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# Synthesis and Transformations of Triphenylpropargylphosphonium Bromide

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**Abstract**—A method of the synthesis of triphenylpropargylphosphonium bromide is developed. Its isomerization and hydration in various solvents are studied, and reactions with secondary amines, triethylamine, and triphenylphosphine are carried out. It is established that secondary amines add to the intermediate allene isomer with subsequent migration of the formed double bond to the phosphorus atom. The reaction of triethylamine with triphenylpropargyl and triphenylethynyl bromides occurs similarly to alkaline hydrolysis involving attack of the amine on the phosphorus atom. Triphenylphosphine forms with triphenylpropargylphosphonium bromide a bis-salt with a terminal methylene group. Experimental evidence is obtained showing that for phosphoxazole derivatives to form from oximes derived from triphenyl-(oxomethyl)phosphonium salts that latter should bear an aryl substituent at the keto group.

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Reactions of unsaturated phosphonium salts with nucleophilic reagents hold a special place among transformations of organophosphorus compounds. A great number of works have been devoted to reactions of NH-, CH-, OH-, SH-, and PH-nucleophiles with phosphonium salts containing α- and β-acetylene (vinylacetylene) and α-allene (enallene) groups.

In these reactions, triphenylethynylphosphonium bromide and triphenylpropargylphosphonium bromide and its tautomers prepared from phenylpropargyl bromide: triphenylpropargyl-, triphenylpropadienyl-, and triphenyl(prop-1-ynyll)phosphonium bromides, were best studied.

Goffmann and Forster [1] examined reactions of nucleophiles with propargylphosphonium salts. They established that the latter give the same products as their isomeric α-acetylenic salts. An essential difference consists in the fact that in the first case the reactions proceeds easier, since they involve, in the authors' opinion, the intermediate active allenic intermediates. Thus, the propargyl group is equivalent to prop-1-ynyl and, at the same time, reacts more effectively, which makes application of propargyl salts preferable.

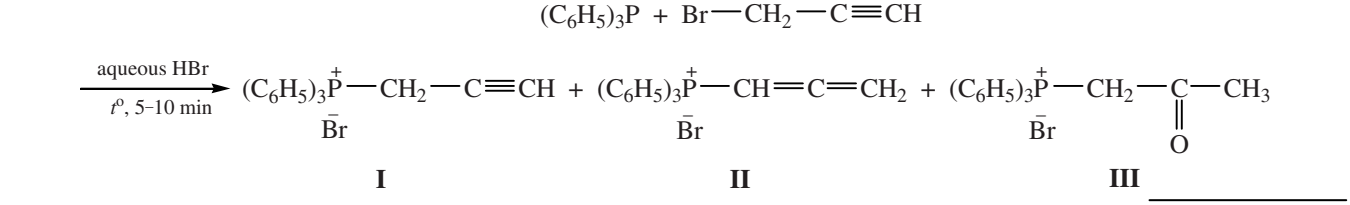
Schweitzer, Koff, and Murray [3] obtained decisive evidence to show that the reaction of triphenylpropargylphosphonium bromide with methanol involves an allenic intermediate. The authors showed that the reaction easily proceeds under reflux for 24 h to form an adduct by the β,γ-unsaturated group. The latter transforms into an α,β isomer upon addition of catalytic quantities of a base. The reaction with deuteromethanol leads to a β,γ isomer completely deuterated into the α and β positions. However, treatment of the β,γ isomer with deuteromethanol does not lead to the above-mentioned deuterated product. Hence, the authors fairly conclude that deuteration occurs in the intermediately formed allenic salts.

The present work is devoted to the development of a procedure for synthesis of triphenylpropargyl-phosphonium bromide (**I**) and to the study of its reaction with certain P- and N-nucleophiles.

