

## Synthesis of Allyl 2-Dialkylamino-4-pentenoates and Their Analogs via Stevens Rearrangement

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**Abstract**—Stevens rearrangement of ammonium salts containing an allyloxycarbonylmethyl group in benzene in the presence of sodium phenoxide yields allyl 2-dialkylamino-4-pentenoates. The rearrangement in the presence of sodium methoxide is accompanied by transesterification to afford methyl 2-dialkylamino-4-pentenoates.

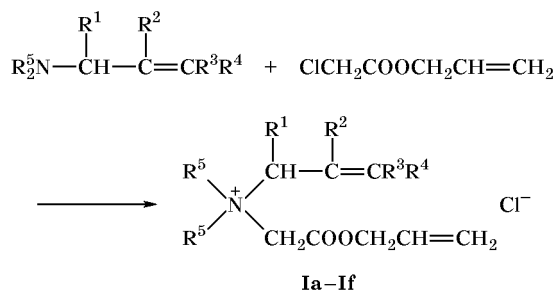
Ammonium salts containing a methoxycarbonylmethyl group are known to undergo rearrangement by the action of sodium methoxide to give methyl 2-dialkylamino-substituted carboxylates in good yields [1]. The rearrangement of the same compounds in the presence of other alkoxides leads to formation of the corresponding transesterification products whose yield attains 75–85% [2]. Using allyl(dimethyl)-(methoxycarbonylmethyl)ammonium bromide as an example, we showed that the reaction in the presence of sodium phenoxide as basic reagent gives the respective rearrangement product without transesterification [2].

In the present work we studied the Stevens rearrangement of ammonium salts **Ia–If** containing an allyloxycarbonylmethyl group. Initial salts **Ia–If**

were synthesized in 86–94% yield by reaction of the corresponding alkenylamines with allyl chloroacetate (Scheme 1, Table 1).

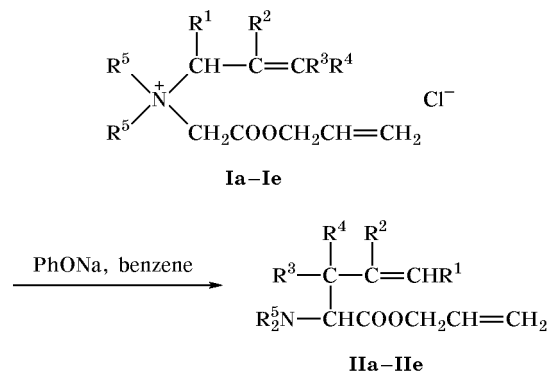
As follows from the data of [2, 3], the Stevens rearrangement of salts **Ia–If** by the action of alkali metal hydroxides should result in complete hydrolysis of the ester group, while the reaction with alkali metal alkoxides should lead mainly to transesterification. Therefore, an appropriate basic reagent for salts **Ia–If** may be sodium phenoxide. In fact, the rearrangement of salts **Ia–Ie** in benzene in the presence of sodium phenoxide was not accompanied by transesterification, and the products were allyl 2-dialkylamino-4-pentenoates **Ia–Ie** (Scheme 2, Table 2).

Scheme 1.



**I**,  $R^1 = R^2 = R^3 = R^4 = H$ ,  $R^5 = Me$  (**a**);  $R^1 = R^3 = R^4 = H$ ,  $R^2 = R^5 = Me$  (**b**);  $R^1 = R^2 = R^3 = H$ ,  $R^4 = R^5 = Me$  (**c**);  $R^1 = R^2 = R^3 = H$ ,  $R^4 = Ph$ ,  $R^5 = Me$  (**d**);  $R^1 = R^2 = H$ ,  $R^3 = R^4 = Me$ ,  $R^5 = (CH_2)_5$  (**e**);  $R^1 = CH_2CH=CH_2$ ,  $R^2 = R^3 = R^4 = H$ ,  $R^5 = Me$  (**f**).

