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THE PECULIARITIES OF THE INTERACTION OF A SERIES OF β,γ-UNSATURATED PHOSPHONIUM SALTS AND DEHYDROBROMINATION OF THE OBTAINED DIBROMO DERIVATIVES

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By bromination of but-, 3-phenylprop-, hex- and cyclohex-2-enyltriphenylphosphonium bromides with molecular bromine in chloroform the corresponding 2,3-dibromo derivatives have been obtained. It is established that 2,3-dibromo-butyl- and 3-phenylpropyl-triphenylphosphonium bromides under the action of sodium carbonate are dehydrobrominated with participation of the hydrogen atom in α-position of the side chain forming the corresponding α,β-unsaturated phosphonium salts. As a result of the interaction of 2,3-dibromobutyltriphenylphosphonium bromide with triethylamine, 3-bromobut-2-enyltriphenylphosphonium bromide was unexpectedly obtained The formation of the latter apparently takes place due to the “reverse prototropic isomerization” of the initially formed 3-bromobut-1-enyltriphenylphosphonium bromide.

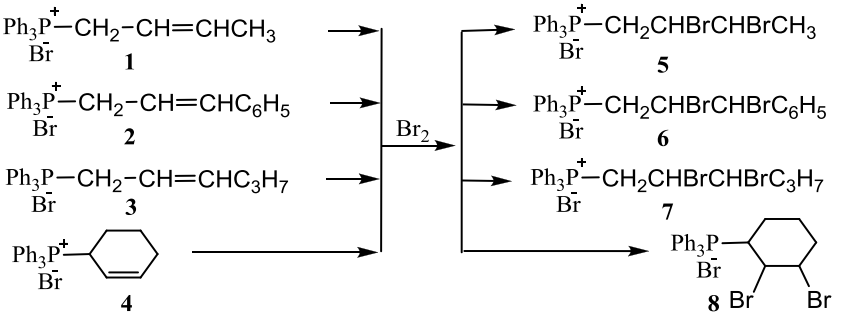
References 8.

Recently, we have found that prop-2-enyltributyl- and triphenylphosphonium bromides are easily brominated by the β,γ-double bond with molecular bromine in the cold (-3÷-5^{o}C) in a chloroform solution with formation of the corresponding adducts with almost quantitative yields. It should also be noted that, according to X-ray structural analysis, the triphenylphosphonium analogue is a mixture of R- and S-conformers with a synclinic arrangement of bromine atoms [1].

In continuation of these studies we have synthesized but-2-enyl- (**1)** [2], 3-phenylprop-2-enyl- (**2)** [3] and hex-2-enyltriphenylphosphonium (**3**) bromides, as well as a cyclic analog of allylphosphonium salt – cyclohex-2-enyltriphenylphosphonium bromide (4) [4] in high yields by interaction of triphenylphosphine with the appropriate allyl halogenides. It should be noted that

phosphonium salt **1**, according to the ^{1}H and ^{13}C NMR spectral data, is the mixture of two geometric isomers in the 67:33 ratio.

Our investigations have shown that all of the above β,γ-unsaturated phosphonium salts **1-4** are easily brominated with the molecular bromine in the cold to form the corresponding 2,3-dibromo derivatives of phosphonium salts **5-8**, respectively, in high yields.

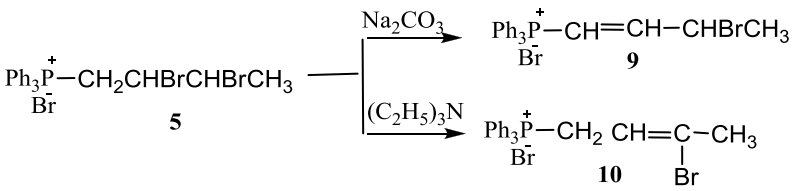


It should be noted that phosphonium salts **1** and **2** are also easily brominated under the action of hν-irradiation in chloroform. In both cases, there is the formation of a mixture of diastereomers with signals in ^{31}P NMR spectra at 23.70, 24.25 (**5**) and 23.69, 23.73 (**6**) ppm, respectively. From the obtained diastereomers mixture of phosphonium salt **6** by adding acetonitrile, we have succeeded in isolating one diastereomer in a pure form with a signal in ^{31}P spectrum at 23.69 ppm.

