148 *Russian Chemical Bulletin, International Edition, Vol. 51, No. 1, pp. 148—150, January, 2002*

Reactions of tautomeric quaternary phosphonium salts based on triphenylphosphine and 3-phenylpropargyl bromide with nitrogen nucleophiles

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Triphenyl(3-phenylprop-1-ynyl)phosphonium bromide (**3**) was isolated. This compound is a third isomer for the tautomeric system triphenyl(3-phenylpropadienyl)phosphonium bromide (**1**) $\rightleftharpoons$ triphenyl(3-phenylprop-2-ynyl)phosphonium bromide (**2**). Salts **1** and **2** smoothly react with secondary amines to give adducts with an α,β-double bond, while salt **3** changes to an allene ylide. Addition of phenylhydrazine and triphenyl(phenylethynyl)phosphonium bromide to salts **1** and **2** and addition of dimethylformamide to salt **2** were performed.

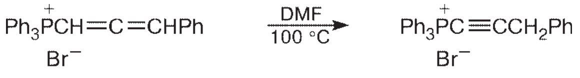
Key words: triphenyl(3-phenylprop-2-ynyl)phosphonium bromide, triphenyl(3-phenylpropadienyl)phosphonium bromide, triphenyl(3-phenylprop-1-ynyl)phosphonium bromide, isomerization, amines, ylide, phenylhydrazine.

Earlier,[1,2] we have found that 3-phenylprop-2-ynyl bromide reacts with triphenylphosphine to give, depending on the solvent, either individual salts containing an α-allene (**1**) or a β-acetylene group (**2**) or their mixture. It was also shown that the β-acetylene salt **2** completely changes to allene **1** on storage in acetonitrile, ether, ethanol, and dimethylformamide. The reverse reaction occurs in aqueous HBr, in trichloroacetic acid at a melting point, and, surprisingly, in $CHCl_3$.

The goal of the present work was to perform a detailed study of mutual transformations in a system containing salts with α-allene and β-acetylene groups.

Results and Discussion

It was shown that the heating of salt **1** in DMF at ~100 °C yields triphenyl(3-phenylprop-1-ynyl)phosphonium bromide (**3**) with an α-triple bond, which is a third isomer for the tautomeric system triphenyl(3-phenylpropadienyl)phosphonium bromide (**1**) $\rightleftharpoons$ triphenyl(3-phenylprop-2-ynyl)phosphonium bromide (**2**).



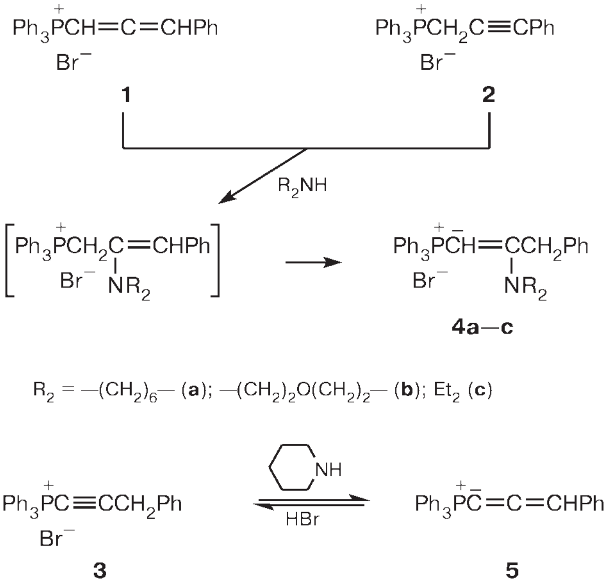
$$\underset{Br^-}{Ph_3\overset{+}{P}CH{=}C{=}CHPh} \xrightarrow[100\ °C]{DMF} \underset{Br^-}{Ph_3\overset{+}{P}C{\equiv}CCH_2Ph}$$

1 **3**

The structure of salt **3** was determined from ^1H NMR and Raman spectroscopy data.