Some authors [7–9] reported the synthesis of triphenylpropargylphosphonium bromide (**I**) by reacting the components in dioxane in the presence of HBr. Conditions applied by different authors differed only by the concentration of HBr which was probably added to prevent prototropic isomerization, and by the solvent for recrystallization. In all the cases, the

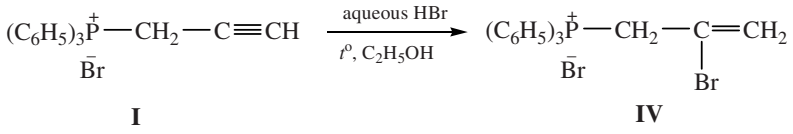
postreaction mixture was heated at 100°C for 5–10 min and the salt was filtered off and recrystallized from ethanol or isopropanol. The yields varied in the range 13–75 %. The melting points of the prepared salt varied from work to work.

We failed to obtain salt **I** in a satisfactory yield by any of these methods. In all the cases, the isomeric allenic salt **II** and the hydration product, acetonyltriphenylphosphonium bromide (yields 23–45%) formed along with salt **I**.

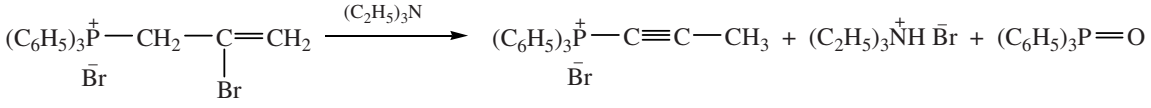



The yield of salt **I** in mixture with the allenic isomer was no higher than did not exceed 16%. The resulting data can be explained by transformations of salt **I** during heating with HBr and recrystallization. Actually, we managed to obtain a pure salt **I** in a yield of 75% by performing the reaction at room temperature and without subsequent recrystallization.

It is interesting that the reaction of salt **I** with HBr mixed with ethanol under heating for 1 h gave (2-bromoprop-2-enyl)triphenylphosphonium bromide (**IV**) in a yield of 38%. Compound **IV** could be formed exclusively by hydrobromination of the allenic isomer, involving nucleophilic attack of the bromide ion on the $sp^2$-carbon atom.

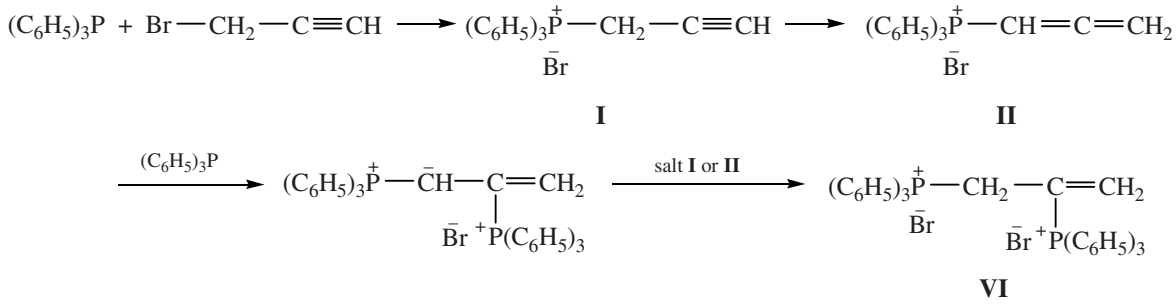



Along with $^1$H and $^{13}$C NMR, the structure of compound **IV** was established by its dehydrobromination to triphenyl(prop-1-ynyl)phosphonium bromide (**V**) under the action of triethylamine.