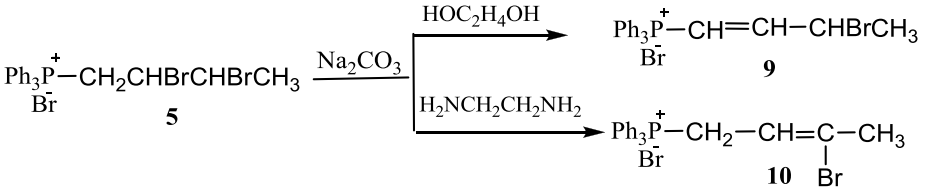
In our previous report [1], it was found that triphenyl-2,3-dibromopropylphosphonium bromide under the action of sodium carbonate in chloroform undergoes dehydrobromination to form 3-bromoprop-1-enyltriphenylphosphonium bromide in ~75% yield. The data obtained indicate that dehydrobromination proceeds with the participation of the most mobile α-hydrogen atom of the side radical.

In this paper, it is shown that in a similar way, phosphonium salt **5** under the action of the fourfold amount of sodium carbonate in chloroform at room temperature is dehydrobrominated to form 3-bromobut-1-enyltriphenylphosphonium bromide (**9**) in 71% yield.

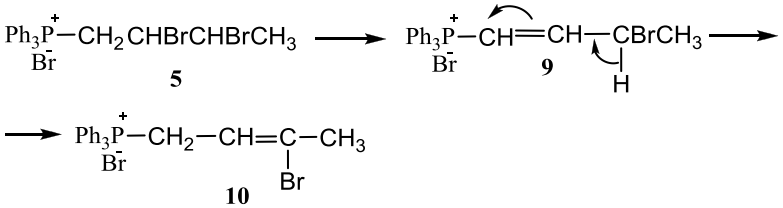
When carrying out the same reaction using triethylamine as a dehydrobrominating agent, 3-bromobut-2-enyltriphenylphosphonium bromide (**10**) was unexpectedly isolated in 80% yield and identified.



In continuation of the studies, phosphonium salt **5** was involved in reactions with ethylene glycol and ethylenediamine in the presence of a fourfold excess of soda in order to realize the cyclization reaction in the side radical by means of double nucleophilic substitution of vicinal bromine atoms. However, as a result of the conducted reactions, only dehydrobromination products **9** and **10** were obtained.



Comparing the obtained results on the behavior of phosphonium salt **5** in relation to the used dehydrobrominating agents, it can be assumed that in all cases at the first stage dehydrobromination of salt **5** with participation of the most mobile α-hydrogen atom takes place. Then the formed α,β-unsaturated phosphonium salt under the action of nitrogenous bases - triethylamine and ethylenediamine is subjected to the reverse prototropic isomerization according to the following Scheme:

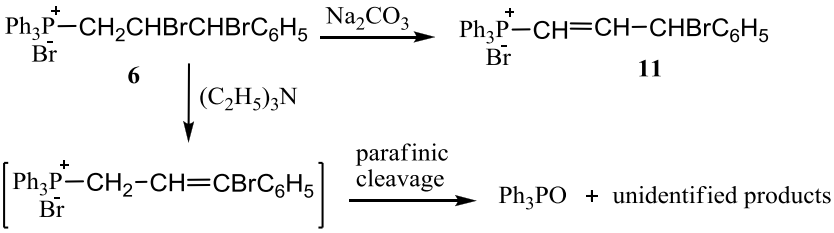


By a specially set experiment it was actually established that 3-bromobut-1-enyltriphenyl-phosphonium bromide (**9**) under the action of triethylamine underwent the reverse prototropic isomerization to form phosphonium salt **10**.

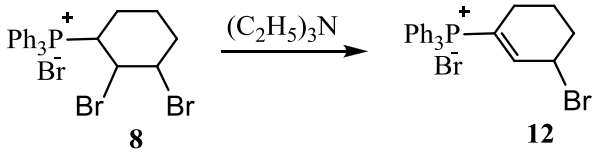
In the literature, there are examples of prototropic isomerization of β,γ-unsaturated phosphonium salts to the α,β-unsaturated analogs [5-7], however, examples of the reverse isomerization are not known to us.

