*ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 10, pp. 1938–1940. © Pleiades Publishing, Ltd., 2014.*
*Original Russian Text © A.Kh. Gyul'nazaryan, T.A. Sahakyan, G.T. Sargsyan, J.V. Grigoryan, A.G. Aivazyan, R.A. Tamanyan, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 10, pp. 1660–1662.*

# Synthesis, X-Ray Structure, and Stevens Rearrangement of 1,1-Di(prop-2-yn-1-yl)-2,5-dihydro-1*H*-pyrrol-1-ium Bromide

**A. Kh. Gyul'nazaryan, T. A. Sahakyan, G. T. Sargsyan,
J. V. Grigoryan, A. G. Aivazyan, and R. A. Tamanyan**

*Institute of Organic Chemistry, Scientific and Technological Center of Organic and Pharmaceutical Chemistry,
National Academy of Sciences of Armenia,
26 Azatutyan ave., Yerevan, 0014 Armenia
e-mail: ara.gyulnazaryan@gmail.com*

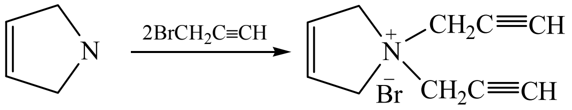
Received July 10, 2014

**Abstract**—1,1-Di(prop-2-yn-1-yl)-2,5-dihydro-1*H*-Pyrrol-1-ium bromide was obtained with interaction of 3-pyrroline with propargyl bromide and its structure was studied by X-ray analysis. It has been shown that the Stevens rearrangement of obtaining salt leads to the formation of 1-(hexa-4,5-dien-1-yn-3-yl)-2,5-dihydro-1*H*-pyrrol.

**Keywords**: 1,1-Di(prop-2-yn-1-yl)-2,5-dihydro-1*H*-pyrrol-1-ium bromide, Stevens rearrangement, X-ray analysis, 2,5-dihydro-1*H*-pyrrole, synthesis

**DOI:** 10.1134/S1070363214100132

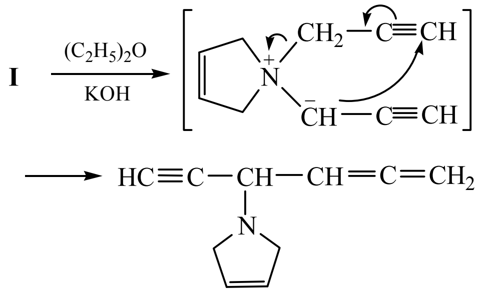
Quaternary ammonium compounds with heterocyclic ammonium group are of interest both as potential biologically active compounds and as precursors in the synthesis of unsaturated heterocyclic amines. In continuation of our studies on the synthesis and transformations of these compounds [1, 2] in the present work we report on the synthesis of 1,1-di(prop-2-yn-1-yl)-2,5-dihydro-1*H*-pyrrol-1-ium bromide (**I**) as yellow needle crystals with mp 190–192°C.



There are no data in the literature on the X-ray diffraction (XRD) analysis of ammonium salts having the unsaturated pyrrolinium ring in the molecule. In order to establish the structure of compound **I** we have performed its XRD analysis.

The structure of molecule **I** is shown in Fig. 1. The molecules in the crystal lattice are bound by electrostatic interactions between quaternary nitrogen atoms and bromide ions. In the three-dimensional packing each bromine atom is coordinated to four nitrogen atoms as in tetrahedron. The neighboring tetrahedra have common edge and form columns in the [100] direction (Fig. 2a). These columns are bound with each other chequerwise by common vertices in the (100) plane (Fig. 2b).

One of typical reactions of ammonium salts is Stevens rearrangement consisting in their transformation into amines with the migration of one of radicals at the nitrogen atom to the neighboring carbon atom under the action of strong bases. For compound **I** either the formation of the disubstituted pyrroline with the propargyl groups at the nitrogen atom and the 2 position of the pyrroline ring could be anticipated, or, by analogy with [3], the migration of one of the propargyl groups to the carbon atom of the second propargyl group. There are no data in the literature on Stevens rearrangement of ammonium salts having two propargyl groups in one molecule. We tried to perform the rearrangement of salt **I** using the ether suspension of potassium hydroxide. However, instead of the Stevens rearrangement product, the compound was obtained, which, according to the IR spectroscopy data, contained both the allene and the terminal acetylene group typical for amines [3]. Taking into account a high degree of unsaturation and to avoid tarring of the product, it was not distilled, but the data of the IR spectroscopy, determination of molecular weight by titration and elemental analysis are indicative of the formation of 1-(hexa-4,5-dien-1-yn-3-yl)-2,5-dihydro-1*H*-pyrrol (**II**), apparently by the following scheme:



