## Stevens Rearrangement of Ammonium Salts Containing 2-Propynyloxy or *tert*-Butoxycarbonylmethyl Groups

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**Abstract** — The Stevens rearrangement of ammonium salts containing 2-alkenyl, 2-alkynyl, or benzyl groups along with 2-propynyloxy or *tert*-butoxycarbonylmethyl was studied. Under the action of a suspension of sodium phenolate in benzene the salts containing a 2-propynyloxycarbonylmethyl group form 2-propynyl esters of 2-dialkylamino-4-pentenoic acids, whereas with sodium methylate as the basic reagent, rearrangement is preceded by an almost complete transesterification. The salts containing a *tert*-butoxycarbonylmethyl group undergo almost no transesterification under the action of sodium methylate. The *tert*-butyl fragment in the ester group of the salt with a benzyl group exerts a fairly strong effect on the regiochemistry of the rearrangement and on the prototropic isomerization of the 3,2-Stevens rearrangement of the salts with 2-butynyl or 3-phenyl-2-propynyl groups.

Ammonium salts containing an alkoxycarbonylmethyl group undergo complete hydrolysis by the ester group under the action of alkali metal hydroxides [1], whereas sodium alcoholates produce their transesterification [2, 3]. Appropriate choice of the basic component may allow rearrangement without transesterification. Kocharyan *et al.* could effect rearrangement of allyldimethyl(methoxycarbonyl)ammonium bromide without transesterification under the action of sodium phenolate [3].

The present work was devoted to the Stevens rearrangement of ammonium salts **Ia–Ip** containing 2-propynyloxy- or *tert*-butoxycarbonylmethyl groups. The salts were prepared in high yields by reactions of unsaturated tertiary amines with propynyl [4] (**Ia–Ig**) or *tert*-butyl [5] (**Ih–II**) esters of monochloroacetic acid (Table 1).

$$R_{2}^{1}NCHR^{2}CR^{3}=CR^{4}R^{5}+CICH_{2}COOR^{6}\longrightarrow R_{2}^{1}N \stackrel{CHR^{2}CR^{3}=CR^{4}R^{5}}{Ci} \xrightarrow{R^{7}ONa} \xrightarrow{R^{4}R^{5}CCR^{3}=CHR^{2}}{R_{2}^{1}NCHCOOR^{6}}$$

$$Ia-II \qquad IIa-III$$

It was shown that the reaction of salts **Ia–If** with a benzene suspension of sodium phenolate takes exclusively the way of the 3,2-Stevens rearrangement to form propynyl 2-dialkylamino-4-pentenoates **IIa–IIf** (Table 2). The rearrangement of salt **Ig** under the same conditions yields 2-propynyl 2-dimethylamino-4,7-octadienoate (**IIg**) (Table 2).

 $\xrightarrow{CH_2CH=CH_2}_{(CH_3)_2N} \xrightarrow{CH_2CH=CH_2}_{(CH_3)_2N} \xrightarrow{CH_2COOCH_2C\equiv CH}_{Ig} \xrightarrow{C_6H_5ONa}_{benzene} (CH_3)_2NCH-CH_2CH=CHCH_2CH=CH_2}_{COOCH_2C\equiv CH}_{IIg}$ 

<u></u>	<b>V</b> : 11.0/		Found, %		Earneyla	Calculated		
Comp. no.	rield, %	mp, °C	Cl	N	Formula	Cl	N	
Ia Ib Ic Id Ie If Ig Ih I	75 80 82 85 86 87 78 90	a a 125–128 118–120 a 123–125 96–98	16.08 15.20 15.18 12.02 12.98 12.29 13.65 15.01	6.37 6.01 5.99 4.65 5.11 4.69 5.37 5.89	$\begin{array}{c} C_{10}H_{16}CINO_2\\ C_{11}H_{18}CINO_2\\ C_{11}H_{18}CINO_2\\ C_{16}H_{20}CINO_2\\ C_{14}H_{22}CINO_2\\ C_{15}H_{24}CINO_2\\ C_{13}H_{20}CINO_2\\ C_{11}H_{22}CINO_2\\ C_{11}H_{22}CINO_2\\$	16.29 15.30 15.30 12.07 13.04 12.40 13.75 15.07	6.43 6.05 6.05 4.77 5.15 4.90 5.43 5.94	
li Ij Ik Il Im In Io Ip	89 86 70 94 68 93 60 92	105-107 $132-133$ $151-153$ $163-164$ $135-137$ $145-146$ $125-126$ $65-66$	14.15 14.19 12.21 11.45 14.28 11.41 24.94 12.40	5.58 5.57 4.80 4.38 5.59 4.48 4.88 4.88	$\begin{array}{c} C_{12}H_{24}CINO_2\\ C_{12}H_{24}CINO_2\\ C_{15}H_{28}CINO_2\\ C_{17}H_{26}CINO_2\\ C_{12}H_{22}CINO_2\\ C_{17}H_{24}CINO_2\\ C_{12}H_{23}Cl_2NO_2\\ C_{15}H_{24}CINO_2\\ \end{array}$	14.23 14.23 12.26 11.39 14.34 11.47 25.00 12.43	5.61 5.61 4.84 4.49 5.66 4.52 4.93 4.90	