Proceeding from the above-mentioned, it should be assumed that the action of different bases, in our case, soda or triethylamine on phosphonium salt **6** would make it possible to obtain phenyl analogues of salts **9** or **10**, respectively.

However, if, in the case of using soda as a dehydrobrominating agent, an analogue of salt **9** -3-bromo-3-phenylprop-1-enyltriphenylphosphonium bromide (**11**) was actually obtained, then in the case of triethylamine the reaction product was exclusively triphenylphosphine oxide, formed, most likely, according to the Scheme below:



In continuation of the research, we found that phosphonium salt **8** under the action of the excess of triethylamine in chloroform at room temperature was dehydrobrominated to form 3-bromocyclohex-1-enyltriphenylphosphonium bromide, which, according to ^{31}P NMR, was a mixture of two geometric isomers in the 95:5 ratio.



8 **12**

Experimental Section

^{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 an internal standard, respectively.

2,3-Dibromobutyltriphenylphosphonium bromide (5).

1. Bromination of but-2-enyltriphenylphosphonium bromide (**1**). To a solution of 2 *g* (5 *mmol*) of phosphonium salt (**1**) in 20 *ml* of chloroform 0.8 *g* (5 *mmol*) of bromine was added at -3÷-5°C. Then the solvent was evaporated and the residue was washed with benzene, abs. ether and dried in vacuo, affording 2.8 *g* (100%) of phosphonium salt **5** with mp 195-196°C. Found, %: Br^- 14.65. $C_{22}H_{23}Br_3P$. Calcd.,%: Br^- 14.37. ^{1}H NMR, δ, ppm, *Hz*: 1.73 (d, CH_3, J =7.0, 47%); 1.85 (d, CH_3, J =7.0, 53%); 4.2-4.96 (m, 4H, CH_2CHBr-CHBr); 7.7-8.05 (m, 15H, Ph_3P^+). ^{31}P NMR, δ, ppm: 23.70 (47%) (s) and 24.25 (53%) (s).

2. Bromination of but-2-enyltriphenylphosphonium bromide (**1**) **under hν-irradiation**. To a vigorously stirred solution of 1 *g* (2.5 *mmol*) of phosphonium salt **1** in 15 *ml* of chloroform 0.4 *g* (2.5 *mmol*) of bromine was added during hν-irradiation. The reaction mixture was refluxed for 5 *h*, then the solvent was evaporated and the residue was washed with benzene, abs. ether and dried in vacuo, affording 1.4 *g* (100%) of phosphonium salt **5**.

2,3-Dibromo-3-phenylpropyltriphenylphosphonium bromide (6).

1. The experiment was carried out similarly to the described above. 3 *g* (6.5 *mmol*) of 3-phenylprop-2-enyltriphenylphosphonium bromide (**2**) and 1 *g* (6.5 *mmol*) of bromine yielded 3.2 *g* (80%) of phosphonium salt **6** with mp 108-109°C. Found, %: Br^- 13.04. $C_{27}H_{24}Br_3P$. Calcd., %: Br^- 12.92. ^{1}H NMR, δ, ppm, *Hz*: 4.2-5.39 (m, 3H, CH_2CHBr); 5.95 (d, 1H, CHBrPh, J =7.5, 38%), 6.35 (d, 1H,

CHBrPh, J =2.2, 62%); 7.19-7.39 (m, 5H, Ph, 62%); 7. 5-7.63 (m, 5H, Ph, 38%); 7.69-8.02 (m, 15H, Ph_3P^+). ^{31}P NMR, δ, ppm: 23.69 (38%) (s) and 23.73 (62%) (s).