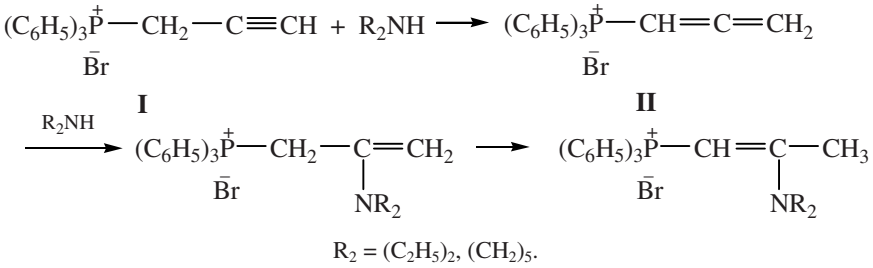

Attempted preparation of salt **I** by the reaction of the components in absolute ether at a room temperature gave [2-(triphenylphosphonio)prop-2-enyl]triphenylphosphonium dibromide (**VI**) in a yield of 44%. The same result was obtained when the reaction was carried out in absolute benzene.

Apparently, the reaction scheme involves formation of salt **I** followed by allene formation and triphenylphosphine addition.



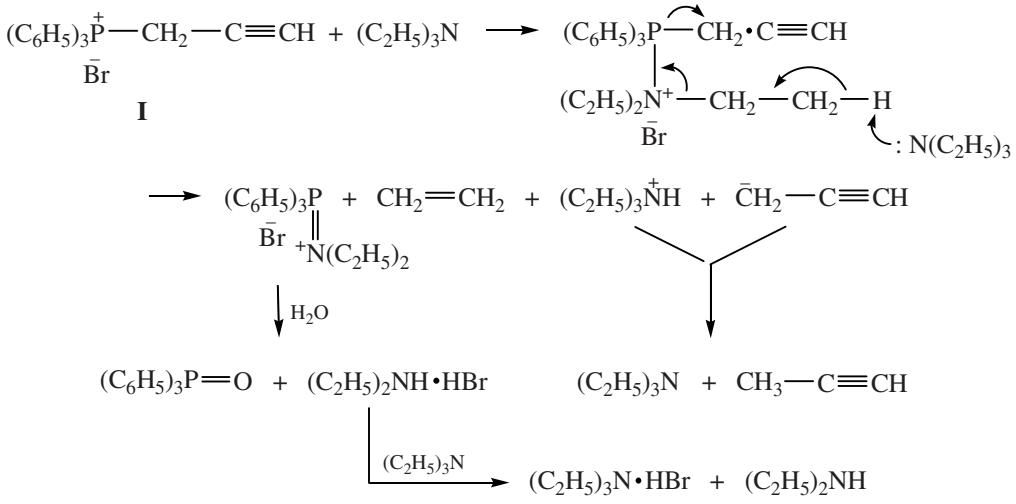
As would be expected, compound **VI** was also obtained by the reaction of salt **I** with triphenylphosphine in acetonitrile. The different behavior of triphenylphosphine toward propargyl bromide in the presence and in the absence of HBr is most likely explained by the prototropic isomerization of salts **I** into the allenic isomer in the second case. The latter reacts with triphenylphosphine by the nucleophilic addition scheme.

We studied reactions of salt **I** with such N-nucleophiles as diethylamine, piperidine, and triethylamine. In the first two cases, addition products were obtained according to the following scheme:

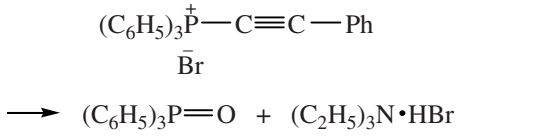



$R_2 = (C_2H_5)_2, (CH_2)_5$.

In the reaction with diethylamine, the product of addition across the triple bond and subsequent prototropic isomerization was isolated. The reaction with piperidine resulted in isolation of a 9 : 1 mixture of a similar adduct and piperidine hydrobromide. The reaction of salt **I** with triethylamine took an interesting pathway leading to triphenylphosphine oxide and triethylamine hydrobromide in yields of 70 and 84.5%, respectively. These products are likely to be formed by a scheme similar to that of alkaline hydrolysis of phosphonium salts, that involves nucleophilic attack on the phosphorus atom.



