Russian Journal of General Chemistry, Vol. 74, No. 9, 2004, pp. 1376–1382. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 9, 2004, pp. 1484–1490.
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1,5-Hydride Shift in Products of Stevens 3,2-Rearrangement of Methyl(alkyl)(alkoxycarbonylmethyl)-(3-phenyl-2-propynyl)ammonium Bromides

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Received November 5, 2002

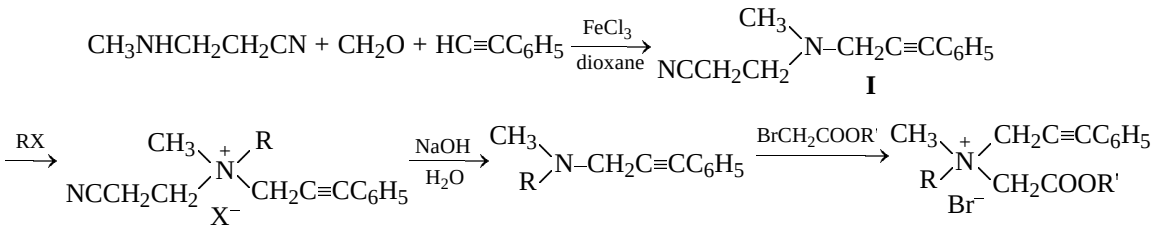
Abstract — The products of the Stevens 3,2-rearrangement of ammonium salts containing methyl and other (ethyl, propyl, butyl) alkyl groups along with 3-phenylprop-2-ynyl, under the reaction conditions undergo, roughly by half, intramolecular hydride shift with intermediate formation of immonium salts. The latter convert into enamino esters whose hydrolysis involving alkyl groups at the nitrogen atom gives rise to lower aliphatic aldehydes and the corresponding amino esters. Treatment with dilute hydrochloric acid of the reaction mixture containing enamino esters results in formation of hydrogenated and nonhydrogenated alkyl esters of α-keto acids. This mixture was reacted with concentrated hydrochloric acid to obtain 3-hydroxy-5-methyl-4-phenylfuran-2(5*H*)-one from the nonhydrogenated keto ester and to isolate pure the hydrogenated keto ester.

Earlier we showed that the products of the Stevens 3,2-rearrangement of ammonium salts containing methoxy(ethoxy)carbonylmethyl, pent-4-en-2-ynyl, and alkyl (alkyl ≥ C_2H_5) groups undergo 1,5-hydride shift to form hydrogenated and nonhydrogenated keto esters [1, 2].

Proceeding with this research we synthesized and studied ammonium bromides containing, along with methyl, alkoxycarbonylmethyl, and 3-phenylprop-2-ynyl groups, ethyl, propyl, or butyl groups.

The synthesis of starting amines **IIIa**–**IIIc** (Tables 1 and 2) and target ammonium salts **IVa**–**IVf** (Tables 3 and 4) was performed by Scheme 1.

Scheme 1.



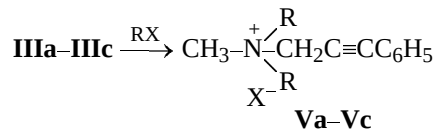
I–**IV**, R = C_2H_5 (**a**), C_3H_7 (**b**), C_4H_9 (**c**); **IV**, R' = CH_3 (**a, c, e**), C_2H_5 (**b, d, f**); **II**, X = Br (**a, b**), I (**c**).

In the synthesis of amines **IIIa**–**IIIc** we made use of the fact that ammonium salts exceptionally easily lose the 2-cyanoethyl group on thermal and alkaline cleavage. According to published data, the thermal cleavage of acrylonitrile begins at 75–80°C and vigorously proceeds at 100–110°C [3]. We found that the retro Michael reaction of (2-cyanoethyl)ammonium salts **IIa**–**IIc** occurs already at 45–50°C. It should be noted that the synthesis of salts **IIa**–**IIc** involves formation of salts **Va**–**Vc** with two identical alkyl groups. The formation of the latter salts can be explained by the fact that salts **IIa**–**IIc** readily split off acrylonitrile to give amines **IIIa**–**IIIc** which further react *in situ* with one more alkyl halide molecule, yielding ammonium salts **Va**–**Vc** (Scheme 2).