2. The experiment was carried out similarly to the described above. 0.8 *g* (1.7 *mmol*) of 3-phenyl-prop-2-enyltriphenylphosphonium bromide (**2**) and 0.28 *g* (1.7 *mmol*) of bromine under hν-irradiation afforded 0.96 *g* (91.4%) of phosphonium salt **6.**

2,3-Dibromohexyl triphenylphosphonium bromide (7). The experiment was carried out similarly to the described above. 0.14 *g* (0.33 *mmol*) of hex-2-enyltriphenylphosphonium bromide (**3**) and 0.053 *g* (0.33 *mmol*) of bromine yielded 0.2 *g* (100%) of phosphonium salt **7** with mp 108-109°C. Found, %: Br^- 13.35. $C_{24}H_{26}Br_3P$. Calcd., %: Br^- 13.68. ^1H NMR, δ, ppm, *Hz*: 0.93 (t, 3H, J =6.9); 1.28-1.99 (m, 4H, CH_2CH_2); 4.28-4.8 (m 4H, CH_2CHBr-CHBr); 7.67-8.03 (m, 15H, Ph_3P^+). ^{31}P NMR, δ, ppm: 23.80 (s).

2,3-Dibromocyclohexyltriphenylphosphonium bromide (8). The experiment was carried out similarly to the described above. 3 *g* (7.1 *mmol*) of cyclohex-2-enyltriphenylphosphonium bromide (**4**) and 1.1 *g* (7.1 *mmol*) of bromine yielded 3.3 *g* (80.5%) of phosphonium salt **8** with mp 154-155°C. Found, %: Br^- 13.35. $C_{24}H_{26}Br_3P$. Calcd., %: Br^- 13.68. ^1H NMR, δ, ppm, *Hz*: 1.88-2.48 (m, 6H, cyclohexyl); 4.45-4.56 (m, 1H, CHBr-cyclohexyl.); 4.84-4.94 (m, 2H, Ph_3P^+-CH-CHBr-cyclohexyl); 7.74-7.99 (m, 15H, Ph_3P^+). ^{13}C NMR, δ, p.p.m, *Hz*: 20.17 (d, J_{pc} =13.2); 22.79 (d, J_{pc} =2.5); 34.85 (d, J_{pc} =54.2); 49.43 (d, J_{pc} =3.1); 52.64 (d, J_{pc} =10.5); 115.78 (d, J_{pc} =84.7); 130.19 (d, J_{pc} =12.5); 134.05 (d, J_{pc} =9.7); 135.01 (d, J_{pc} =3.0). ^{31}P NMR, δ, ppm: 26.17 (s).

3-Bromobut-1- enyltriphenylphosphonium bromide (9). To a solution of 0.5 *g* (1 *mmol*) of phosphonium salt **5** in 10 *ml* of chloroform 0.38 *g* (3.6 *mmol*) of sodium carbonate was added at room temperature, and the reaction mixture was stirred for 12 *h*. The solvent was filtered and evaporated, then the residue was washed with benzene, abs. ether and dried in vacuo to afford 0.43 *g* (92.3%) of phosphonium salt **9** with mp 117-119°C. Found, %: Br^-17.05. $C_{22}H_{21}Br_2P$. Calcd., %: Br^- 16.81. ^1H NMR, δ, ppm, *Hz*: 1.91 (d, 3H, J =7.0); 5.28-5.4 (m, 1H, -CHBr); 6.7 (ddd, 1H, CH=C<u>H</u>, J_1=20.2, J_2=16.4, J_3=8.4); 7.71-7.79 (16H, C<u>H</u>=CH, Ph_3P^+). ^{13}C NMR, δ, ppm, *Hz*: 23.41 (s); 45.66 (d, J_{pc} =21.7); 109.53 (d, J_{pc} =83.4); 117.45 (d, J_{pc} =90.4); 129.98 (d, J_{pc} =13.0); 133.64 (d, J_{pc} =10.8); 134.83 (d, J_{pc} =3.0); 159.27 (d, J_{pc} =3.6). ^{31}P NMR, δ, ppm: 19.34 (s).

3-Bromobut-2-enyltriphenylphosphonium bromide (10). To a solution of 0.5 *g* (0.89 *mmol*) of phosphonium salt **5** in 10 *ml* of acetonitrile 0.18 *g* (1.78 *mmol*) of triethylamine was added at room temperature, and the reaction mixture was stirred for 18 *h*. The reaction mixture was then washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was washed with benzene, abs. ether and dried in a vacuum, affording 0.4 *g* (95.2%) of phosphonium salt **10** with mp 163-165°C. Found, %: Br^-17.13. $C_{22}H_{21}Br_2P$. Calc., %: 16.81. ^1H NMR, δ, ppm, *Hz*: 2.31 (dq, 3H, CH_3, J_1=6.4, J_2=1.2); 4.65 (dd, 2H, C<u>H</u>$_2$CH=, J_1=15.9, J_2=7.5); 5.89-5.98 (m, 1H, CH_2C<u>H</u>=); 7.62-7.97 (m, 15 H, Ph_3P^+). ^{31}P NMR, δ, ppm: 22.07 (s).