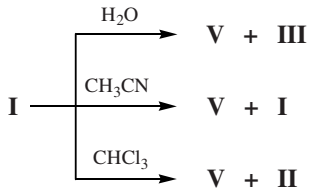

The same reaction pathway with triethylamine was observed in going from salt **I** to triphenyl(phenylethynyl)phosphonium bromide.




We reported earlier [6] a similar reaction pathway with the attack of amine on the phosphorus atom.

Previously we established that unsaturated phosphonium salts undergo a facile prototropic isomerization in various solvents. The isomerization involves shifts of the multiple bond from the β,γ into α,β position to phosphorus and back. In particular, it was found phenylpropargyl bromide reacts with triphenylphosphine in ether, benzene, or acetonitrile to form triphenyl(3-phenylpropadienyl)phosphonium bromide. The same reaction in chloroform results in a pure salt with a phenylpropargyl group. Regularities of

interconversions of these isomeric phosphonium salts were revealed [10]. Proceeding with this research, we established that salt **I** on boiling in water gives a mixture of acetonyl and prop-1-ynyl salts **III** and **V**, in acetonitrile, a mixture of prop-1-ynyl and starting salts **V** and **I**, and in chloroform, a mixture of prop-1-ynyl and propadienyl salts **V** and **II**.




According to published data and our results triphenylphosphonium salts containing an aroylmethyl group undergo a facile heterocyclization under action of 10 N alkali both at low and at room temperatures to form phosphoxazole derivatives. We failed to carry out a similar reaction with oxime derived from salt **III**: The oxime was always recovered unchanged. Apparently, for heterocyclization to occur an aryl-substituted keto group is necessary.

## EXPERIMENTAL

The NMR spectra are recorded on a Varian Mercury 300 spectrometer at 300.08, 121.75 and 75.46 MHz for $^{1}H$, $^{31}P$, and $^{13}C$ and 2D-COSY, respectively, at 303K. The chemical shifts were measured against internal TMS ($^{1}H$ and $^{13}C$) and external orthophosphoric acid ($^{31}P$). The IR spectra were recorded on UR-20 and Specord IR-75 instruments.

**Reaction of triphenylphosphine with propargyl bromide.** *a*. A replica of the experiment in [7, 9] was made. A mixture, 5.8 g (16.6%), of triphenylpropargylphosphonium bromide (**I**) and propadienyltriphenylphosphonium bromide (**II**) and 16.7 g (45.5%) of acetonyltriphenylphosphonium bromide (**III**) was prepared from 24 g of triphenylphosphine, 45 ml of dry 1,4-dioxane, 10 ml of 52% HBr, and 11.3 g propargyl bromide. Salt **I**. IR spectrum of salt **I**, ν, $cm^{-1}$: 2100 (–C≡CH), 3140 (≡CH). $^{1}H$ NMR spectrum (DMSO), δ, ppm, (*J*, Hz): 3.02 d.t (1H, $^{4}J_{PH}$ 6.9, $^{4}J_{HH}$ 2.7, –C≡CH), 5.19 d.d (2H, $^{2}J_{PH}$ 16.6, $^{2}J_{HH}$ 2.7, $PCH_2$), 7.7–7.95 m (15H, $C_6H_5$). $^{31}P$ NMR spectrum (DMSO), δ, ppm: 27.7. Salt **II.** IR spectrum, ν, $cm^{-1}$: 1960 ($CH=C=CH_2$). $^{1}H$ NMR spectrum (DMSO), δ, ppm, (*J*, Hz): 5.49 d.d (2H, $^{4}J_{PH}$ 13.1, $^{4}J_{HH}$ 6.5, $=CH_2$), 7.7–7.93 m (16H, $C_6H_5$ and $P^{+}CH=$). $^{31}P$ NMR spectrum (DMSO), δ, ppm: 23.95. Salt **III.** IR spectrum, ν, $cm^{-1}$: 1720 (C=O ). $^{1}H$ NMR spectrum ($CDCl_3$), δ, ppm, (*J*, Hz): 6.02 d (2H, $^{2}J_{PH}$ 11.4, $PCH_2$), 2.59 d (3H, $^{4}J$ 2.6, $CH_3$), 7.5–8.1 m (15 H, $C_6H_5$). $^{13}C$ NMR spectrum ($CDCl_3$), δ, ppm, 32.78 d ($CH_3$, $^{3}J_{PC}$ 6.5), 40.89 d ($CH_2$, $^{1}J_{PC}$ 58.4), 118.79 d ($3C_{ipso}$, $^{1}J_{PC}$ 89.2), 130.24 d (6C, $^{2}J_{PC}$ 13.0), 134.04 d (6C, $^{3}J_{PC}$ 10.7), 134.81 d (3C, $^{4}J_{PC}$ 3.0), 200.98 d (CO, $^{2}J_{PC}$ 6.8). $^{31}P$ NMR spectrum ($CDCl_3$), δ, ppm: 21.8. Found, %: Br 20.60. $C_{21}H_{20}BrOP$. Calculated, %: Br 20.05. mp 223–224°C. The product gave no melting point depression in a mixture with an authentic sample.