Table 1. Yields, constants, and elemental analyses of amines **I** and **IIIa**–**IIIc**

Starting salt	Amine	Yield, %	bp, °C (1 mm Hg)	n_D^{20}	Found, %			Formula	Calculated, %			*M*
					C	H	N		C	H	N	
–	**I**	58	153–156	1.5375	78.39	7.10	13.72	$C_{13}H_{14}N_2$	78.79	7.07	14.14	198
IIa	**IIIa**	52.6	96–99	1.4971	82.67	8.19	7.71	$C_{12}H_{15}N$	83.24	8.67	8.09	173
IIb	**IIIb**	72	97–100	1.5292	82.93	9.53	7.02	$C_{13}H_{17}N$	83.42	9.09	7.49	187
IIc	**IIIc**	52.7	102–105	1.5302	84.07	9.04	6.54	$C_{14}H_{19}N$	83.58	9.45	6.97	201

Scheme 2.



IIIa–**IIIc** $\xrightarrow{RX}$ CH_3–$\overset{+}{N}(R)(R)$–$CH_2C{\equiv}CC_6H_5$ X^-

Va–**Vc**

V, R = C_2H_5 (**a**), C_3H_7 (**b**), C_4H_9 (**c**); X = Br (**a, b**), I (**c**).

To bring ammonium salts **IVa**–**IVf** into Stevens rearrangement, a suspension of sodium alcoholate in ether or benzene was used. The rearrangement results are shown in Table 4 and its proposed directions, in Scheme 3.

Route *A* involves hydride shift in the 3,2-rearrangement products, resulting in formation of immonium salts **VIIa**–**VIIf**. The latter react with base for a mixture of amino esters **VIIIa**–**VIIIf** and their prototropic rearrangement products **IXa**–**IXf** (route *b*) [2]. Route *B* involves exclusively the prototropic rearrangement of the rest part of 3,2-rearrangement products **VIa**–**VIf**, affording amino esters **XIIIa**–**XIIIf**. In both cases, acid treatment of the reaction mixtures gave hydrogenated amino esters **Xa**, **Xb** and keto esters **XIIa**, **XIIb**, as well as nonhydrogented keto esters **XIVa**, **XIVb**, lower aliphatic aldehydes, and primary and secondary amines (Table 4). Keto esters **XIVa**, **XIVb** were also obtained by independent synthesis,

Table 2. Yields, constants, and elemental analyses of salts **Va**–**Vc**

Salt[a]	Yield, %	Found, %		Formula	Calculated, %	
		Br (I)	N		Br (I)	N
Va	23	28.97	5.41	$C_{14}H_{20}BrN$	28.37	4.96
Vb	26	26.52	4.32	$C_{16}H_{24}BrN$	27.03	4.73
Vc	21.5	(26.03)	3.57	$C_{18}H_{28}IN$	(26.62)	2.94

[a] The salts are hygroscopic.

specifically, by the Stevens rearrangement of dimethylalkoxycarbonylmethyl(3-phenyl-2-propynyl)ammonium bromides followed by hydrolysis of the rearrangement products, dienic amino esters (Scheme 4).

Keto ester **XIVa** we prepared earlier [4].

As seen from the ^{1}H NMR spectrum of the Stevens rearrangement products of salt **IVa**, the integral intensity of vinyl proton signals is larger that expected. Furthermore, on the assumption that the hydride shift involves no other intermediates than **VIIa**, the percentage of amine reaction products (83%) should be much lower than is actually observed.