While α-allene and β-acetylene salts **1** and **2** smoothly react with secondary amines (piperidine, morpholine, and diethylamine) to give similar adducts **4a—c** involving the α,β-unsaturated bond, the reaction of α-acetylene salt **3** with piperidine affords allene-type ylide **5**. Salt **3** is recovered when ylide **5** is treated with aqueous HBr. The reactions of salt **2** with amines seem to include prototropic isomerization into salt **1** (Scheme 1).

Scheme 1



It should be noted that the intermediate formation of isomeric allenylphosphonium salts was suggested earlier for the reactions of prop-2-ynylphosphonium salts with

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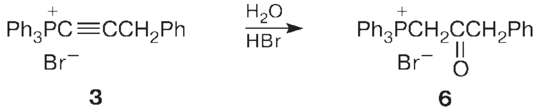
† Deceased.

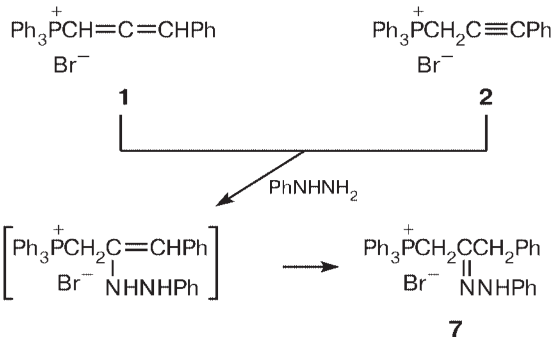
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 139—141, January, 2002.

nucleophiles[3—11] and unambiguously proved by studying the reaction of triphenylprop-2-ynylphosphonium bromide with methanol.[4] We found that salt **3** reacts with aqueous HBr to give a hydration product, namely, triphenylphosphonium salt **6** with a phenylacetonyl group.

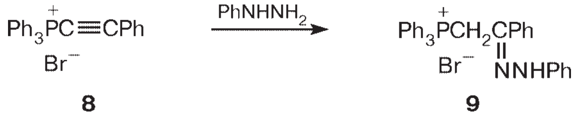


The reactions of salts **1** and **2** with phenylhydrazine yielded triphenyl(3-phenyl-2-phenylhydrazonopropyl)phosphonium bromide (**7**) (Scheme 2).

Scheme 2

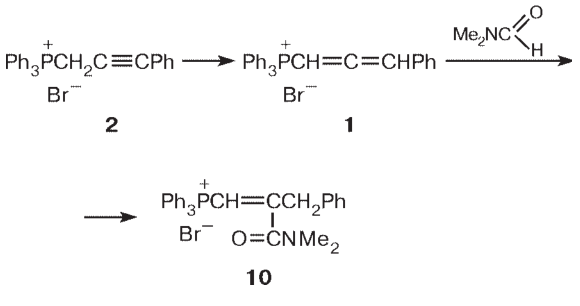


Analogously, triphenyl(2-phenyl-2-phenylhydrazonoethyl)phosphonium bromide (**9**) was obtained from triphenyl(phenylethynyl)phosphonium bromide (**8**) and phenylhydrazine.



Previously, we found that the allene group neighboring to the positive phosphonium center in salt **1** makes the multiple bonds strongly deficient in electrons so that weak nucleophiles such as acetone, acetophenone,[12] and phenylacetylene[13] can add to the salt. In the present work, the reaction of salt **2** with DMF was carried out; apparently, **2** → **1** isomerization takes place to give adduct **10** at the α,β-double bond (Scheme 3).

Scheme 3



However, it is surprising that the reaction of preliminarily prepared salt **1** with DMF under the same conditions affords, as noted above, exclusively salt **3**.

Experimental

^1H NMR spectra were recorded on a Mercury-300 Varian instrument (300 MHz) with Me_4Si as the internal standard. IR spectra were recorded on a Specord M-80 instrument. Raman spectra were recorded on a DFS-24 instrument (λ_{exc} = 441 nm). Salts **1**, **2**, and **8** were prepared according to the known procedures.[1—3] Their purity was checked by TLC and ^1H and ^{31}P NMR spectroscopy.