Interaction of phosphopnium salt 5 with ethylene glycol. To a solution of 0.1 *g* (1.4 *mmol*) of ethylene glycol in 10 *ml* of chloroform 0.6 *g* (5.6 *mmol*) of sodium carbonate was added at room temperature and stirred for 30 *min*. Then to the resulting solution 0.8 *g* (1.4 *mmol*) of phosphonium salt **5** was added dropwise, and the reaction mixture was stirred for 12 *h* at the same temperature. The solution was filtered, evaporated and the residue washed with benzene, abs. ether and dried in a vacuum to yield 0.55 *g* (82.1%) of phosphonium salt **9**.

Interaction of phosphopnium salt 5 with ethylenediamine. To a solution of 1 *g* (1.8 *mmol*) of phosphonium salt **5** in 20 *ml* of chloroform 0.11 *g* (1.8 *mmol*) of ethylenediamine was added at room temperature and the reaction mixture was stirred for 3 *h*. Then to the reaction mixture 0.76 *g* (7.2 *mmol*) of sodium carbonate was added and stirred for 3 *h* at the same temperature. The solvent was filtered and evaporated and the residue washed with benzene, abs. ether and dried in vacuo to afford 0.66 *g* (76.7%) of phosphonium salt **10**.

Interaction of phosphopnium salt 9 with triethylamine. To a solution of 1 *g* (1.8 *mmol*) of phosphonium salt **9** in 15 *ml* of acetonitrile, 0.36 *g* (3.6 *mmol*) of triehtylamine was added at room temperature, and the reaction mixture was stirred for 6 *h*. The solvent was evaporated and the residue washed with abs. ether and dried in vacuo to afford 0.95 *g* (95%) of phosphonium salt **10**.

3-Bromo-3-phenylprop-1-enyltriphenylphosphonium bromide (11). To a solution of 2 *g* (3.2 *mmol*) of phosphonium salt **6** in 25 *ml* of chloroform, 1.02 *g* (9.7 *mmol*) of sodium carbonate was added at room temperature and the reaction mixture was stirred for 18 *h*. The solution was filtered, evaporated and the residue washed with benzene, abs. ether and dried in vacuo. By fractional recrystallization of the residue, 0.88*g* (52%) of phosphonium salt **11** was obtained. Found, %: Br^-14.49 $C_{27}H_{23}Br_2P$. Br^- 14.87. ^{1}H NMR, δ, ppm, *Hz*: 6.55 (d, 1H, J=8.6, CHBr); 7.02 (ddd, 1H, J_1=20.3, J_2=16.3, J_3=8.5, CH=C<u>H</u>,); 7.44-7.62 (m, 6H, CH=C<u>H</u>C$_6$<u>H</u>$_5$); 7.7-8.0 (m, 15H, Ph_3P^+). ^{31}P NMR, δ, ppm: 19.0 (s).

Interaction of phosphopnium salt 6 with triethylamine. To a solution of 1 *g* (1.6 *mmol*) of phosphonium salt **6** in 15 *ml* of chloroform 0.4 *g* (4 *mmol*) of triehtylamine was added at room temperature and the reaction mixture was stirred for 3.5 *h*. The latter was then washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue washed with abs. ether and dried in vacuo to afford 0.38 *g* (86.4%) of triphenylphosphinoxide with mp 155-156^{o}C.

3-Bromocyclohex-1-enyltriphenylphosphonium bromide (12). The experiment was carried out similarly to the described above. 0.5 *g* (0.86 *mmol*) of 2,3-dibromocyclohexylptriphenylphosphonium bromide (**8**) and 0.13 *g* (1.3 *mmol*) of triethylamine in 15 *ml* of chloroform yielded 0.4 *g* (93%) of phosphonium salt **12** with mp 146-148^{o}C. Found, %: Br^-14.02. $C_{24}H_{24}Br_2P$. Calcd.,%: 13.72. ^{1}H NMR, δ, ppm, *Hz*: 1.91-2.53 (m, 6H, CH_2-cyclohexyl); 5.08-5.14 (m, 1H, -CHBr-cyclohexyl); 6.59-6.72 (m, 1H, =CH-cyclohexyl); 7.7-7.99 (m, 15H, Ph_3P^+). ^{31}P NMR, δ, ppm: 23.85 (95%) (s) and 23.19 (5%) (s).