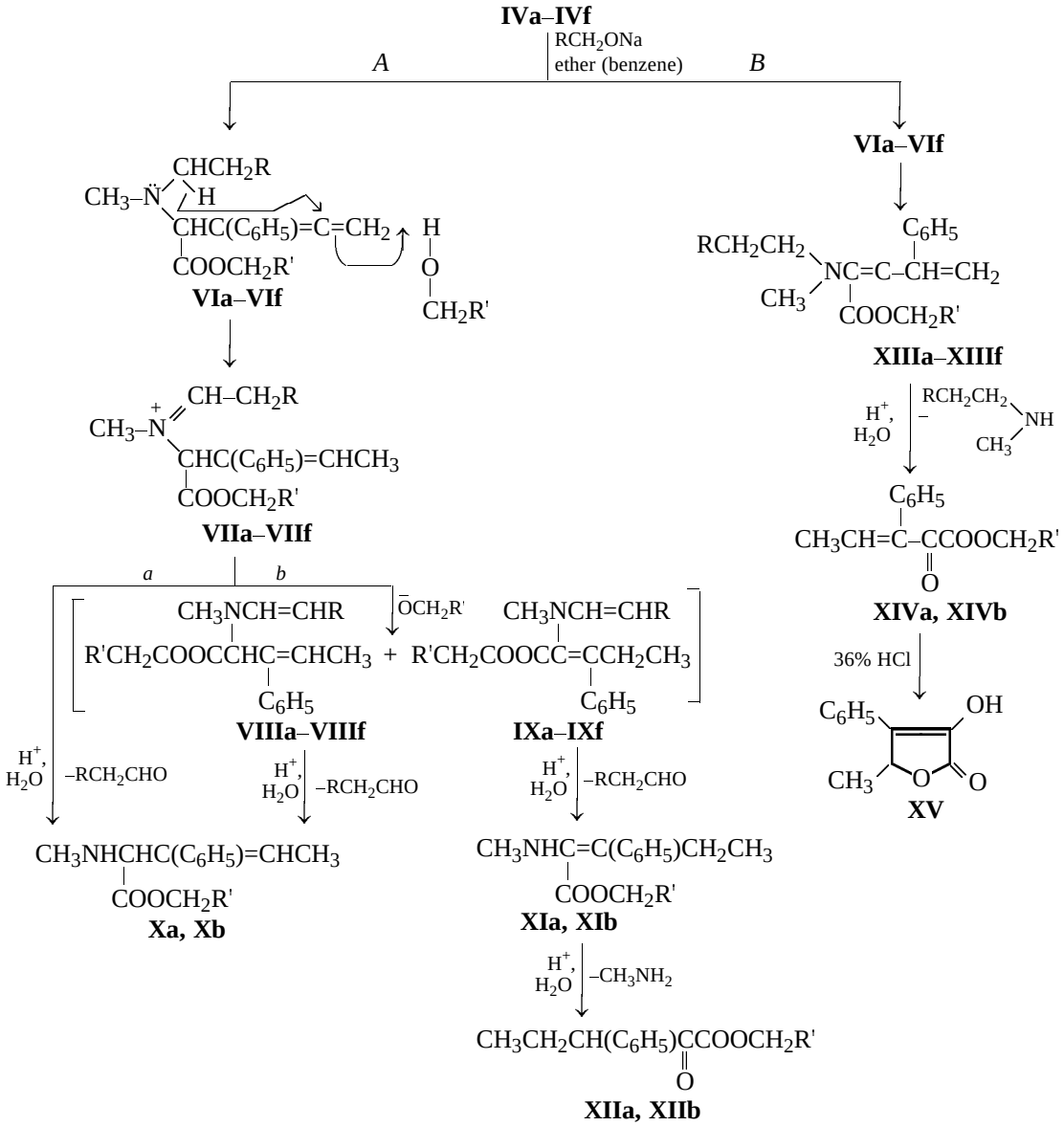
Thus, the obtained evidence suggests that under the action of the basic agent immonium salt **VIIa**

