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НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ
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ПИСЬМА В РЕДАКЦИЮ

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SYNTHESIS AND PECULIARITIES IN THE REACTION OF CYCLOHEX-2-ENYLTRIPHENYLPHOSPHONIUM BROMIDE WITH SH- AND NH-CONTAINING COMPOUNDS

Among numerous transformations of organophosphorus compounds the reactions of phosphonium salts, particularly their α,β-unsaturated representatives with NH-, SH-, OH-, PH- and CH-acids are of definite interest [1-7]. The subject of our scientific research is cyclohex-2-enyltriphenylphosphonium bromide (**1**) synthesized by interaction of triphenylphosphine with cyclohex-2-enylbromide in boiling benzene. It should be noted that for the first time the mentioned phosphonuim salt was obtained by McIntosh and Stevens in acetonitrile [8]. The authors note that the mentioned synthesis in benzene results in complete decomposition of the stated salt, which we did not observe.

According to the RSA data, phosphonium salt **1** has the following structure:

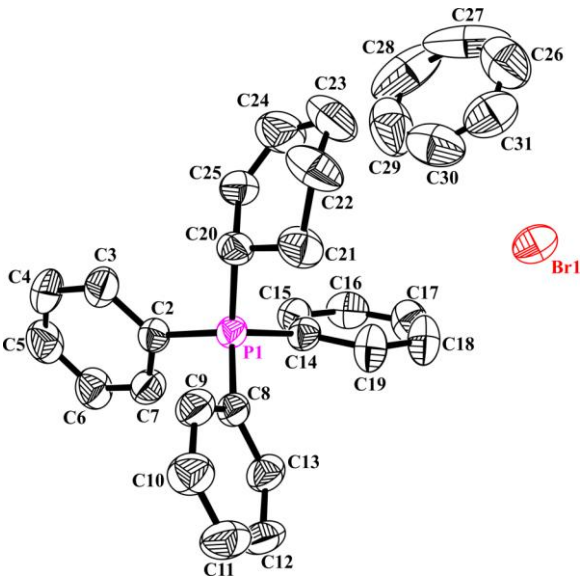


Fig. The molecular structure of compound **1** with thermal displacement ellipsoids drawn at the 50% probability level.

The diffraction measurements were carried out at room temperature on a Enraf-Nonius CAD-4 autodiffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ-scan). The monoclinic unit cell parameters were measured and refined using the diffraction angles of 24 reflections ($11.9<\theta<15.0$). The structure were solved by direct method and refined using the software package SHELXTL [9]. The absorption correction was made by psi-scan method [10]. All non-hydrogen atoms were refined in anisotropic approximation by full-matrix least squares methods. The hydrogen atoms were positioned geometrically and refined using riding model, with C-H=0.93-0.97, $U_{iso}(H)=1.2U_{eq}(C)$.

Crystallographic and experimental data are listed in table. The full crystallographic data in CIF format available free of charge via internet at: http://www.ccdc.cam.ac.uk/products/csd/request/, deposition number: CCDC 1847884.

Table

Crystallographic and experimental data

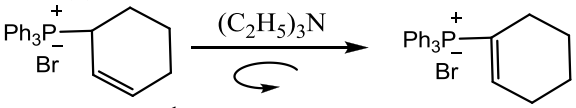
Crystal Data	
Formula	$C_{24}H_{24}P^+$, Br^-, C_6H_6
Formula Weight	501.41
Crystal System	Monoclinic
Space group	Cc
a, b, c [Å]	16.662(3), 9.870(2), 16.475(3)
α, β, γ [deg.]	90, 109.67(3), 90
V [$Å^3$]	2551.3(10)
Z	4
D(calc) [g/cm^3]	1.305
μ(MoKα) [mm^{-1}],T_{min}, T_{max}	1.689, 0.34958, 0.46885
F(000)	1040
Crystal Size [mm]	0.30x0.26x0.20
Data Collection	
Temperature (K)	293(2)
Radiation [Å]	MoKα 0.71073
θ_{min}, θ_{max} [Deg]	2.4, 30.0
Dataset	$-23\leq h\leq 23$; $0\leq k\leq 13$; $-23\leq l\leq 23$
Tot., Uniq. Data, R(int)	7652, 7422, 0.014
Observed data [$I > 2.0\ \sigma(I)$]	5291
Refinement	
Nref, Npar	7422, 289
R, wR2, S	0.0421, 0.1045, 1.01

The molecular structure of the compound **1** is shown in Fig.

