH ₃), 2.46 q (4H, NC <u>H₂</u> CH ₃ , ³ <i>J</i> 7.1), 3.17 t (2H, C <u>H₂</u> NMe ₂ , ⁵ <i>J</i> 2.0), 3.35 t (2H, C <u>H₂</u> NEt ₂ , ⁵ <i>J</i> 2.0); $\delta_{\text{C}:}$ 12.2 (CH ₂ CH ₃), 43.2 (C, NCH ₃), 46.4 (N <u>C</u> H ₂ CH ₃), 39.9 (NCH ₂), 47.2 (NCH ₂), 78.7 and 78.9 (C=C)				
IIIa	890, 920, 1650, 3015, 3085 (C=C); 2250 (C=C)	$\delta_{\text{H}:}$ 1.01 t (6H, CH ₂ C <u>H₃</u> , ³ <i>J</i> 7.2), 2.15 s (6H, NCH ₃), 2.27 m (2H, CH ₂), 2.46 q (4H, NC <u>H₂</u> CH ₃ , ³ <i>J</i> 7.2), 3.29 d.d.t (1H, CH, ³ <i>J</i> 8.0, 7.2, ⁵ <i>J</i> 1.8), 3.37 d (2H, NCH ₂ , ⁵ <i>J</i> 1.8), 4.98 d.d.t (1H, =CH ₂ , ³ <i>J</i> 10.2, ² <i>J</i> 2.0, ⁴ <i>J</i> 1.2), 5.05 d.d.t (1H, =CH ₂ , ³ <i>J</i> 17.2, ² <i>J</i> 2.0, ⁴ <i>J</i> 1.5), 5.80 d.d.t (1H, =CH, ³ <i>J</i> 17.2, 10.2, 6.8)				
IIIb	915, 975, 1640, 3015, 3085 (C=C); 2245 (C≡C)	$δ_{\rm H}$: 1.01 t (6H, CH ₂ CH ₃ , ³ J 7.1), 1.74 t (3H, CH ₃ , ⁴ J 1.2), 2.16 s (6H, NCH ₃), 2.19–2.27 m (2H, CH ₂), 2.45 q (4H, NCH ₂ CH ₃ , ³ J 7.1), 3.36 d (2H, NCH ₂ , ⁵ J 1.8), 3.43 d.d.t (1H, CH, ³ J 8.3, 7.0, ⁵ J 1.8), 4.72 q (2H, =CH ₂ , ⁴ J 1.2)				
IIIc	920, 1640, 3015, 3090 (C=C); 2240 (C=C)	$δ_{\rm H}$: 1.03 t (6H, CH ₂ CH ₃ , ³ J 7.1), 1.06 d (3H, CH ₃ CH, ³ J 6.7), 2.14 s (6H, NCH ₃), 2.19–3.32 m (1H, CH ₂ CH ₃), 2.48 q (4H, NCH ₂ CH ₃ , ³ J 7.1), 2.94 d.t (3H, NCH, ³ J 10.1, ⁵ J 1.8), 3.37 d (2H, CH ₂ NEt ₂ , ⁵ J 1.8), 4.87–5.05 m (2H, CH ₂), 5.78 d.d.d (1H, =CH, ³ J 17.2, 10.4, 7.5)				
IIId	920, 1640, 3025, 3085 (C=C); 720, 765, 1500, 1600, 3020, 3065 (C ₆ H ₅); 2235 (C=C)	$ \begin{split} &\delta_{H:} 1.02 \text{ t (6H, CH}_2\text{C}_{\underline{H}_3}, {}^{3}J 7.1), 2.21 \text{ s (6H, NCH}_3), 2.50 \text{ q (4H, NC}_{\underline{H}_2\text{C}}\text{H}_3, {}^{3}J 7.1), 3.19 \text{ d (2H, C}_{\underline{H}_2\text{NEt}_2}, {}^{5}J 2.0), 3.34 \text{ d.d.t (1H, CH, }^{3}J 11.0, 7.6, {}^{4}J 1.0), 3.59 \text{ d.t (1H, NCH, }^{3}J 11.0, {}^{5}J 2.0), 4.87 \text{ d.d.d (1H, =CH}_2, {}^{3}J 18.0, {}^{2}J 1.8, {}^{4}J 1.0), 4.95 \text{ d.d.d (1H, =CH}_2, {}^{3}J 10.3, {}^{2}J 1.8, {}^{4}J 1.0), 6.08 \text{ d.d.d (1H, =CH, }^{3}J 18.0, 10.3, {}^{7}G), 7.11-7.34 \text{ m (5H, C}_{6}H_5) \end{split} $				

60 ml min⁻¹]. The TLC analysis was carried out on Silufol UV-254 plates in an *n*-butanol–ethanol–water–acetic acid system (10:7:6:4) detecting with iodine vapor.

The starting 1-dimethylamino-4-diethylaminobut-2yne was obtained by the Mannich reaction [8].

Synthesis of ammonium salts IIa–IId. To a solution of 0.045 mol of 1-dimethylamino-4-diethyl-aminobut-2-yne in 10 ml of anhydrous ether was added dropwise 0.015 mol of the corresponding 2-alkenyl halide dissolved in 10 ml of anhydrous ether. The reaction mixture was kept for 24 h at room temperature. The resulting salt was washed several times with anhydrous ether and dried in a desiccator over CaCl₂. The obtained compounds are waxy substances.

The Stevens rearrangement of salts IIa–IId. To a suspension of 0.01 mol of II in 10 ml of anhydrous benzene was added by portions 0.02 mol of the powdered potassium hydroxide. The mixture was carefully triturated until the exothermic reaction completed. After adding 2–3 drops of methanol the mixture was refluxed for 10 min. Then the mixture was cooled and treated with water. The benzene layer was separated, and the aqueous layer was extracted twice

with ether. The combined extracts were dried with magnesium sulfate. After the solvent removal the residue was distilled in a vacuum.

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