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LETTERS TO THE EDITOR

Stevens Rearrangement of Ammonium Salts Containing a Hydrazinocarbonylmethyl Group

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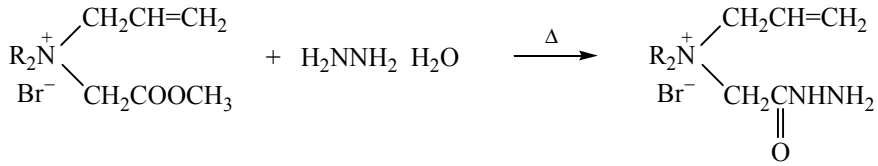
The Stevens rearrangement of quaternary ammonium salts that combine a variety of migrating and host groups opens a wide possibilities for the synthesis of substances with a large range of practically important features, including fragrances, analytical reagents for the photometric determination of the noble and transition metals, antistatic agents, inhibitors of acid corrosion of metals, substances with wide spectrum of biological activity, etc.

In this work we attempted to bring into the Stevens rearrangement the previously unexplored ammonium salts **IIa–IId**, which combine allyl and hydrazinocarbonylmethyl groups. We expected as a result the formation of unsaturated α-dialkylaminocarboxylic acid hydrazides, the intermediates in organic synthesis, in particular, in the synthesis of hydrazones of aromatic aldehydes. The latter are known to be highly selective agents for the analytical determination of gold in the presence of accompanying elements in different environments, and can be used in metallurgy [1].

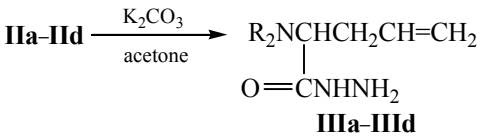
The target ammonium compounds **IIa–IId** were synthesized in a high yield according to [2] in the reaction of dialkylallylcarbonylmethylammonium salts **Ia–Id** with hydrazine hydrate at prolonged heating.



Ia–Id **IIa–IId**

R = CH_3 (**a**), C_2H_5 (**b**); R_2 = $(CH_2)_5$ (**c**), $O(CH_2CH_2)_2$ (**d**).

The Sevens rearrangement of the salts **IIa–IId** was carried out by heating them in anhydrous acetone under the influence of dry powdered potassium carbonate. The 2-amino-4-pentadienic acid hydrazides **IIIa–IIId** were obtained in a high yield. Purity of the obtained compounds was checked by GLC, the structure proved by IR and ^{1}H NMR spectroscopy.



IIIa–IIId

Analysis of the data obtained shows that the steric radius of alkyl groups at the ammonium nitrogen have a noticeable effect on the yield of the rearrangement products. Thus, in going from the methyl and ethyl derivatives to the piperidine and morpholine analogs the yield fails, which can be explained by the steric influence of these groups on the formation of the carbonate–proton complex, thus hampering the rearrangement.

EXPERIMENTAL

IR spectra were recorded on UR-20 and Specord 75IR spectrometers from thin layers or pasts in liquid

paraffin. The ^{1}H NMR spectra were obtained on a Perkin-Elmer R-12B spectrometer with an operating frequency 60 MHz relative to TMS in CCl_4.

Analysis by the GLC method was carried out on a LKhM-8MD instrument with a katharometer detector (temperature 170–200°C, column 2000×3 mm, 10% Apieson-L on Inerton AW, carrier gas He, flow rate 60 ml min^{-1}).

Synthesis of ammonium salts IIa–IId. A mixture of 0.01 mol of salt **Ia–Id** and 0.02 mol of hydrazine hydrate in 30 ml of methanol was heated under reflux on a boiling water bath for 20–25 h. Then the rest of hydrazine hydrate and the solvent were removed in a moderate vacuum (40–50 mm Hg), the residue was washed repeatedly with anhydrous ether, and dried. The salts **IIa–IId** are honey-like hygroscopic masses. Yield 86–92%, elemental analysis corresponds to the calculated one. The IR spectra of the compounds obtained show no absorption at 1675–1680 cm^{-1} characteristic of the carboxy group.