Triphenyl(3-phenylprop-1-ynyl)phosphonium bromide (3). Triphenyl(3-phenylpropadienyl)phosphonium bromide (**1**) (10 g, 0.022 mol) was heated in 70 mL of DMF in a water bath for 12 h. The solvent was removed *in vacuo*, and the precipitate that formed was washed with boiling anhydrous acetone and, on cooling, with anhydrous ether, and dried *in vacuo*. The yield of salt **3** was 6.8 g (68%), m.p. 234—235 °C. Found (%): C, 70.55; H, 4.45; Br, 17.36. $C_{27}H_{22}BrP$. Calculated (%): C, 70.89; H, 4.81; Br, 17.50. IR (CH_2Cl_2), ν/cm^{-1}: 2250 (C≡C). ^1H NMR (CD_3OD), δ: 4.0 (s, 2 H, CH_2Ph); 7.2—7.7 (m, 20 H, 4 Ph). Raman spectrum, ν/cm^{-1}: 2250 ($P^+C{\equiv}C$).

Reaction of triphenyl(3-phenylprop-1-ynyl)phosphonium bromide (3) with piperidine. A mixture of salt **3** (1 g, 0.0022 mol) and piperidine (0.2 g, 0.0023 mol) in 8 mL of benzene was refluxed for 7 h. The solvent was decanted, and the residue was washed with anhydrous ether and dried *in vacuo*. The yield of piperidine hydrobromide was 0.34 g (93.9%), m.p. 222—223 °C. A mixture of this product with an authentic sample did not depress the melting point. Found (%): C, 35.80; H, 7.55; Br, 48.40. $C_5H_{12}BrN$. Calculated (%): C, 36.14; H, 7.22; Br, 48.19. The solvent was removed from the benzene layer to give triphenylphosphonium (3-phenylpropadien-1-yl) ylide (**5**), yield 0.74 g (90%). Found (%): C, 86.44; H, 5.50. $C_{27}H_{21}P$. Calculated (%): C, 86.17; H, 5.58. IR (CH_2Cl_2), ν/cm^{-1}: 1590 (benzene ring); 1940 (allene). ^1H NMR (CD_3OD), δ: 7.0—7.6 (m, 20 H, Ph, 1 H, =CHPh).

A 40% aqueous solution of HBr (0.0011 mol) was added to a solution of ylide **5** (0.4 g, 0.0011 mol) in 1 mL of CH_2Cl_2. After ~15 h, the precipitate that formed was separated by decanting, washed with ether, and dried *in vacuo*. The yield of triphenyl(3-phenylprop-1-ynyl)phosphonium bromide (**3**) was 0.24 g (50%), m.p. 234—235 °C. A mixture of this product with an authentic sample did not depress the melting point. ^1H NMR (DMSO-d_6), δ: 4.0 (s, 2 H, CH_2P); 7.0—7.8 (m, 20 H, 4 Ph).

Reaction of triphenyl(3-phenylpropadienyl)phosphonium bromide (1) with phenylhydrazine. A mixture of phosphonium salt **1** (1.3 g, 0.003 mol) and phenylhydrazine (0.3 g, 0.003 mol) was refluxed in 10 mL of MeCN. The solvent was removed, and the residue was washed with anhydrous ether and dried *in vacuo*. The yield of salt **7** was 1.5 g (96.2%), m.p. 200—202 °C. Found (%): C, 70.25; H, 5.15; Br, 14.49. $C_{33}H_{30}BrN_2P$. Calculated (%): C, 70.0; H, 5.30; Br, 14.15. IR, ν/cm^{-1}: 1580 (benzene ring); 1680 (β,γ-C=C). ^1H NMR ($CDCl_3$), δ: 4.2 (s,

Table 1. Yields, elemental analysis data, and ^{1}H NMR data for adducts of secondary amines with salts **1** and **2**