X-ray diffraction studies showed that in the crystal lattice of the investigated compound, beside of basic compound ($C_{24}H_{24}P^+$, Br^-), the solvent molecule benzene is present as well. The results of X-ray diffraction analysis showed that in compound **1** the positive charge on the phosphorus atom is compensated by the negative charge of the bromine ion. In the molecule of the compound **1** all phenyl rings are perfectly planar, the maximum deviation of atoms from mean-squared plane not exceeding 0.0213(2). The cyclohexene ring shows well expressed "half-chair" conformation. The four atom (C20, C23, C24, C25) of the ring lie in the same plane and atoms C21 and C22 out of plane are shifted on 0.3663(2)Å and -0.3481(2)Å respectively. The molecule has a chiral center at C20 atom. According to results of structure determination only the molecules of *L*-configuration are present in crystal structure.

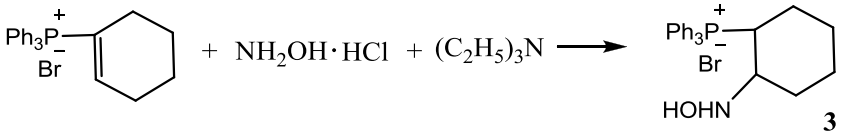
In the three-dimensional packing of molecules, intermolecular interactions are mainly described by van der Waals forces.

First, phosphonuim salt **1** under the action of triethylamine in acetonitrile solution was transformed into α,β-unsaturated isomer, cyclohex-1-enyltriphenyl-phosphoniumbromide (**2**).



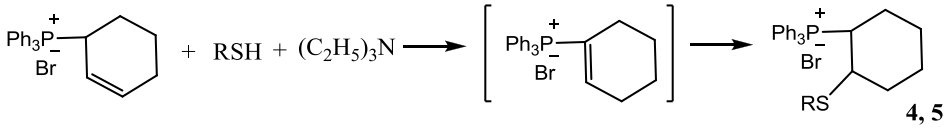
1 **2**

However, contrary to our expectations, our first attempts to involve phosphonium salt **2** into reactions with such reactive OH-, NH- and PH-containing compounds as ethanol, diethylamine, phenyl-, benzylhydrazines and diethylphosphite, were not successful. It should be also noted that the initial phosphonium salt **2** is completely returned. Unlike this, we managed to realize addition of hydroxylamine to phosphonium salt **2** in the presence of triethylamine at room temperature. The yield of resultant 1:1 adduct **3** was about 44%.



3

Analogically we have realized nucleophilic addition of ethyl- and β-hydroxyethyl-mercaptans in the presence of triethylamine to phosphonium salt **1**, which is potential α,β-unsaturated phosphonium salt **2**; reagents being at a 1:2:1 ratio. As a result of reactions realized, 1:1 adducts **4** and **5** were obtained in 82.5% and 92.4% yields, correspondingly. By realization of the same reactions at 1:1:1 ratio of reagents, half quantity of the initial phosphonium salt returns without any transformation.



4, 5

R = C_2H_5 (**4**); R = C_2H_4OH (**5**).

Thus, based on the conducted research we may conclude that contrary to linearly built α,β-unsaturated phosphonium salts, cyclohex-1-enyltriphenylphosphonium bromide is less reactive with respect to A-H compounds, possibly because of the structural peculiarities.

Experimental part

^{1}H, ^{13}C and ^{31}P spectra were recorded on a Varian "Mercury" in DMSO-d_6:CCl_4 (1:3) at 300 *MHz* and 121 *MHz*, using TMS and 85% H_3PO_4 as internal standards, respectively.

Cyclohex-2-enyltriphenylphosphonium bromide (1). The solution of 8.6 *g* (33 *mmol*) of triphenylphosphine and of 5.3 *g* (33 *mmol*) of cyclohex-2-enylbromide in 50 *ml* benzene was refluxed for 15 *h*. The precipitated phosphonuim salt was filtered, washed with benzene, abs. ether and dried in a vacuum. 12 *g* (86%) of phosphonium salt **1** with m.p. 222-224 ^{o}C was obtained. Found, %: Br 18.75. $C_{24}H_{24}BrP$. Calc., %: Br 18.91. ^{1}H NMR, δ, p.p.m, *Hz*: 1.51 - 2.38 (m, 6H, 3x CH_2); 5.6 – 5.78 (m, 2H, $P^{+}CH$, =CH); 6.03–6.16 (m,1H, $P^{+}CHCH$=); 7.69–8.0 (m, 15H, Ph_3P^{+}).^{13}C NMR, δ, p.p.m, *Hz*: 19.73 (d, CH_2, J_{pc}=10.0); 22.02 (d, CH_2, J_{pc} =2.3); 23.54 (d, CH_2, J_{pc} =2.5); 29.72 (d, CH, J_{pc} =48.0); 117.08 (d, CH, J_{pc} =83.0); 117.89 (d, CH, J_{pc} =5.9); 129.77 (d, CH, J_{pc} =12.2); 133.65 (d, CH, J_{pc} =9.3); 134.3 (d, CH, J_{pc} =2.8); 134.77 (d, CH, J_{pc} =11.7). ^{31}P NMR: δ 26.65 (s).