**II**

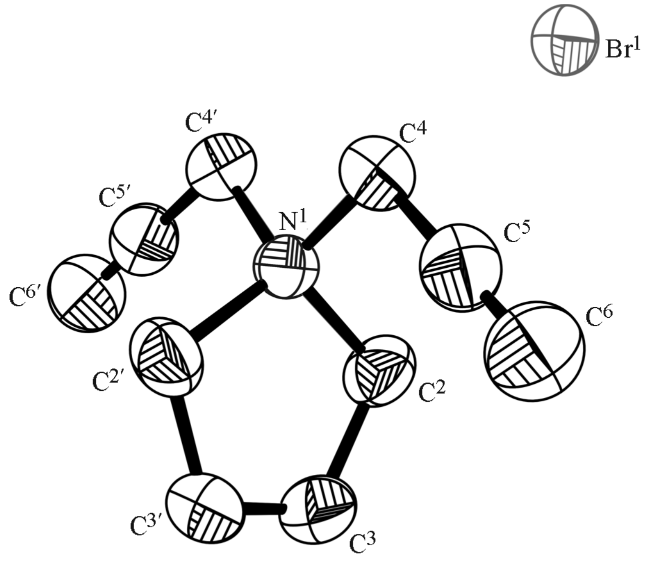


**Fig. 1.** Structure of molecule **I**. Ellipsoids of anisotropic thermal vibrations are given with 50% probability, symmetry code (*i*): *x*; 0.5 – *y*; 0.5 – *z*.

## EXPERIMENTAL

IR spectra were obtained on a Specord 75 IR spectrometer from mulls in mineral oil. $^1$H NMR spectra were registered on a Varian-Mercury-300 spectrometer with working frequency 300.77 MHz in $(CD_3)_2SO$. Chemical shifts are given with respect to TMS as an internal refernce. TLC analysis was performed on Silufol UV-254 plates in the system of solvents butanol–ethanol–water–acetic acid, 10 : 7 : 6 : 4, development in iodine vapor. Melting points were measured on a Boetius-PHMK-05 heating block. XRD analysis was performed on an autodifractometer Enraf-Nonius CAD-4 (graphite monochromator, Mo$K_\alpha$ radiation, $\theta/2\theta$-scanning) at room temperature and refined for 22 reflections with $14.8 < \theta < 15.4$. The set of diffraction reflections was measured on the same instrument. The structure was solved by the direct method, coordinates of hydrogen atoms were determined from difference Fourier maps. The structure was refined by full-matrix least-squares method in anisotropic approximation for non-hydrogen atoms and in isotropic, for all hydrogen atoms. All calculations were performed using the SHELXTL program [5]. An empirical extinction correction based on azimuthal

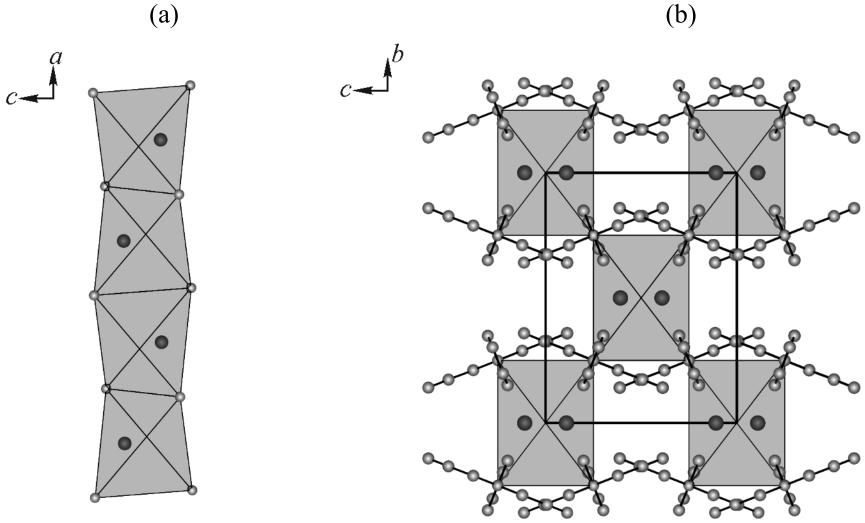


**Fig. 2.** Packaging of molecule I in crystal. (a) Columns formed by tetrahedral and (b) chequerwise packing of the columns in the (100) plane.