Table 1. Yields, constants, and elemental analyses of salts Ia-Ip

<sup>a</sup> Hygroscopic substances.

Table 2. Yields, constants, and elemental analyses of products of rearrangement of salts Ia-Ip

Starting	Rearrangement	Yield,	mp, °C	n <sub>D</sub> <sup>20</sup>	Found, %		Formula	Calculated			
salt no.	product no.	%	( <i>p</i> , mm Hg)		С	Н	N	Formula	С	Н	N
Ia Ib Ic Id Ie If Ig Ih Ii Ij Ik Il	IIa IIb IIc IId IIf IIf IIg IIh IIi IIj IIk III	32 30 29 40 34 35 47 51 66 46 52 70 48	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.4752 1.4792 1.4747 1.4948 1.4898 1.4835 1.4886 1.4330 1.4356 1.4360 1.4554 a 1.4554 a	65.90 67.15 67.80 75.02 71.03 72.66 70.98 65.99 65.83 67.21 70.98 75.01 (8.02	8.42 8.45 8.53 6.88 8.62 8.87 8.35 10.41 10.37 10.53 10.52 8.42 0.82	7.33 7.44 6.88 5.15 6.09 5.25 5.97 7.29 6.90 6.39 5.41 4.77 6.41	$\begin{array}{c} C_{10}H_{15}NO_2\\ C_{11}H_{17}NO_2\\ C_{11}H_{17}NO_2\\ C_{16}H_{19}NO_2\\ C_{15}H_{23}NO_2\\ C_{13}H_{19}NO_2\\ C_{11}H_{21}NO_2\\ C_{12}H_{23}NO_2\\ C_{12}H_{23}NO_2\\ C_{12}H_{23}NO_2\\ C_{15}H_{27}NO_2\\ C_{15}H_{27}NO_2\\ C_{17}H_{25}NO_2\\ C_{11}H_{25}NO_2\\ C_{11$	66.30 67.70 74.71 71.49 72.29 70.59 66.33 67.60 67.60 71.15 74.18 68.25	8.29 8.72 8.72 7.39 8.94 9.24 8.60 10.55 10.79 10.79 10.67 9.09	7.73 7.18 7.18 5.45 5.96 5.62 6.33 7.04 6.57 6.57 5.53 5.09
Im In Io Ip	IIM IIn IIo IIp	48 54 58 49	$\begin{array}{c} 67-68 & (3) \\ 143-142 & (2) \\ 64-65 & (1) \\ 110-111 & (1) \end{array}$	1.4578 1.4626 1.4840 1.4844	68.02 74.38 68.67 71.93	9.82 8.53 9.55 9.11	6.41 5.40 6.43 5.18	$C_{12}H_{21}NO_2$ $C_{17}H_{23}NO_2$ $C_{12}H_{21}NO_2$ $C_{15}H_{23}NO_2$	68.25 74.72 68.25 72.30	9.95 8.42 9.95 9.24	6.63 5.13 6.63 5.62

<sup>a</sup> Compound III is a crystalline substance, mp 44-45°C.

The example of salt Ia was used to show that under the action of sodium methylate rearrangement is accompanied by an almost complete transesterification. According GLC and <sup>1</sup>H NMR data, the content of the

rearrangement-without-transesterification product in the mixture is 5.5%.