Cyclohex-1-enyltriphenylphosphonium bromide (2). To a solution of 2 *g* (4.7 *mmol*) of phosphonuim salt **1** in 15 *ml* acetonitrile 0.48 *g* (4.7 *mmol*) of triethylamine was added and the solution was stirred at room temperature for 12 *h*. The solvent was evaporated and residue was washed with benzene, abs. ether and dried in a vacuum. 1.8 *g* (90%) of phosphonium salt **2** with m.p. 187-188^{o}C was obtained. Found, %: Br 18.63. $C_{24}H_{24}BrP$. Calc., %: Br 18.91. ^{1}H NMR, δ, p.p.m, *Hz*: 1.78 – 1.93, 2.01-2.31, 2.44-2.57 (m, 8H, 4x CH_2); 6.78 (d.d, 1H, =CH, , $J_{нн}$ =6.78, $J_{рн}$ =22.8); 7.69 –7.98 (m, 15H, Ph_3P^{+}). ^{13}C NMR, δ, p.p.m, *Hz*: 19.92 (d, CH_2, J_{pc} =1.9); 21.41(d, CH_2, J_{pc} =8.5); 25.80 (d, CH_2, J_{pc} =8.9); 27.88 (d, CH, J_{pc} =15.0); 116.70(d, CH, J_{pc} =88.0); 117.83(d, CH, J_{pc} =78.8);129.98 (d, CH, J_{pc} =12.6); 133.97(d, CH, J_{pc} =10.2); 134.59 (d, CH, J_{pc} =2.9); 155.11(d, CH, J_{pc} =7.9).^{31}P NMR, δ, p.p.m: 23.76 (s).

2-Hydroxyaminocyclohexyltriphenylphosphonium bromide (3). To a suspension of 0.21 *g* (1.9 *mmol*) hydroxylamine hydrochloride and 0.19 *g* (1.9 *mmol*) triethylamine in 10 *ml* chloroform a solution of 0.8 *g* (1.9 *mmol*) of phosphonium salt **2** in 10 *ml* chloroform was added. The reaction mixture was stirred at room temperature for 7 *h* and was washed with water. Organic layer was dried and chloroform evaporated. By fraction recrystallization from ethylacetate:acetonitrile (5:1) 0.38 *g* (44%) of phosphonium salt **3** with m.p. 145-146^{o}C was obtained. Found, %: Br 17.93. $C_{24}H_{27}BrNOP$. Calc.,%: Br 17.54. ^{1}H NMR, δ, p.p.m.: 1.22-1.83 (m, 8H, 4x CH_2); 4.42-4.54 (m, 1H, CHN); 5.36-5.42 (m,

1H, CHP); 6.93 (br.s., 1H, NH); 7.6– 8.03 (m, 15H, Ph_3P^+). ^{31}P NMR, δ, p.p.m: δ 31.24 (s). 0.4 *g* (50%) of the initial phosphonium salt **2** was retured.

2-Ethylsulphanylcyclohexyltriphenylphosphonium bromide (4). A solution of 1.5 *g* (3.5 *mmol*) of phosphnium salt **1**, 0.44 *g* (7.0 *mmol*) of ethylmercaptane and 0.36 *g* (3.5 *mmol*) of triethylamine in 15 *ml* chloroform was stirred at room temperature for 13 *h*. The solvent was evaporated and residue was washed with benzene, abs. ether and dried in a vacuum. 1.4 *g* (82.5%) of phosphonium salt **4** with m.p. 148-150^{o}C was obtained. Found, %: Br 16.73. $C_{26}H_{30}BrPS$. Calc.,%: Br 16.49. ^1H NMR, δ, p.p.m, *Hz*: 0.9 (t, 3H, CH_3, Jнн =7.4); 1.5-1.68, 1.73-1.91, 2.22-2.38 (m, 8H, 4x CH_2); 1.92-2.2 (m, 2H, CH_2S); 3.39-3.46 (m, 1H, CHS); 5.12-5.22 (m, 1H, CHP); 7.62– 8.02 (m, 15H, Ph_3P^+).^{31}P NMR, δ, p.p.m: 29.89 (s).