*b*. A mixture of 9.55 g of triphenylphosphine and 17.5 ml of dry 1,4-dioxane was stirred for 40 min at room temperature, after which 5.8 g of 42% HBr was added dropwise, and the mixture was stirred until homogeneous (50 min). A solution of 4.34 g of propargyl bromide in 5 ml of dioxane was added dropwise to the resulting solution. At the next day the precipitate that formed was filtered off, washed with absolute ether and benzene, and dried under a vacuum to obtain 10.5 g (75.6%) of triphenylpropargyl-phosphonium bromide, mp 168–169ºC. The IR, $^{1}H$, and $^{31}P$ NMR spectra were coincident with those of salt **I** obtained in the previous experiment. Found, %: Br 20.8, $C_{21}H_{20}BrP$. Calculated, %: Br 20.99.

**Alkaline hydrolysis of triphenylpropargylphosphonium bromide (I).** To a solution of 1.2 g of salt **I** in 26 ml of water, 13.1 ml of 10% NaOH was added, and the mixture was refluxed for 4 h. The aquoeus layer was decanted. The precipitate was washed with ether several times. The ethereal extracts were reduced by distillation, and the residual substance and the powder at the bottom of the flask were washed with absolute acetone and dried to obtain 0.81 g (97.1%) of triphenylphosphine oxide, mp 152–153ºC. The product gave no melting point depression in a mixture with an authentic sample.

**Reaction of triphenylpropargylphosphonium bromide (I) with 42% HBr.** Hydrobromic acid, 1.1 ml, was added dropwise to 1.2 g of salt **I** in 10 ml of ethanol, and the mixture was refluxed for 1 h. The alcohol was removed by distillation. The residual white precipitate was washed with several portions of distilled water and then with ether, and dried to obtain 5.5 g of a mixture of (2-bromoprop-2-enyl)triphenylphosphonium bromide (**IV**) and acetonyltriphenylphosphonium bromide (**III**) in a 95 : 5. Salt **IV.** IR spectrum, ν, $cm^{-1}$: 1620 ($C=CH_2$). $^{1}H$ NMR spectrum (DMSO), δ, ppm, (*J*, Hz): 5.49 d (2H, $^{2}J_{PH}$ 15.5, $PCH_2$), 5.70 d.d (1H, $^{4}J_{PH}$ 4.3, $^{2}J_{HH}$ 1.9, $C=CH_2$), 6.26

d.d (1H, $^4J_{PH}$ 5.0, $^2J_{HH}$ 1.9, C=$CH_2$), 7.65–7.98 m (15H, $C_6H_5$). $^{31}$P NMR spectrum (DMSO), δ, ppm: 26.95. Salt **III.** IR spectrum, ν, $cm^{-1}$: 1720 (C=O). $^1$H NMR spectrum (DMSO), δ, ppm, (*J*, Hz): 6.03 d (2H, $^2J_{PH}$ 12.2, $PCH_2$), 2.44 d (3H, $^4J_{PH}$ 2.6, $CH_3$), 7.5–8.1 m (15H, $C_6H_5$). $^{31}$P NMR spectrum (DMSO), δ, ppm: 25.32.