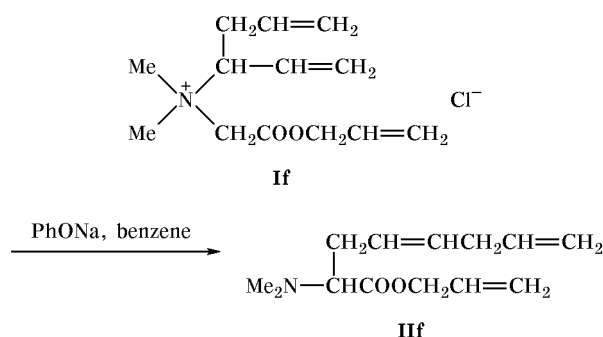
Scheme 2.



**II**,  $R^1 = R^2 = R^3 = R^4 = H$ ,  $R^5 = Me$  (**a**);  $R^1 = R^3 = R^4 = H$ ,  $R^2 = R^5 = Me$  (**b**);  $R^1 = R^2 = R^3 = H$ ,  $R^4 = R^5 = Me$  (**c**);  $R^1 = R^2 = R^3 = H$ ,  $R^4 = Ph$ ,  $R^5 = Me$  (**d**);  $R^1 = R^2 = H$ ,  $R^3 = R^4 = Me$ ,  $R^5 = (CH_2)_5$  (**e**).

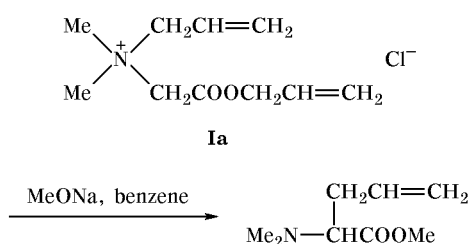
Under the same conditions, from ammonium salt **If** we obtained allyl 2-dimethylamino-4,7-octadienoate (**IIf**) (Scheme 3).

Scheme 3.



Using salt **Ia** as an example, we showed that the rearrangement in the presence of sodium methoxide instead of phenoxide is accompanied by almost complete transesterification (Scheme 4). The fraction of the resulting methyl 2-dimethylamino-4-pentenoate in the product mixture reaches 92% according to the GLC and  $^1\text{H}$  NMR data.

Scheme 4.



In order to elucidate the reaction sequence, i.e., whether the Stevens rearrangement is followed by transesterification or *vice versa*, we examined the

reaction of amino ester **Ia** with sodium methoxide under the rearrangement conditions. According to the  $^1\text{H}$  NMR and GLC data, initial ester **Ia** was recovered from the reaction mixture after appropriate treatment. Therefore, the transesterification precedes the rearrangement.

## EXPERIMENTAL

The IR spectra were recorded on UR-20 and Specord IR-75 spectrometers. The  $^1\text{H}$  NMR spectra were measured on Perkin-Elmer R-12B and Varian Mercury-300 instruments operating at 60 and 300 MHz, respectively. Tetramethylsilane was used as internal reference, and carbon tetrachloride, as solvent. GLC analysis was performed on an LKhM-80 chromatograph equipped with a 2000  $\times$  3-mm column which was packed with 10% of Apiezon L on Inerton A-W (0.20–0.25 mm); oven temperature programming from 100 to 220°C at 16 deg/min; carrier gas helium, flow rate 60 ml/min. The purity of the products was checked by TLC on Silufol UV-254 plates using butanol–ethanol–water–acetic acid (10:7:6:4) as eluent and iodine vapor as developer. Allyl chloroacetate was prepared by the procedure described in [4].

### Allyloxycarbonylmethylammonium salts **Ia–If**.

A mixture of 0.02 mol of the corresponding tertiary amine and 0.02 mol of allyl chloroacetate was kept at room temperature. The resulting salt was filtered off, washed with dry diethyl ether, and dried. The yields and analytical data of salts **Ia–If** are given in Table 1. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 925, 985, 990, 1635, 3010, 3030, 3080 (C=C); 1140, 1150, 1200, 1725 (ester).