2-Hydroxyethylsulphanylcyclohexyltriphenylphosphonium bromide (5). A solution of 0.8 *g* (1.9 *mmol*) of phosphonium salt **1**, 0.3 *g* (3.8 *mmol*) of 2-hydroxyethylmercaptane and 0.19 *g* (1.9 *mmol*) of triethylamine in 10 *ml* chloroform was stirred at 60^{0}C for 8 *h*. The solvent was evaporated and residue was washed with benzene, abs. ether and dried in a vacuum. 0.88 *g* (92.4%) of phosphonium salt **5** with m.p. 255-256^{0}C was obtained. Found, %: Br 16.23. $C_{26}H_{30}BrOPS$. Calc.,%: Br 15.97. ^1H NMR, δ, p.p.m, *Hz*: 1.22-1.85 (m, 8H, 4x CH_2); 1.99-2.28 (m, 3H, $CHSCH_2$); 3.09-3.22 (m, 2H, OCH_2); 4.48 (t, 1H, OH, Jнн =6.8); 4.51-4.68 (m, 1H, Ph_3P^+CH); 7.65-7.87 (m, 9H, Ph_3P^+); 7.91-8.0 (m, 6H, Ph_3P^+). ^{13}C NMR, δ, p.p.m, *Hz*: 24.46 (d, CH_2, J_{pc} =2.5); 24.55 (d, CH_2, J_{pc} =13.8); 25.078 (d, CH_2, J_{pc} =2.6); 28.78 (d, CH_2, J_{pc} =2.4); 34.016 (s, CH_2); 34.59 (d, CH, J_{pc} =10.0); 35.48 (d, CH, J_{pc} =48.2); 59.77 (s, CH_2); 119.02 (d, CH, J_{pc} =89.0); 129.50 (d, CH, J_{pc} =12.5); 133.386 (d, CH, J_{pc} =10.3); 133.754 (d, CH, J_{pc} =2.8). ^{31}P NMR, δ, p.p.m: 29.09 (s).

All the relativities are made on the basis of double resonance.

ՏՐԻՖԵՆԻԼՑԻԿԼՈՀԵՔՍ-2-ԵՆԻԼՖՈՍՖՈՆԻՈՒՄԱՅԻՆ ԲՐՈՄԻԴԻ ՍԻՆԹԵԶԸ ԵՎ ՏԻ- ԵՎ ՈՒ-ՄԻԱՑՈՒԹՅՈՒՆՆԵՐԻ ՀԵՏ ՓՈԽԱԶԴԵՑՈՒԹՅԱՆ ԱՌԱՆՁՆԱՀԱՏԿՈՒԹՅՈՒՆՆԵՐԸ

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Առաջին անգամ տրիֆենիլցիկլոհեքս-2-ենիլֆոսֆոնիումային բրոմիդի պրոտոտրոպ իզոմերիզացիայով տրիէթիլամինի ներկայությամբ ստացվել է տրիֆենիլցիկլոհեքս-1-ենիլֆոսֆոնիումային բրոմիդ: Իրականացվել է տրիֆենիլցիկլոհեքս-2-ենիլֆոսֆոնիումային բրոմիդի ռենտգեն կառուցվածքային անալիզը: Տրիֆենիլցիկլոհեքս-1-ենիլֆոսֆոնիումային բրոմիդի և հիդրօքսիլամինի, ինչպես նաև էթիլ-, 2-հիդրօքսիէթիլմերկապտանների փոխազդեցության արդյունքում սինթեզվել են 1:1 համապատասխան միացման արգասիքներ:

СИНТЕЗ И ОСОБЕННОСТИ РЕАГИРОВАНИЯ ТРИФЕНИЛЦИКЛОГЕКС-2-ЕНИЛФОСФОНИЙ БРОМИДА С SH- И NH-СОДЕРЖАЩИМИ СОЕДИНЕНИЯМИ

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Впервые прототропной изомеризацией трифенилциклогекс-2-енилфосфоний бромида в присутствии триэтиламина получен трифенилциклогекс-1-енилфосфоний бромид. Взаимодействием трифенилциклогекс-1-енилфосфоний бромида с гидроксиламином, этил- и 2-гидроксиэтилмеркаптанами синтезированы соответствующие продукты присоединения.

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