The example of salts of Ih-Ip containing a tert-

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 74 No. 8 2004

 $(CH_3)_2 \overset{+}{\underset{Cl}{N}} \overset{CH_2CH=CH_2}{(CH_3CH_2C)} \xrightarrow{CH_3ONa} (CH_3)_2 \overset{-}{\underset{benzene}{N}} (CH_3)_2 \overset{-}{\underset{benzene}{N}} \overset{CH_2CH=CH_2}{(CH_3)_2 N} \xrightarrow{LH_2CH=CH_2} IIa$ 

butoxycarbonylmethyl substituent was used to elucidate the effect of steric and electronic factors on the Stevens rearrangement and rearrangement–transesterification product ratio. As known, *tert*-butyl esters of carboxylic acids are hardly transesterified [6]. We found that salts **Ih–II** under the action of sodium methylate undergo 3,2-Stevens rearrangement to form *tert*-butyl 2-dialkylamino-4-pentenoates **IIh–III** (Table 2). Therewith, the content of transesterification– rearrangement products in the mixture is no higher than 5–8%. To obtain pure target products, salts **Ih**–**Ip** were subjected to rearrangement under the action of sodium *tert*-butylate in *tert*-butanol.

We earlier showed that the methoxycarbonylmethyl analog of aminoester **III** undergoes thermal isomerization to form a 1,2-Stevens rearrangement product [7]. It was found that aminoester **III** is more susceptible to thermal isomerization than its methoxycarbonylmethyl analog, which appears to be explained by the steric effect of the ester *tert*-butyl group (Tables 2 and 3).



The rearrangement of 2-butynyl- and 3-phenyl-2propynyl-containing salts **Im** and **In** under the action of a basic agent gives rise to allenic aminoesters **IIm** and **IIn**. It should be noted that with sodium methylate or *tert*-butylate as basic agents, the regiochemistry of the rearrangement of these salts is the same (3,2 rearrangement). However, rearrangement products **IIm** and **IIn** with a *tert*-butoxycarbonyl group undergo no allene–diene prototropic isomerization, as observed earlier [8], whereas the transesterification–rearrangement product isomerizes into conjugated diene **II'm**. The content of compound **II'm** in the mixture is 7% (GLC). With salt **In**, we failed to isolate the dienic aminoester because of its tarring [8]. The different behaviors of the allenic methyl and *tert*-butyl esters can be explained in terms of the steric effect of the *tert*-butyl group that prevents access of the basic reagent to the  $\alpha$ -proton of the 3,2-rearrangement product and renders isomerization impossible.

With salt **Ip** containing a 3-chloro-2-butenyl group, two rearrangement pathways (a and b) are theoretically possible. The formation of 1,3-dienic aminoester **IIp** from salt **Ip** rules out pathway b that leads to allenic aminoester **IIm**, as with salt **Im**.

Table 3. IR and <sup>1</sup>H NMR spectra of compounds IIa–IIp and II'l

Comp. no.	IR spectrum, v, cm <sup>-1</sup>	<sup>1</sup> H NMR spectrum (CCl <sub>4</sub> ), δ, ppm ( <i>J</i> , Hz)
IIa	915, 985, 1640, 3030, 3085 (CH=CH <sub>2</sub> ); 1075, 1130, 1730 (COO); 2130, 3300 (C≡CH)	2.23 s (6H, NCH <sub>3</sub> ), 1.9–2.55 m (2H, CH <sub>2</sub> ), 2.65–3.60 m (2H, NCH, $\equiv$ CH), 4.20 m (2H, OCH <sub>2</sub> ), 4.40–5.40 m (2H, CH <sub>2</sub> =), 5.40–6.20 m (1H, CH=)
IIb	890, 1640, 3085 (C=CH <sub>2</sub> ); 1040, 1070, 1150, 1730 (COO); 2125, 3300 (C≡CH)	1.77 s (3H, CH <sub>3</sub> ), 2.22–2.53 m (2H, CH <sub>2</sub> ), 2.34 s (6H, NCH <sub>3</sub> ), 2.72 m (1H, $\equiv$ CH), 3.43 t (1H, NCH, <i>J</i> 7.2), 4.12 m (2H, OCH <sub>2</sub> ), 4.77 m (2H, CH <sub>2</sub> =)
IIc	920, 990, 1640, 3030, 3085 (CH=CH <sub>2</sub> ); 1070, 1130, 1730 (COO); 2120, 3300 (C≡CH)	0.71 and 0.83 d (3H, $CH_3$ CH, $J$ 7.0), 2.26 s (6H, NCH <sub>3</sub> ), 2.71 m (1H, $\equiv$ CH), 2.8 m (NCHCH), 4.50–4.72 m (2H, OCH <sub>2</sub> ), 4.80–5.20 m (2H, CH <sub>2</sub> =), 5.20–6.03 m (1H, CH=)