ՄԻ ՇԱՐՔ β,γ-ՉՀԱԳԵՑԱԾ ՖՈՍՖՈՆԻՈՒՄԱՅԻՆ ԱՂԵՐԻ ՄՈԼԵԿՈՒԼՅԱՐ ԲՐՈՄՈՎ ԲՐՈՄԱՑՄԱՆ ԵՎ ՍՏԱՑՎԱԾ ԴԻԲՐՈՄԱԾԱՆՑՅԱԼՆԵՐԻ ԴԵՀԻԴՐՈԲՐՈՄԱՑՄԱՆ ՌԵԱԿՑԻԱՆԵՐԻ ԱՌԱՆՁՆԱՀԱՏԿՈՒԹՅՈՒՆՆԵՐԸ

Մ. Ժ. ՀՈՎԱԿԻՄՅԱՆ, Գ. Ց. ԳԱՍՊԱՐՅԱՆ, Ա. Ս. ԲԻՉԱԽՉՅԱՆ և Լ. Վ. ԴԵՐՁՅԱՆ

Բուտ-, 3-ֆենիլպրոպ-, հեքս- և ցիկլոհեքս-2-ենիլֆոսֆոնիումային բրոմիդների բրոմացմամբ մոլեկուլյար բրոմով, քլորոֆորմի մեջ ստացվել են համապատասխան 2,3-դիբրոմածանցյալներ: Ցույց է տրվել, որ 2,3-դիբրոմբուտիլ- և -3-ֆենիլպրոպիլ-տրիֆենիլֆոսֆոնիումային բրոմիդները α-ջրածնի ատոմի հաշվին նատրիումի կարբոնատի ազդեցությամբ դեհիդրոբրոմանում են, առաջացնելով համապատասխան α,β-չհագեցած ֆոսֆոնիումային աղեր: 2,3-դիբրոմբուտիլտրիֆենիլֆոսֆոնիումային բրոմիդի և տրիէթիլամինի փոխազդեցության արդյունքում անսպասելիորեն ստացվել է 3-բրոմբուտ-2-ենիլտրիֆենիլֆոսֆոնիումային բրոմիդ: Վերջինիս առաջացումը, ամենայն հավանականությամբ, տեղի է ունենում սկզբնական փուլում ստացված 3-բրոմբուտ-1-ենիլտրիֆենիլֆոսֆոնիումային բրոմիդի, հետադարձ պրոտոտրոպ իզոմերիզացիայի արդյունքում:

ОСОБЕННОСТИ РЕАГИРОВАНИЯ РЯДА β,γ-НЕПРЕДЕЛЬНЫХ ФОСФОНИЕВЫХ СОЛЕЙ С МОЛЕКУЛЯРНЫМ БРОМОМ И ДЕГИДРОБРОМИРОВАНИЕ ПОЛУЧЕННЫХ ДИБРОМПРОИЗВОДНЫХ

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Бромированием бут-, 3-фенилпроп-, гекс- и циклогекс-2-енилтрифенилфосфоний бромидов молекулярным бромом в хлороформе получены соответствующие 2,3-дибромпроизводные. Установлено, что 2,3-дибромбутил- и -3-фенилпропилтрифенилфосфоний бромиды под действием карбоната натрия дегидробромируются с участием α-водородного атома боковой цепи, образуя соответствующие α,β-ненасыщенные фосфониевые соли. В результате же взаимодействия 2,3-дибромбутилтрифенилфосфоний бромида с триэтиламином неожиданным образом получен 3-бромбут-2-енилтрифенилфосфоний бромид. Образование последнего, по-видимому, имеет место в результате “обратной прототропной изомеризации” первоначально образовавшегося 3-бромбут-1-енилтрифенилфосфоний бромида.

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