Table 3. Yields, constants, and elemental analyses of salts **IVa**–**IVf**

Salt	mp, °C	Yield, %	IR spectrum, ν, cm^{-1}	Found, %		Formula	Calculated, %	
				Br	N		Br	N
IVa[a]	–	76	1745 (COO), 2230 (C≡C)	24.93	4.90	$C_{15}H_{20}BrNO_2$	25.54	4.29
IVb[a]	–	72	1740 (COO), 2235 (C≡C)	23.90	3.75	$C_{16}H_{22}BrNO_2$	23.53	4.12
IVc	112–114	75	1750 (COO), 2240 (C≡C)	23.13	4.52	$C_{16}H_{22}BrNO_2$	23.53	4.12
IVd	107–109	60	1745 (COO), 2230 (C≡C)	22.12	4.43	$C_{17}H_{24}BrNO_2$	22.60	3.95
IVe	110–111	85	1750 (COO), 2230 (C≡C)	22.20	4.35	$C_{17}H_{24}BrNO_2$	22.60	3.95
IVf	115–116	93	1750 (COO), 2235 (C≡C)	22.29	3.25	$C_{18}H_{26}BrNO_2$	21.74	3.80

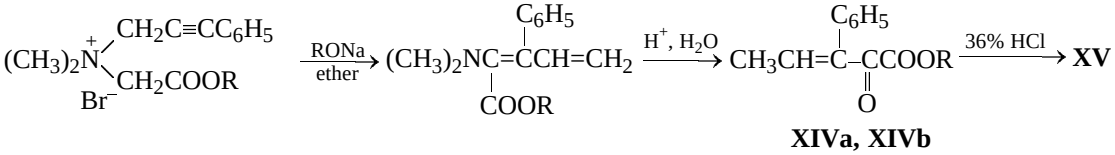
[a] The salts are hygroscopic.

Scheme 3.



IV, VI–IX, XIII, R = R' = H (**a**), R = H, R' = CH_3 (**b**), R = CH_3, R' = H (**c**), R = R' = CH_3 (**d**), R = C_2H_5, R' = H (**e**), R = C_2H_5, R' = CH_3 (**f**); **X–XII, XIV**, R' = H (**a**), CH_3 (**b**).

Scheme 4.



XIV, R = CH_3 (**a**), C_2H_5 (**b**).

mostly converts into amino esters **VIIIa**, **IXa** by route *b*.

Hydrogenated reaction products are partially formed by route *a*. Thus by treatment of the dry reaction residue of salt **IVa** with dilute hydrochloric acid we obtained trace amounts of compounds **Xa**, **XIIa**, as well as acetaldehyde as 2,4-dinitrophenylhydrazone.

The structure of the synthesized compounds was

Table 4. Hydrogenated and nonhydrogenated Stevens rearrangement products of salts **IVa**–**IVf**

Salt	Amino ester	Yield, %	Ratio of hydrogenated and starting amines in the mixture	bp, °C (*p*, mm Hg)	Found, %			Formula	Calculated, %		
					C	H	N		C	H	N
IVa	**IXa**	15.5	93 : 7	97–105 (2)	71.37	7.31	6.13	$C_{13}H_{17}NO_2 + C_{12}H_{15}N$	71.91	7.81	6.49
IVb	**IXb**	14.4	95 : 5	100–108 (1)	73.07	7.71	5.59	$C_{14}H_{19}NO_2 + C_{12}H_{15}N$	72.52	8.17	6.09
IVc	**IXc**	12.7	93 : 7	98–106 (1)	71.31	7.49	6.04	$C_{13}H_{17}NO_2 + C_{13}H_{17}N$	71.97	7.84	6.46
IVd	**IXd**	13	94 : 6	103–109 (1.5)	73.05	7.68	5.74	$C_{14}H_{19}NO_2 + C_{13}H_{17}N$	72.65	8.20	6.08
IVe	**IXe**	15	96 : 4	99–105 (1)	71.06	7.33	7.02	$C_{13}H_{17}NO_2 + C_{14}H_{19}N$	71.69	7.82	6.41
IVf	**IXf**	14.8	93 : 7	102–108 (1)	72.27	7.79	5.68	$C_{14}H_{19}NO_2 + C_{14}H_{19}N$	72.80	8.23	6.07

Table 4. (Contd.)