Compound	Yield from **1** (**2**) (%)	Found / Calculated (%)*	^{1}H NMR (CD_3OD), δ (*J*/Hz)
4a	93.0 (68.9)	15.00, 15.19 15.09	1.40—1.65 (m, 6 H, CH_2 piperidine); 3.40—3.60 (m, 4 H, CH_2 piperidine); 3.80 (s, 2 H, CH_2Ph); 4.50 (d, 1 H, PCH, $^2J_{PH}$ = 20); 7.00—8.00 (m, 20 H, Ph)
4b	90.0 (92)	15.05, 14.85 14.75	3.42 (m, 4 H, CH_2O); 3.60 (m, 4 H, CH_2N); 3.75 (s, 2 H, CH_2Ph); 4.80 (d, 1 H, PCH, $^2J_{PH}$ = 20); 6.80—7.80 (m, 20 H, Ph)
4c	86.1 (82.0)	14.55, 14.85 14.68	1.10 (m, 6 H, $NCH_2\underline{Me}$); 3.40 (q, 4 H, $NC\underline{H}_2Me$, *J* = 7.3); 3.60 (s, 2 H, CH_2Ph); 4.25 (d, 1 H, PCH, $^2J_{PH}$ = 12.7); 6.80—7.60 (m, 20 H, Ph)

* For Br.

CH_2Ph); 5.1 (d, 2 H, PCH_2, $^2J_{PH}$ = 17 Hz); 6.7—8.0 (m, 25 H, 5 Ph); 10.1 (s, NH).

Reaction of triphenyl(3-phenylprop-2-ynyl)phosphonium bromide (2) with phenylhydrazine. Analogously, phosphonium salt **7** was obtained from salt **2** (1.1 g, 0.0025 mol) in 15 mL of acetonitrile and phenylhydrazine (0.3 g, 0.0027 mol). The yield of **7** was 1.2 g (90%). The characteristics of the product were identical with those described above.

Reaction of triphenyl(phenylethynyl)phosphonium bromide (8) with phenylhydrazine. A solution of phenylhydrazine (0.3 g, 0.0027 mol) in 7 mL of MeCN was added to a solution of phosphonium salt **8** (1 g, 0.0022 mol) in 10 mL of MeCN. The reaction mixture was refluxed in a water bath for 4 h, concentrated, and worked up with anhydrous ether. The yield of salt **9** was 0.7 g (71%), m.p. 212—215 °C. Found (%): C, 69.45; H, 4.56; P, 5.35; Br, 14.83. $C_{32}H_{27}BrN_2P$. Calculated (%): C, 69.80; H, 4.91; P, 5.63; Br, 14.53. ^{1}H NMR (DMSO-d_6), δ: 5.8 (d, 2 H, PCH_2, $^2J_{PH}$ = 16 Hz); 7.0—8.0 (m, 25 H, Ph).

Reaction of triphenyl(3-phenylprop-2-ynyl)phosphonium bromide (2) with DMF. Salt **2** (13 g, 0.0284 mol) was heated in DMF (90 mL) in a boiling water bath for 12 h. The liquid was decanted, and the precipitate was refluxed with acetone for 2 h. Then the acetone was removed, and the product was washed with anhydrous ether and dried *in vacuo*. The yield of triphenyl[3-phenyl-2-(*N,N*-dimethylcarbamoyl)prop-1-enyl]phosphonium bromide (**10**) was 6.1 g. The dimethylformamide solution was slightly concentrated, and an additional amount (0.6 g) of the salt was precipitated with ether. The total yield of product **10** was 6.7 g (44.5%), m.p. 246 °C. Found (%): C, 67.45; H, 5.81; Br, 14.93; P, 5.38. $C_{30}H_{29}BrNOP$. Calculated (%): C, 67.90; H, 5.47; Br, 15.09; P, 5.85. ^{1}H NMR ($CDCl_3$), δ: 3.1 and 3.2 (s, 6 H, NMe_2); 3.8 (s, 2 H, CH_2Ph); 4.1 (d, PCH=, $^2J_{PH}$ = 13.8 Hz); 6.6—7.8 (m, 20 H, Ph).

Reactions of triphenyl(3-phenylpropadienyl)phosphonium bromide (1) and triphenyl(3-phenylprop-2-ynyl)phosphonium bromide (2) with secondary amines (general procedure). An equimolar amount of a corresponding amine in MeCN was added to a solution of a phosphonium salt in MeCN. The mixture was refluxed in a water bath. The solvent was removed, and the residue was repeatedly washed with anhydrous ether and dried *in vacuo*. The yields, elemental analysis data, and ^{1}H NMR spectra of compounds **4a—c** are given in Table 1.

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Received April 2, 2001;
in revised form July 24, 2001