scan curves was performed ($T_{\min}$ = 0.03495, $T_{\max}$ = 0.20260) [6]. Crystallographic data were deposited to Cambridge Crystallographic Data Center, CCDC number 1002749.

**1,1-Di(prop-2-yn-1-yl)-2,5-dihydro-1*H*-pyrrol-1-ium bromide (I).** To the solution of 6.9 g (0.1 mol) of 3-pyrroline in 50 mL of alcohol 23.8 g (0.2 mol) of propargyl bromide was added. After 1 day of staying at room temperature the solvent was removed in a vacuum (40–50 mmHg). The precipitated salt was washed with anhydrous ether and dried in a desiccator over $CaCI_2$. 16 g (85%) of *N,N*-dipropargylpyrrolinium bromide **I** was obtained with mp 190–192°C. $R_f$ = 0.61. Found, %: N 6.15, $Br^-$ 36.0. $C_{10}H_{12}NBr$. Calculated, %: N 6.19, $Br^-$35.40. *M* 226.12. *M* (by titration 225.10). IR spectrum, ν, $cm^{-1}$: 1620 (C=C), 2110, 3160 (C≡C). $^1H$ NMR, δ, ppm, *J*, Hz: 3.77 t (2H, *J* = 2.5, ≡CH), 4.56 br.s (4H, $CH_2C$=), 4.70 d (4H, *J* = 2.5, C≡), 5.99 (2H, br.s , =CH).

**1-(Hexa-4,5-dien-1-yn-3-yl)-2,5-dihydro-1*H*-pyrrol (II).** To the suspension of 0.01 mol of salt **I** in 15 mL of anhydrous ether 0.02 mol of sodium ethoxide was added, and the mixture was thoroughly grownd. After the exothermic reaction was completed, the mixture was heated on a water bath for 3–4 h, cooled, and treated with water. The ether layer was separated, the residue was several times extracted with ether, and dried over $MgSO_4$. After removal of solvent 1.2 g (73.6%) of 3-pyrrolinyldi-4,5-enehex-1-yne (**II**) was obtained as viscous oil. Found, %: N 9.69. $C_{10}H_{11}N$. Calculated, %: N 9.66. *M* 145.20. *M* (by titration 143.27). IR spectrum, ν, $cm^{-1}$: 1620, 3090 (C=C), 1960 (C=C=CH).

## REFERENCES

1. Sahakyan, T.A., Gyul'nazaryan, A.Kh., and Manukyan, M.O., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 10, p. 1952. DOI: 10.1134/S1070363213100265.
2. Gyul'nazaryan, A.Kh., Sahakyan, T.A., and Manukyan, M.O., *Nekotorye uspekhi organicheskoi i farmatsevticheskoi khimii* (Some Successes of Organic and Pharmaceutical Chemistry), Yerevan: Center of Molecular Structure Investigation, Scientific and Technological Center of Organic and Pharmaceutical Chemistry, National Academy of Sciences of Armenia, 2012, p. 111.
3. Manukyan, M.O., Barsegyan, K.S., Shakhatuni, A.A., Babahanyan, A.V., and Gyul'nazaryan, A.Kh., *Khim. Zh. Armenii*, 2014, vol. 67, no. 1, p. 103.
4. Kinoyan, F.S., *Khim. Zh. Armenii*, 2011, vol. 64, no. 4, p. 565.
5. North, A.C.T., Phillipsand, D.C., and Mathews, F.S., *Acta Crystallogr. A*, 1968, vol. 24, p. 351. DOI: 10.1107/S0567739468000707.
6. Sheldrick, G.M., *SHELXS97 and SHELXL97*, 1997, University of Göttingen, Germany.