Salt	Keto esters	**XI** : **XII** ratio, %	Total yield, %	bp, °C (*p*, mm Hg)
IVa	**XIa**–**XIIIa**	45 : 55	33.5	112–118 (3)
IVb	**XIb**–**XIIIb**	42 : 58	36.2	119–125 (2)
IVc	**XIa**–**XIIIa**	26 : 74	40.4	106–112 (1)
IVd	**XIb**–**XIIIb**	21 : 79	41.8	112–116 (1)
IVe	**XIa**–**XIIIa**	39 : 61	43.4	110–116 (2)
IVf	**XIb**–**XIIIb**	43 : 57	50.3	112–117 (1)

Salt	Found, %		Formula	Calculated, %		Aldehyde, %	mp, °C[a]	Amines		
	C	H		C	H			CH_3NH_2, %	CH_3NHR	
									%	R
IVa	58.31	7.43	$C_7H_{10}O_3 + C_7H_{12}O_3$	58.76	7.66	CH_3CHO	163–164	19	23	C_2H_5
IVb	60.71	8.09	$C_8H_{12}O_3 + C_8H_{14}O_3$	61.07	8.40	CH_3CHO	163	18	21	C_2H_5
IVc	58.02	7.92	$C_7H_{10}O_3 + C_7H_{12}O_3$	58.47	8.11	C_2H_5CHO	154	17	20	C_3H_7
IVd	60.55	8.44	$C_8H_{12}O_3 + C_8H_{14}O_3$	60.84	8.74	C_2H_5CHO	154–155	19.5	22	C_3H_7
IVe	57.97	7.52	$C_7H_{10}O_3 + C_7H_{12}O_3$	58.60	7.92	C_3H_7CHO	121–122	22	25	C_4H_9
IVf	61.38	7.91	$C_8H_{12}O_3 + C_8H_{14}O_3$	61.13	8.31	C_3H_7CHO	121–122	21	24.5	C_4H_9

[a] Melting point of 2,4-dinitrophenylhydrazone.

established by ^1H and IR spectroscopy (Table 5), and their purity was controlled by GLC.

EXPERIMENTAL

The IR spectra were recorded on UR-20 and Specord IR-75 instruments. The ^1H NMR spectra were obtained Perkin–Elmer R-12B and Varian Mercury-300 spectrometers at 60 and 300 MHz, internal reference TMS in CCl_4 and D_3CSOCD_3.

Gas chromatography was performed on an LKhM-80 chromatograph, thermal conductivity detector, oven temperature 30–220°C (16 deg min^{-1}), 2000 × 3 mm, 10% of Apieson L on Inerton-AW (0.20–0.25 mm), carrier gas (helium) 60 ml min^{-1}.

***N*-(2-Cyanoethyl)-*N*-methyl-*N*-(3-phenylprop-2-ynyl)amine (I)** was prepared by the Mannich reaction [5] from 54.3 g of *N*-(2-cyanoethyl)-*N*-methylamine, 65.9 g of phenylacetylene, 29.1 g of Paraform, 2 g of $FeCl_3 \cdot 7H_2O$, and 180 ml of dioxane. Yield 31.7 g (58%), bp 154–157°C (1 mm Hg), n_D^{20} 1.5395. Found, %: C 78.36; H 6.68; N 13.69. $C_{13}H_{14}N_2$. Calculated,

Table 5. IR and ^{1}H NMR spectra of compounds **I, IIIa–IIIc, Va–Vc, Xa, Xb, XIIa, XIIb, XIVa**, and **XIV**, **XIVb**