2-Amino-4-pentadienic acids IIIa–IIId. To a suspension of 0.015 mol of salt **IIa–IId** in 15–20 ml of anhydrous acetone was added 0.03 mole of dry powdered potassium carbonate. After keeping the mixture for 30 min at room temperature it was heated under reflux on a boiling water bath for 4 h. Then the reaction mixture was diluted with water and extracted with ether. The ether layer was dried over anhydrous magnesium sulfate and after removal of the ether the residue was distilled in a vacuum.

2-Dimethylamino-4-pentadienic acid hydrazide (IIIa). Yield 82.8%, bp 146–147°C (9 mm Hg), n_D^{20} 1.5022. IR spectrum, ν, cm^{-1}: 930, 970.1640, 3070 (CH=CH_2), 1660 (C=O), 3200–3400 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.20 s (6H, NCH_3), 2.35–2.70 m (2H, C*H*$_2$CH=), 3.40–3.45 m (1H, NH), 4.90 m and 4.98 m (2H, =CH_2), 5.68 d.d.t. (1H, CH=, J_1 16.8, J_2 9.7, J_3 6.3), 7.3–7.7 m (2H, NH_2). Found, % C 53.21, H 9.48, N 26.80. $C_7H_{15}N_3O$. Calculated, % C 53.50, H 9.55, N 26.75.

2-Diethylamino-4-pentadienic acid hydrazide (IIIb). Yield 73.5%, bp 138–139°C (5 mm Hg), n_D^{20} 1.4895. IR spectrum, ν, cm^{-1}: 930, 970, 1645, 3065 (CH=CH_2), 1660 (C=O), 3200–3400 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.01 t (6H, CH_2CH_3, *J* 7.0), 2.55 q (2H, C*H*$_2$CH$_3$, *J* 7.0), 2.35–2.60 m (2H, C*H*$_2$CH=), 3.31 m (1H, NCH), 5.01 m and 5.05 m (2H, =CH_2), 5.81 d.d.t (1H, CH=, J_1 17.6, J_2 9.3, J_3 6.3), 7.45–7.7 m (2H, NH_2). Found, %: C 58.30; H 10.11; N 22.51. $C_9H_{19}N_3O$. Calculated, %: C 58.38; H 10.27; N 22.70.

2-Piperidino-4-pentadienic acid hydrazide (IIIc). Yield 70.4%, bp 171–175°C (7 mm Hg), mp 68–69°C. IR spectrum, ν, cm$^{-1:}$ 940, 960, 1640, 3070 (CH=CH_2), 1655 (C=O), 3200–3400 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.41–1.82 m (6H, β,γ-CH_{2ring}), 2.35–2.60 m (2H, C*H*$_2$CH=), 3.22–3.63 m (4H, α-CH_{2ring}), 3.31 m (1H, NCH), 5.98 m and 5.02 m (2H, =CH_2), 5.71 d.d.t (1H, CH=, J_1 17.6, J_2 9.3, J_3 6.3), 7.45–7.7 m (2H, NH_2). Found, %: C 60.85,H 9.59; N 21.42. H 9.59, N 21.42. $C_{10}H_{19}N_3O$. Calculated, %: C 60.91, H 9.64; N 21.32.

2-Morpholino-4-pentadienic acid hydrazide (IIId). Yield 60.4%, bp 190–191°C (7 mm Hg), mp 93–94°C. IR spectrum, ν, cm^{-1}: 930, 970, 1645, 3070 (CH=CH_2), 1660 (C=O), 3200–3400 (NH). ^{1}H NMR spectrum, δ, ppm *(J,* Hz): 1.62–2.0 m (4H, β-CH_{2ring}), 2.35–2.60 m (2H, C*H*$_2$CH=), 3.31 m (1H, NCH), 3.32–3.71 m (4H, α-CH_{2ring}), 5.01 m and 5.5 m (2H, =CH_2), 5.81 d.d.t (1H, CH=, J_1 17.6, J_2 9.3, J_3 6.3), 77.45–7.72 m (2H, NH_2). Found, %: C 60.09, H 9.45; N 23.40. $C_9H_{17}N_3O_2$. Calculated, %: C 60.34, H 9.50, N 23.46.

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