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 74 No. 8 2004

Table 5. (Conta.)	Table	3.	(Contd.)
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Comp. no.	IR spectrum, v, cm <sup>-1</sup>	<sup>1</sup> H NMR spectrum (CCl <sub>4</sub> ), $\delta$ , ppm ( <i>J</i> , Hz)
IId	700, 770, 1600, 3030, 3090 ( $C_6H_5$ ); 915, 985, 1640 (CH=CH <sub>2</sub> ); 1130, 1730 (COO); 2120, 3300 (C=CH)	2.32 s (6H, CH <sub>3</sub> ), 3.05–4.20 m (5H, CH <sub>2</sub> , CHCH, NCH), 4.79 m (2H, CH <sub>2</sub> =), 5.42–6.03 m (1H, CH=), 7.20 s (5H, C <sub>6</sub> H <sub>5</sub> )
IIe	920, 980, 1640, 3030, 3085 (CH=CH <sub>2</sub> ); 1025, 1140, 1730 (COO); 2120, 3305 (C≡CH)	0.72 and 0.85 d (3H, CH <sub>3</sub> CH, J 7.0), 1.03–1.97 m (6H, $\beta$ ,γ-CH <sub>2</sub> ), 2.05–2.65 m (4H, α-CH <sub>2</sub> ), 2.75 m (3H, NCHCH, =CH), 4.45–4.70 m (2H, OCH <sub>2</sub> ), 5.20 m (2H, CH <sub>2</sub> =), 5.65–6.20 m (1H, CH=)
IIf	915, 985, 1640, 3025, 3085 (CH=CH <sub>2</sub> ); 1070, 1130, 1730 (COO); 2125, 3305 (C≡CH)	0.93 and 0.98 s (6H, CH <sub>3</sub> C), 1.2–1.7 m (6H, $\beta$ , $\gamma$ -CH <sub>2</sub> ), 2.05–2.65 m (4H, $\alpha$ -CH <sub>2</sub> ), 2.71 m (1H, =CH), 2.85 s (1H, NCH), 4.42–4.68 m (2H, OCH <sub>2</sub> ), 5.15 m (2H, CH <sub>2</sub> =), 5.72–6.30 m (1H, CH=)
IIg	920, 990, 1640, 1645, 3035, 3085 (CH=CH <sub>2</sub> , CH=CH); 1070, 1135, 1730 (COO); 2130, 3300 (C≡CH)	2.28 s (6H, NCH <sub>3</sub> ), 2.20–2.50 m (4H, CH <sub>2</sub> ), 3.18 t (1H, NCH, J 7.3 ), 4.15 s (2H, OCH <sub>2</sub> ), 4.4–6.2 m (5H, CH <sub>2</sub> =, CH=)
IIh	925, 990, 1630, 1830, 3015, 3085 (CH=CH <sub>2</sub> ); 1035, 1060, 1250, 1710 (COO)	1.29 s [9H, C(CH <sub>3</sub> )3], 2.17 s (6H, NCH <sub>3</sub> ), 1.85–2.25 m (2H, CH <sub>2</sub> ), 2.95 t (1H, NCH, J 8.0), 4.55–5.10 m (2H, CH <sub>2</sub> =), 5.20–5.65 m (1H, CH=)
IIi	890, 1630, 1800, 3080 (C=CH <sub>2</sub> ); 1035, 1065, 1245, 1705 (COO)	1.19 s [9H, C(CH <sub>3</sub> )3], 1.43 d.d (3H, CH <sub>3</sub> C=, $J_1$ 0.8, $J_2$ 1.2), 1.80–2.09 m (2H, CH <sub>2</sub> ), 2.1 s (6H, NCH <sub>3</sub> ), 2.89 t (1H, NCH, $J$ 7.8), 4.20 m (2H, CH <sub>2</sub> =)