Comp. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz)
I	690, 730, 770, 1610, 3030, 3065, 3085 (C_6H_5), 2240 (C≡C), 2230 (C≡N)	2.11 s (3H, NCH_3), 1.9–3.0 m (4H, NCH_2CH_2), 3.51 s (2H, $NCH_2C{\equiv}C$), 7.18 m (5H, C_6H_5)
IIIa	695, 730, 770, 1605, 3035, 3070, 3085 (C_6H_5), 2240 (C≡C)	1.00 t (3H, CH_3CH_2, *J* 7.1), 2.30 s (3H, NCH_3), 2.50 q (2H, CH_3CH_2), 3.50 s (2H, NCH_2), 7.25–7.41 m (5H, C_6H_5)
IIIb	690, 725, 770, 1610, 3035, 3075, 3080 (C_6H_5), 2240 (C≡C)	0.81 t (3H, $CH_3CH_2CH_2$, *J* 7.0), 1.25 m (2H, $CH_2CH_2CH_3$), 2.30 t (2H, $CH_2CH_2CH_3$, *J* 7.3), 2.33 s (3H, NCH_3), 3.50 s (2H, $CH_2C{\equiv}C$), 7.24–7.40 m (5H, C_6H_5)
IIIc	700, 730, 770, 1610, 3030,3070, 3085 (C_6H_5), 2240 (C≡C)	0.71 t (3H, $CH_3CH_2CH_2CH_2$, *J* 7.1), 1.21 m (4H, $CH_2CH_2CH_2 \cdot H_3$), 2.28 t (3H, NCH_2, *J* 7.3), 2.31 s (3H, NCH_3), 3.51 s (2H, $NCH_2C{\equiv}C$), 7.23–7.40 m (5H, C_6H_5)
Va	690, 760,1595, 3030, 3075 (C_6H_5), 2220 (C≡C)	1.24 t (6H, NCH_2CH_3, *J* 7.0), 3.0 s (3H, NCH_3), 3.42 q (4H, NCH_2CH_3), 4.20 s (2H, $NCH_2C{\equiv}C$), 7.35 m (5H, C_6H_5)
Vb	695, 760, 1598, 3030, 3075 (C_6H_5), 2225 (C≡C)	0.95 t (6H, $NCH_2CH_2CH_3$, *J* 7.1), 1.20 m (4H, $NCH_2CH_2CH_3$), 2.8–3.4 m (7H, $NCH_2CH_2CH_3$, NCH_3), 4.20 s (2H, $NCH_2C{\equiv}C$), 7.37 m (5H, C_6H_5)
Vc	695, 760, 1598, 3030, 3075 (C_6H_5), 2225 (C≡C)	0.93 t (6H, $NCH_2CH_2CH_2CH_3$, *J* 7.1), 1.22 m (8H, $NCH_2CH_2 \cdot CH_2CH_3$), 2.8–3.5 m (7H, $NCH_2CH_2CH_2CH_3$, NCH_3), 4.17 s (2H, $NCH_2C{\equiv}C$), 7.34 m (5H, C_6H_5)
Xa	690, 730, 770, 1610, 3030, 3065, 3085 (C_6H_5), 790, 830, 1640 (CH=C), 1070, 1145, 1240, 1735 (COO), 3330 (NH)	2.36 s (3H, NCH_3), 1.54 br.s (1H, NH), 1.73 d (3H, CH_3CH=, *J* 8), 3.53 s (3H, OCH_3), 4.17 s (1H, NCH), 5.68 q (1H, CH=), 7.16 m (5H, C_6H_5)
Xb	695, 730, 1610, 3035, 3065, 3080 (C_6H_5), 790, 835, 1640, (CH=C), 1070, 1140, 1245, 1735 (COO), 3330 (NH)	1.22 t (3H, CH_3CH_2O, *J* 7), 2.31 s (3H, NCH_3), 1.54 br.s (1H, NH), 1.73 d (3H, CH_3CH=, *J* 8), 3.53 q (2H, CH_3CH_2O), 4.17 s (1H, NCH), 5.68 q (1H, CH_3CH=), 7.15 m (5H, C_6H_5)
XIIa	695, 730, 1610, 3030, 3065, 3085 (C_6H_5), 1675, (C=O), 1075, 1140, 1245, 1735 (COO)	0.85 t (3H, CH_3CH_2, *J* 7), 1.77 and 2.07 m (2H, CH_3CH_2), 3.75 s (3H, OCH_3), 4.29 m (1H, CH), 7.10–7.45 m (5H, C_6H_5)
XIIb	690, 730, 770, 1605, 3035, 3070, 3080 (C_6H_5), 1675 (C=O), 1070, 1140, 1240, 1735 (COO)	0.90 t (3H, CH_3CH_2, *J* 7), 1.23 t (3H, CH_3CH_2O, *J* 7), 1.75 and 2.06 (2H, CH_3CH_2), 4.16 q (2H, CH_3CH_2O), 4.25 m (1H, CH), 7.09–7.44 m (5H, C_6H_5)
XIVa	700, 730, 770, 1610, 3035, 3065, 3080 (C_6H_5) 790, 835, 1640 (CH=C), 1675 (C=O), 1070, 1140, 1240, 1735 (COO)	1.93 d (3H, CH_3CH=, *J* 8), 3.85 s (3H, OCH_3), 7.0 q (1H, CH=), 7.10–7.45 m (5H, C_6H_5)
XIVb	700, 720, 770, 1605, 3035, 3070, 3080 (C_6H_5), 790, 835, 1640 (CH=C), 1675 (C=O), 1070, 1145, 1240, 1735 (COO)	1.32 t (3H, CH_3CH_2O, *J* 7), 1.92 d (3H, CH_3CH=, *J* 8), 4.32 q (2H, CH_3CH_2O), 7.04 q (1H, CH_3CH=), 7.09–7.44 m (5H, C_6H_5)