**Reaction of (2-bromoprop-2-enyl)triphenylphosphonium bromide (IV) with triethylamine.** To a heterogeneous mixture of 0.5 g of salt **IV** and 8 ml of dry acetonitrile, 0.11 g of triethylamine was added, and the resulting mixture was refluxed for 1 h. After removal of the solvent, the residue was washed with a water–chloroform mixture. From the aquoeous layer, 0.15 g (82.4%) of triethylamine hydrobromide was isolated, mp 245ºC. The product gave no melting point depression in a mixture with an authentic sample Found, %: Br 43.3. $C_6H_{16}BrN$. Calculated, %: Br 43.9. From the chloroform layer, 0.2 g of a mixture ($^1$H and $^{31}$P NMR spectra) of triphenyl(prop-1-ynyl)phosphonium bromide (**V**) and triphenylphosphine oxide was isolated in a 1 : 1 ratio. Salt **V.** IR spectrum, ν, $cm^{-1}$: 2220 (–C ≡C–). $^1$H NMR spectrum (DMSO), δ, ppm, (*J*, Hz): 2.59 d (3H, $^4J_{PH}$ 4.7, $CH_3$), 7.42–7.98 m (15H, $C_6H_5$ of salt and 15H, $C_6H_5$ of oxide). $^{31}$P NMR spectrum (DMSO), δ, ppm: 10.5 (salt) and 30.7 (oxide).

**Reaction of triphenylphosphine with propargyl bromide in ether.** Propargyl bromide, 3 g, was added dropwise to a solution of 6.6 g of triphenylphosphine in 30 ml of absolute ether under nitrogen. At the next day, the precipitate was filtered off, washed in succession with several portions of absolute ether, a minimum of dry acetonitrile, and ether and dried under a vacuum to obtain 4.0 g (44.0%) of [2-(triphenylphosphonio)prop-2-enyl]triphenylphosphonium dibromide (**VI**), mp 275ºC. IR spectrum, ν, $cm^{-1}$: 1620, (C=$CH_2$). $^1$H NMR spectrum (DMSO), δ, ppm, (*J*, Hz): 5.14 d.d (2H, $^2J_{PH}$ 15.4, $^3J_{PH}$ 9.7, $PCH_2$), 6.41 d.t (1H, $^3J_{PH}$ 22.1, $^2J_{HH}$ = $^4J_{PH}$ = 3.1, C=$CH_2$), 6.58 d.t (1H, $^3J_{PH}$ 46.2, $^2J_{HH}$ = $^4J_{PH}$ = 3.1, C=$CH_2$), 7.61–7.96 m (30H, $C_6H_5$). $^{13}$C NMR spectrum (DMSO), δ, ppm, 23.8 d.d ($CH_2$, $^1J_{PC}$ 49.0, $^2J_{PC}$ 12.8), 119.2 d.d (=C, $^1J_{PC}$ 78.5, $^2J_{PC}$ 7.0), 146.8 (=$CH_2$), 115.4 d ($C_{ipso}$, $^1J_{PC}$ 88.1), 117.1 d ($C_{ipso}$, $^1J_{PC}$ 86.0), 130.4 d ($^2J_{PC}$ 12.8), 130.4 d ($^2J_{PC}$ 12.8), 133.9 d ($^3J_{PC}$ 10.6), 134.7 d ($^3J_{PC}$ 10.5), 135.4 d ($^4J_{PC}$ 2.9), 135.6 d ($^3J_{PC}$ 2.9). $^{31}$P NMR spectrum (DMSO), δ, ppm: 28.5 d ($^3J_{PP}$ 24.3), 32.5 d ($^3J_{PP}$ 24.3). Found, %: Br 21.5. $C_{39}H_{34}Br_2P_2$. Calculated, % : Br 22.1. A similar result was obtained in the reaction in absolute benzene.