IIj	920, 990, 1625, 1830, 3015, 3085 (CH=CH <sub>2</sub> ); 1035, 1065, 1250, 1705 (COO)	0.72 d and 0.83 d (3H, $CH_3CH$ , J 7.0), 1.25 s and 1.29 s [9H, $C(CH_3)_3$ ], 2.24 s and 2.29 s (6H, $NCH_3$ ), 2.60 m (1H, $CH_3CH$ ), 3.40 d.d (1H, $NCH$ , J 10.2), 4.60–5.10 m (2H, $CH_2=$ ), 5.20–6.1 m (1H, $CH=$ )
IIk	925, 985, 1625, 1825, 3015, 3085 (CH=CH <sub>2</sub> ); 1035, 1065, 1250, 1710 (COO)	0.71 d and 0.82 d (3H, $CH_3CH$ , J 7.0), 1.1–1.6 m [15H, C(CH <sub>3</sub> )3, $\beta$ , $\gamma$ -CH <sub>2</sub> ], 2.0–2.7 m (5H, CH <sub>3</sub> CH, $\alpha$ -CH <sub>2</sub> ), 3.38 d.d (1H, NCH, J 10.3), 4.50–5.10 m (2H, CH <sub>2</sub> =), 5.20–6.05 m (1H, CH=)
III	690, 765, 1600, 1668, 3035, 3070 (C <sub>6</sub> H <sub>5</sub> ); 925, 990, 1625, 1830, 3015, 3085 (CH=CH <sub>2</sub> ); 1035, 1070, 1250, 1705 (COO)	1.19 s and 1.25 s [9H, C(CH <sub>3</sub> )3], 2.20 s (6H, NCH <sub>3</sub> ), 3.81– 4.02 m (2H, CHCH), 4.80–5.20 m (2H, CH <sub>2</sub> =), 5.81–6.35 m (1H, CH=), 7.15 m (5H, C <sub>6</sub> H <sub>5</sub> )
IIm	870, 1945 (C=C=CH <sub>2</sub> ); 1035, 1070, 1250, 1705 (COO)	1.30 s [9H, C(CH <sub>3</sub> )3], 1.67 t (3H, CH <sub>3</sub> C=, $J$ 3.21), 2.32 s (6H, NCH <sub>3</sub> ), 3.58 d (1H, NCH, $J$ 3.2), 4.52 m (2H, CH <sub>2</sub> =)
IIn	690, 770, 1600, 1668, 3035, 3070 (C <sub>6</sub> H <sub>5</sub> ); 870, 1940 (C=C=CH <sub>2</sub> ); 1035, 1070, 1250, 1705 (COO)	1.41 s [9H, C(CH <sub>3</sub> )3], 2.41 s (6H, NCH <sub>3</sub> ), 4.12 d (1H, NCH, $J$ 3.2), 5.18 s (2H, CH <sub>2</sub> =), 7.21–7.50 m (5H, C <sub>6</sub> H <sub>5</sub> )
IIo	920, 970, 990, 1620, 1630, 1825, 3015, 3085 (C=C-CH=CH <sub>2</sub> ); 1035, 1070, 1250, 1705 (COO)	1.20 s [9H, C(CH <sub>3</sub> )3], 1.60 s (3H, CH <sub>3</sub> C=), 2.20 s (6H, NCH <sub>3</sub> ), 4.1–5.1 m (2H, CH <sub>2</sub> =), 5.8–6.7 m (1H, CH=)
IIp	690, 770, 1600, 1667, 3035, 3070 (C <sub>6</sub> H <sub>5</sub> ); 1035, 1070, 1250, 1710 (COO)	1.18 s [9H, C(CH <sub>3</sub> )3], 2.19 s (6H, NCH <sub>3</sub> ), 2.8–3.2 m (2H, CH <sub>2</sub> ), 3.67 d.d (1H, NCH, $J_1$ 4.5, $J_2$ 9.0), 7.23 m (5H, C <sub>6</sub> H <sub>5</sub> )
11'1	690, 770, 1600, 1668, 3035, 3070 (C <sub>6</sub> H <sub>5</sub> ); 975, 1630 (CH=CH); 1035, 1070, 1250, 1710 (COO)	1.19 s [9H, C(CH <sub>3</sub> )3], 2.08 s (6H, NCH <sub>3</sub> ), 2.0–2.4 m (2H, CH <sub>2</sub> ), 3.02 t (1H, NCH, J 7.0), 5.7–6.6 m (2H, CH=CH), 7.0 m (5H, C <sub>6</sub> H <sub>5</sub> )