%: C 78.78; H 7.07; N 14.14. The ^{1}H NMR and IR spectral data are given in Table 5.

***N*-Alkyl-*N*-methyl-*N*-(3-phenylprop-2-ynyl)-amines IIIa–IIIc** *(general procedure).* Alkyl bromide, 0.17 mol, was added to 0.15 mol of amine **I**, and the mixture was heated at 45–50°C for 15–16 h to obtain a mixture of *N*-alkyl-*N*-(2-cyanoethyl)-*N*-methyl-*N*-(3-phenylprop-2-ynyl)- and *N*,*N*-dialkyl-*N*-methyl-*N*-(3-phenylprop-2-ynyl)ammonium halides, that were thoroughly washed with absolute ether, dried, and treated with 0.3 mol of 20% sodium hydroxide. The reaction mixture was heated at 60–65°C for 30 min and then cooled to room temperature and treated with ether (3 × 15 ml). The combined extracts were dried with magnesium sulfate, and amines **IIIa–IIIc** were distilled. The resulting data are given in Table 1. The aqueous layer was acidified with HBr or HI, and the water was removed in a water-jet-pump vacuum. The residue was diluted with absolute alcohol, and the inorganic salt was filtered off. The alcohol was removed by distillation to obtain compounds **Va–Vc** (Table 2).

***N*-Alkyl-*N*-(alkoxycarbonyl)-*N*-methyl-*N*-(3-phenylprop-2-ynyl)ammonium bromides IVa–IVf.**

Alkyl bromoacetate, 0.025 mol, was added dropwise to 0.025 mol of amine **IIIa**–**IIIc** in 5 ml of absolute ether. The mixture was left to stand for 48 h at room temperature. The salt that formed was washed with several portions of absolute ether, filtered, and dried (Table 3).

Rearrangement of salts IVa–IVf. *a.* Sodium alkoxide obtained from 0.06 mol of sodium was added to a suspension of 0.03 mol of salt **IVa**–**IVf** in 20 ml of absolute ether (benzene). The reaction mixture was shaken and ground. When heat release was no longer observed, the mixture was refluxed for 20 min, after which ether and water were added. The combined ether extracts were acidified with 1.5 N HCl. Nonamine reaction products were extracted with ether (3 × 10 ml), the extracts were dried with magnesium sulfate, and the solvent and low-boiling products were distilled off. In the distillate, aldehydes were determined as 2,4-dinitrophenylhydrazones. The residue was distilled in a vacuum to isolate keto esters **XIIa**, **XIIb**, **XIVa**, and **XIVb** (Tables 2 and 4). The aqueous layer was treated with potash (0–5°C), and amine products were extracted with ether (3 × 10 ml), the extracts were dried with magnesium sulfate, and the solvent was removed. Vacuum distillation gave aminoesters **Xa**, **Xb** and the starting amines. The latter were identified and quantified (7–12% in the mixture) by GLC (Table 4). Alkyl- and dialkylamines were salted out (if required) from the reaction residue and extracted with ether, after which they were identified and quantified by GLC (Table 4).

