

LETTERS
TO THE EDITOR

Behavior of Ammonium Salts Containing Propargyl-type Groups in Rearrangement–Cleavage Reactions

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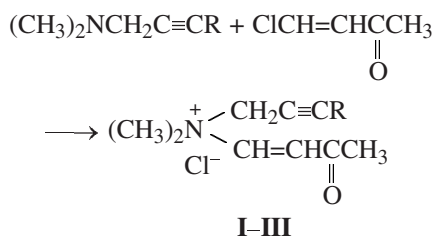
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Quaternary ammonium salts containing a 3-oxobut-1-en-1-yl group together with allyl-type groups undergo rearrangement–cleavage even under the action of such weak nucleophiles as water or ethanol [1, 2]. Quaternary ammonium salts containing propargyl-type groups together with potentially α,β -unsaturated groups form rearrangement–cleavage products in negligible yields [3].

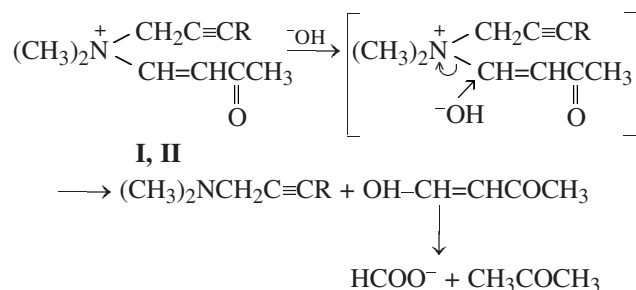
In the present work we studied the behavior of quaternary ammonium salts containing β -ketovinyl and propargyl-type groups in rearrangement–cleavage reaction conditions. In this case, we expected to obtain such interesting compounds as aldoketones. The objects for study were salts **I–III** prepared by the following scheme.



R = C₆H₅ (**I**), CH₃ (**II**), H (**III**).

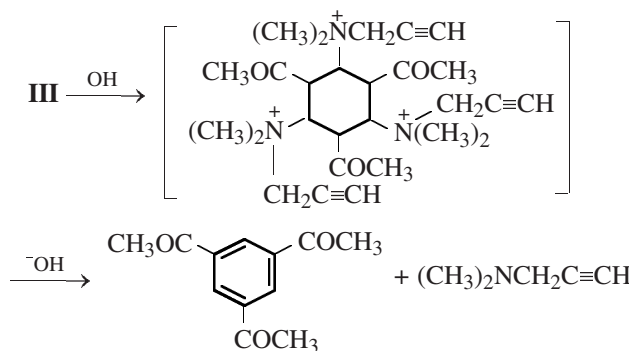
It was found that salts **I–III** do not enter the rearrangement–cleavage reaction. Compound **I** undergoes no changes on standing in aqueous solution for 24 h, while its allyl analog under the same conditions forms a rearrangement–cleavage product in an almost quantitative yield. Heating of salt **I** with aqueous alkali at 90–92°C gives rise to dimethyl(3-phenylprop-2-yn-1-yl)amine (~90%). Among nitrogen-free products, acetone and formic acid are found. The same picture

was observed with salt **II**. The cleavage most probably proceeds according to the following scheme:



R = C₆H₅ (**I**), CH₃ (**II**).

Unlike what is observed with salts **I** and **II**, the reaction of compound **III** with aqueous alkali gives 1,3,5-triacetylbenzene which is probably formed through trimerization of the starting salt followed by cleavage of the cyclic product under the action of alkali. Analogous mechanism for the case of the trimethyl analog of salt **III** was considered in [4].



Starting ammonium salts **I–III** were prepared in quantitative yields by the reactions of equimolar

amounts of corresponding amines with methyl β -chlorovinyl ketone in absolute ether. Their elemental analyses were consistent with calculation. The salts were obtained as hygroscopic syrups, R_f 0.47 (**I**), 0.52 (**II**), and 0.45 (**III**). The IR spectra contained, along with bands at 1620 and 1680 cm^{-1} (C=C, C=O), the following bands: 690, 775, 1450, 1580, 1600, and 2240 cm^{-1} (**I**, monosubstituted benzene ring and disubstituted acetylene); 2230 cm^{-1} (**II**, disubstituted acetylene); and 2190 cm^{-1} (**III**, terminal acetylene).

Aqueous-alkaline cleavage of salts I–III. A solution of 2.64 g of compound **I** was kept at room temperature for 24 h. No formation of amine and carbonyl compound was observed. The reaction mixture was treated with a double molar amount (1.15 g) of potassium hydroxide, left to stand for a day at room temperature, after which it was heated on a boiling water bath for 4 h, extracted with ether, and dried over magnesium sulfate. The ether was removed, and the residue was distilled in a vacuum to obtain 1.45 g (91.2%) of dimethyl(3-phenylprop-2-yn-1-yl)amine, bp 106–107°C (1 mm Hg), n_D^{20} 1.5465 [5], mp 117–118°C (picrate), mixture with an authentic sample gave no melting point depression. Acetone 2,4-dinitrophenylhydrazone, 0.6 g (29%), was precipitated, mp 126–127°C [6]; its mixture with an authentic sample gave no melting point depression. Acidification of the residual reaction mixture and subsequent distillation gave 27% (by titrimetry) of formic acid as a characteristic white precipitate with a mercury dichloride solution.

In a similar way, from 6.1 g of salt **II** we obtained 1.5 g (51.7%) of 1-(dimethylamino)but-2-yne, bp 113–116°C (680 mm Hg), n_D^{20} 1.4970 [7], mp 120–121°C (picrate), mixture with an authentic sample gave no melting point depression, 2.14 g (30.2%) of acetone 2,4-dinitrophenylhydrazone, and 32.1% of formic acid.

In a similar way, from 14.8 g of salt **III** we obtained 4.5 g (70%) of dimethyl(prop-2-yn-1-yl)amine, bp 75–76°C (680 mm), n_D^{20} 1.4186 [8], mp 147–148°C (picrate); mixture with an authentic sample gave no melting point depression. From the residual reaction mixture, 6.6 g (41.5%) of triacetylbenzene, mp 159–160°C [4], was isolated. Its mixture with an authentic sample gave no melting point depression.

The IR spectra were recorded on a Specord 75 IR spectrometer in mineral oil. TLC was carried out on the Silufol UV-254 plates, eluent *n*-butanol–ethanol–water–acetic acid (10:7:6:4 v/v), development in iodine vapor. The melting points were measured on a Boetius hot stage equipped with an RNMK-0.5 microscope.

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