The resulting data suggest that the 3-chloro-2butenyl group is directly involved into the rearrangement of salt **Io** to form a chlorine-containing aminoester that further eliminates hydrogen chloride, yielding dienic aminoester **IIo**.



According to <sup>1</sup>H NMR data, salt **Ip** that contains *tert*-butoxycarbonylmethyl and benzyl groups under the action of sodium *tert*-butylate of the possible Stevens and Sommelet rearrangements is involved exclusively into the former one.



At the same time, it should be noted that the methoxycarbonylmethyl analog of salt **Ip** under the action of sodium methylate forms a mixture of Stevens and Sommelet rearrangement products in a 52:48 ratio [9].

The rearrangement of allyl(methoxycarbonylmethyl)dimethylammonium bromide under the action of sodium *tert*-butylate in *tert*-butanol gave 55% of transesterification–rearrangement product **IIh** and 6.3% of the rearrangement-without-transesterification product (GLC).

$$(CH_3)_2N \xrightarrow{+} CH_2CH=CH_2 \xrightarrow{(CH_3)_3CON_a} (CH_3)_2NCHCH_2CH=CH_2 + (CH_3)_2NCHCH_2CH=CH_2$$
  
$$\stackrel{-}{Br} CH_2COOCH_3 \xrightarrow{(CH_3)_3COH} (CH_3)_2NCHCH_2CH=CH_2 + (CH_3)_2NCHCH_2CH=CH_2$$
  
$$COOC(CH_3)_3 \xrightarrow{(COOCH_3)} (COOCH_3)$$

IIh

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 74 No. 8 2004

To find out whether transesterification precedes rearrangement, aminoester **IIa** was treated with sodium methylate under the rearrangement conditions of salt **Ia**. The lack of transesterification products (<sup>1</sup>H NMR and GLC data) points to the fact rearrangement is preceded by transesterification. The structure of the rearrangement products and their purity were proved by <sup>1</sup>H NMR and IR (Table 3) and GLC data.

## **EXPERIMENTAL**

The IR spectra were obtained on UR-20 and Specord IR-75 spectrophotometers. The <sup>1</sup>H NMR spectra were measured on Perkin–Elmer R-12B (60 MHz) and Varian Mercury-300 (300 MHz) spectrometers in  $CCl_4$  solutions, internal reference TMS. Gas chromatography was performed on an LKhM-80 instrument, thermal conductivity detector, column temperature 100–220°C (16 deg/min), packing 10% Apiezon L on Inerton AW (0.20–0.25 mm), carrier gas helium, rate 60 ml/min.

**Rearrangement of salts Ia–Ip.** A mixture of 0.01 mol of salt **Ia–Ip** and 0.02 mol of sodium phenolate or methylate in 15–20 ml of absolute benzene or sodium *tert*-butylate in 15 ml of absolute *tert*-butanol was intermittently stirred and ground. After heat release had discontinued, the mixture was heated for 15–20 min at 50–55°C, cooled to room temperature, and diluted with water and diethyl ether. The ether layer was separated, and the aqueous layer was extracted with two portions of ether. The combined ethereal extracts were dried over magnesium sulfate, the solvents were removed, and the residue was distilled in a vacuum (Table 2).

With salts **Ih–Im** and **Io**, the residue was subjected to GLC analysis to measure the contents of transesterification–rearrangement and rearrangement-without-transesterification products. The ratio of these two products in the mixture is (5.5–7):(93–94.5)%.

**Rearrangement of allyl(methoxycarbonylmethyl)dimethylammonium chloride under the action of sodium** *tert***-butylate. Sodium** *tert***-butylate obtained by heating of 0.04 mol of sodium in 30 ml of absolute** *tert***-butanol was added to 0.02 mol in 15 ml of absolute benzene. After heat release had discon-** tinued, the mixture was heated for 15 min at 50–55°C and diluted with ether and water. Further workup was performed as described above. According to GLC data, the transesterification-rearrangement and rearrangement-without-transesterification product ratio is (93–95):(5-6)%. Distillation gave 2.1 g (53%) of *tert*-butyl 2-dimethylamino-4-pentenoate (**IIh**), bp 55–57°C (3 mm Hg),  $n_D^{20}$  1.4332 (Table 2).

**Thermal isomerization of aminoester III.** Aminoester **III.** 0.015 mol, was heated at 175–180°C for 12 h in an ampule and then treated with diethyl ether. The solvent was removed to obtain 3.5 g (85%) of *tert*-butyl 2-dimethylamino-5-phenyl-4-pentenoate (**III**), bp 120–122°C (1 mm Hg),  $n_D^{20}$  1.5008 (Table 2). Found, %: C 74.58; H 9.38; N 5.42. C<sub>17</sub>H<sub>25</sub>NO<sub>2</sub>. Calculated, %: C 74.18; H 9.09; N 5.09.

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