b. Sodium alkoxide obtained from 0.06 mol of sodium was added to a suspension of 0.03 mol of salt **IVa** in 20 ml of absolute ether (benzene). When heat release was no longer observed, the mixture was refluxed for 20–30 min in ether or 10–15 min in benzene. The organic layer was separated, and the solid material was washed with absolute ether (3 × 10 ml). Amine products were determined by titration in the organic layer (83%), and evaporated in a vacuum. The residue was analyzed by GLC, ^{1}H NMR, and IR spectroscopy, after which it was acidified with 1.5 N HCl. Further workup was performed as described in procedure *a*.

Dilute HCl was added to the solid reaction residue, and the resulting mixture was treated with ether (3 × 5 ml), the extract was dried with magnesium sulfate, and the solvent was distilled off. Acetaldehyde was determined in the distillate as 2,4-dinitrophenylhydrazone (yield 3.6%, mp 163–164°C). The sample gives no melting point depression in mixture with an authentic sample. The residue was analyzed by GLC and ^{1}H NMR to identify keto ester **XIIa** using as reference the sample prepared by procedure *a*. The aqueous layer was treated with potash (0–5°C) and ether. The ether extract was dried with magnesium sulfate, and the solvent was distilled off. The residue contained amino ester **Xa** (GLC data).

3-Hydroxy-5-methyl-4-phenyl-furan-2(5*H*)-one (XV) was prepared from 5.1 g of methyl 2-oxo-3-phenylpent-3-enoate (**XIVa**) and conc. HCl by the procedure in [2]. Yield 4 g (84%), mp 140–141°C (from alcohol). IR spectrum, ν, cm^{-1}: 710, 775, 1590, 1705, 1960, 3035, 3085 (C_6H_5), 1130, 1080, 1250, 1745, (COO), 3100–3500 (OH). ^{1}H NMR spectrum, δ, ppm: 1.43 d (3H, CH_3CH, *J* 6.6 Hz), 5.10 q (1H, CH_3CH), 7.52 br.s (1H, OH), 7.4 m (5H, C_6H_5). Found, %: C 69.02; H 5.53. $C_{11}H_{10}O_3$. Calculated %: C 69.47; H 5.26.

Lactone **XV** was also prepared from 4.47 g of ethyl 2-oxo-3-phenylpent-3-enoate (**XIVb**). Yield 3.9 g (82%), mp 140–141°C (from alcohol). The sample gave no melting point depression in mixture with that prepared from keto ester **XIVa**.

Reaction of mixture of keto esters XIIa and XIVa with concentrated hydrochloric acid. Concentrated HCl, 3 ml, was added dropwise with stirring to a 45 : 55 mixture of keto esters **XIIa** and **XIVa**. The resulting mixture was stirred at 55–60°C for 10 h and cooled. The precipitate that formed was filtered off and washed with hexane to obtain 1.1 g (70%) of lactone **XV** (per keto ester **XIVa**), mp 140–141°C (from alcohol). The sample gave no melting point depression in mixture with that prepared from keto ester **XIVb**. The ^{1}H and IR spectral data are given above.

The solvent was removed from the filtrate, and the residue was distilled in a vacuum to obtain 0.64 g (46%) of hydrogenated keto ester **XIIa** (per keto ester **XIIa**), bp 96–98°C (1 mm Hg), n_D^{20} 1.5075. The ^{1}H and IR spectral data are given in Table 5.

In a similar way, by the reaction of a 42 : 58 mixture of keto esters **XIIb** and 3 ml of conc. HCl we obtained 1.16 g (70%) of lactone **XV** (per keto ester **XIVb**), mp 140–141°C (from alcohol) and 0.58 g (41%) of hydrogenated keto ester **XIIb** (per keto ester **XIIb**), bp 107–108°C (1 mm Hg), n_D^{20} 1.5173. The ^{1}H and IR spectral data are given in Table 5.

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