**Stevens rearrangement of salts **Ia–If**.** Sodium phenoxide, 0.02 mol, was added to a mixture of 0.01 mol of salt **Ia–If** in 10–15 ml of dry benzene. The mixture was occasionally stirred and, after the

**Table 1.** Yields and elemental analyses of ammonium salts **Ia–If**

Compound no.	Yield, %	Found, %		Formula	Calculated, %	
		N	Cl		N	Cl
<b>Ia</b>	89	6.12	16.00	C <sub>10</sub> H <sub>18</sub> ClNO <sub>2</sub>	6.38	16.17
<b>Ib</b>	86	5.54	14.90	C <sub>11</sub> H <sub>20</sub> ClNO <sub>2</sub>	6.00	15.20
<b>Ic</b>	87	5.59	15.00	C <sub>11</sub> H <sub>20</sub> ClNO <sub>2</sub>	6.00	15.20
<b>Id</b>	94	4.48	11.80	C <sub>16</sub> H <sub>22</sub> ClNO <sub>2</sub>	4.74	12.01
<b>Ie</b>	92	4.50	12.10	C <sub>15</sub> H <sub>26</sub> ClNO <sub>2</sub>	4.87	12.35
<b>If</b>	86	5.10	13.32	C <sub>13</sub> H <sub>22</sub> ClNO <sub>2</sub>	5.39	13.68

**Table 2.** Yields, boiling points, refractive indices, and elemental analyses of compounds **IIa–IIf**

Compound no.	Yield, %	bp, °C ( <i>p</i> , mm)	$n_D^{20}$	Found, %			Formula	Calculated, %		
				C	H	N		C	H	N
<b>IIa</b>	54	62–63 (3)	1.4970	65.11	9.43	7.34	C <sub>10</sub> H <sub>17</sub> NO <sub>2</sub>	65.48	9.28	7.64
<b>IIb</b>	40	69–72 (2)	1.5065	67.51	9.49	7.46	C <sub>11</sub> H <sub>19</sub> NO <sub>2</sub>	66.91	9.64	7.10
<b>IIc</b>	52	68–70 (2)	1.5033	67.43	9.15	6.86	C <sub>11</sub> H <sub>19</sub> NO <sub>2</sub>	66.91	9.64	7.10
<b>IId</b>	65	139–141 (3)	1.5360	74.23	8.51	5.87	C <sub>16</sub> H <sub>21</sub> NO <sub>2</sub>	74.03	8.10	5.40
<b>IIe</b>	50	88–89 (3.5)	1.5293	71.33	9.67	5.76	C <sub>15</sub> H <sub>25</sub> NO <sub>2</sub>	71.61	9.95	5.57
<b>IIf</b>	70	101–104 (3)	1.4982	69.55	8.95	6.05	C <sub>13</sub> H <sub>21</sub> NO <sub>2</sub>	69.86	9.40	6.27

**Table 3.** IR and <sup>1</sup>H NMR spectra of compounds **IIa–IIf**

Compound no.	IR spectrum, $\nu$ , cm <sup>-1</sup>	<sup>1</sup> H NMR spectrum (CCl <sub>4</sub> ), $\delta$ , ppm ( <i>J</i> , Hz)
<b>IIa</b>	920, 985, 1640, 3025, 3085 (CH=CH <sub>2</sub> ); 1080, 1130, 1725 (–COO–)	2.27 s [6H, N(CH <sub>3</sub> ) <sub>2</sub> ]; 2.25–2.53 m (2H, CH <sub>2</sub> ), 3.18 t (1H, NCH, <i>J</i> = 7.4); 4.56 m (2H, CH <sub>2</sub> O); 4.96–5.37 m (4H, CH <sub>2</sub> =); 5.67–5.98 m (2H, CH=)
<b>IIb</b>	890, 1640, 3080 (=CH <sub>2</sub> ); 1070, 1130, 1720 (ester)	1.78 s (3H, CH <sub>3</sub> ); 2.22–2.53 m (2H, CH <sub>2</sub> ); 2.33 s [6H, N(CH <sub>3</sub> ) <sub>2</sub> ]; 3.42 t (1H, NCH, <i>J</i> = 7.2); 4.60 d (2H, OCH <sub>2</sub> , <i>J</i> = 5.7); 4.73 d [2H, CH <sub>2</sub> =C(CH <sub>3</sub> ), <i>J</i> = 5.4]; 5.18–5.40 m (2H, CH <sub>2</sub> =); 5.96 oct (1H, CH=, <i>J</i> <sub>1</sub> = 6.0, <i>J</i> <sub>2</sub> = 10.5, <i>J</i> <sub>3</sub> = 17.3)
<b>IIc</b>	915, 990, 1640, 3030, 3080 (CH=CH <sub>2</sub> ); 1070, 1130, 1730 (ester)	0.7 d and 0.82 d (3H, CH <sub>3</sub> CH, <i>J</i> = 7); 2.23 s and 2.26 s [6H, N(CH <sub>3</sub> ) <sub>2</sub> ]; 2.6 m (2H, NCHCH); 3.61 m (2H, OCH <sub>2</sub> ); 4.5–5.1 m (4H, CH <sub>2</sub> =); 5.6–6.5 m (2H, CH=)
<b>IId</b>	700, 770, 985, 1490, 1600, 3030, 3065, 3085 (C <sub>6</sub> H <sub>5</sub> ); 915, 1640, 3010, 3080 (CH=CH <sub>2</sub> ); 1070, 1130, 1725 (ester)	2.20 s and 2.38 s [6H, N(CH <sub>3</sub> ) <sub>2</sub> ]; 3.60–3.85 m (2H, NCHCH); 4.32 d and 4.61 d (2H, OCH <sub>2</sub> ); 4.95–5.43 m (4H, CH <sub>2</sub> =); 5.60–6.34 m (2H, CH=); 7.15–7.38 m (5H, C <sub>6</sub> H <sub>5</sub> )
<b>IIe</b>	915, 990, 1635, 3025, 3090 (CH=CH <sub>2</sub> ); 1150, 1200, 1720 (ester)	1.0–1.70 m [12H, β-CH <sub>2</sub> , γ-CH <sub>2</sub> , C(CH <sub>3</sub> ) <sub>2</sub> ]; 2.0–3.0 m (5H, NCH <sub>2</sub> , CH); 4.35–4.60 m (2H, OCH <sub>2</sub> ); 4.60–5.40 m (4H, CH <sub>2</sub> =); 5.40–6.30 m (2H, CH=)
<b>IIf</b>	920, 980, 1630, 1640 (CH=CH, CH=CH <sub>2</sub> ); 1025, 1140, 1725 (ester)	2.32 s [6H, N(CH <sub>3</sub> ) <sub>2</sub> ]; 2.20–2.52 m (4H, CH <sub>2</sub> ); 3.20 m (1H, NCH); 4.60 d (2H, OCH <sub>2</sub> , <i>J</i> = 5.7); 4.93–5.40 m (4H, CH <sub>2</sub> =); 5.41–6.05 m (4H, CH=)

exothermic reaction was over, was refluxed for 20–30 min. It was then cooled, and water and diethyl ether were added. The upper (organic) layer was separated and washed with a 10% aqueous solution of sodium hydroxide. The aqueous layer was extracted with diethyl ether. The extracts were combined with the organic phase, dried over magnesium sulfate, and evaporated, and the residue was distilled under reduced pressure. The yields, physical constants, and analytical data of esters **IIa–IIf** are given in Table 2.

#### Reaction of allyl(allyloxycarbonylmethyl)dime-thylammonium bromide with sodium methoxide.

Sodium methoxide, 0.02 mol, was added under intermittent stirring to a mixture of 0.01 mol of salt **Ia** and 10 ml of dry benzene. When the exothermic reaction was over, the mixture was heated for 10 min under reflux and cooled, and water and diethyl ether were added. The organic layer was separated, and the aqueous layer was extracted with ether. The extracts were combined, dried over magnesium sulfate, and

evaporated. The residue was analyzed by GLC. It contained methyl and allyl 2-dimethylamino-4-pentenoates at a ratio of 92:8. Distillation gave methyl 2-dimethylamino-4-pentenoate [1] in 58% yield.

## REFERENCES

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