**Reaction triphenylpropargylphosphonium bromide (I) with triphenylphosphine.** Dry acetonitrile, 10 ml, and 0.68 g of triphenylphosphine were added to 1 g of salt **I**. At the next day, the precipitate that formed was filtered off, washed with several portions of absolute ether, and dried to obtain 0.6 g (31.5%) of salt **VI**, mp 275ºC. The product gave no melting point depression in a mixture with an authentic sample. The IR, $^1$H, $^{13}$C, and $^{31}$P spectra were coincident with those of the sample obtained in the previous experiment.

**Alkaline hydrolysis of bis-salt VI.** To a solution of 1 g of salt **VI** in 22 ml of water, 11 ml of 10% NaOH was added. The mixture was refluxed for 6 h with stirring. The aqueous layer was decanted; the solid residue was washed with several portions of ether and dried under in a vacuum to obtain 0.35 g (46.0%) of triphenylphosphine oxide, mp 152–153ºC. The product gave no melting point depression in a mixture with an authentic sample.

**Reaction of triphenylpropargylphosphonium bromide (I) with diethylamine.** To 1.0 g of salt **I** in 11 ml of dry acetonitrile, 0.21 g of diethylamine was added dropwise. The mixture was refluxed for 1.5 h. At the next day, acetonitrile was removed under a vacuum. The solid residue was washed in succession with several portions of absolute ether, absolute benzene, and absolute ether, and dried to obtain 0.9 g (76.1%) of (2-diethylaminoprop-1-enyl)triphenyl phosphonium bromide, mp 95–96ºC. IR spectrum, ν, $cm^{-1}$: 1615 ($P^+$–CH=C). $^1$H NMR spectrum (DMSO), δ, ppm, (*J*, Hz): 1.27 t (6H, $^3J_{HH}$ 7.1, $CH_3$), 1.87 s (3H, $CH_3$), 3.53 q (4H, $^3J_{HH}$ 7.1, $NCH_2$), 3.96 d (1H, $^2J_{PH}$ 13.9, PCH), 7.66–7.82 m (15H, $C_6H_5$). $^{31}$P NMR spectrum (DMSO), δ, ppm: 21.5. Found, %: Br 18.16. $C_{25}H_{29}BrNP$ . Calculated, %: Br 17.62.

**Reaction of triphenylpropargylphosphonium bromide (I) with piperidine.** Piperidine, 0.4 g, was added to 1.6 g of salt **I** and 10 ml of dry acetonitrile. At the next day, acetonitrile was removed under a vacuum. The precipitate was washed with absolute ether and dried to obtain 1.2 g of a mixture of triphenyl (2-piperidinoprop-1-enyl)phosphonium bromide and piperidine hydrobromide in a 9 : 1. IR spectrum of the mixture, ν, $cm^{-1}$: 1610 ($P^+$–CH=C ). $^1$H NMR spectrum of the salt (DMSO), δ, ppm, (*J*, Hz): 1.65–1.75 m (6H, $CH_2$) and 3.58 m (4H, $NCH_2$ of piperidine), 1.88 s (3H, $CH_3$), 4.20 d (1H, $^2J_{PH}$ 14.1, PCH), 7.66–7.82 m (15H, $C_6H_5$). $^{31}$P NMR spectrum (DMSO), δ, ppm: 22.8 . $^1$H NMR spectrum of piperidine hydrobromide

(DMSO), δ, ppm, (*J*, Hz): 1.80–1.85 m (6H, $CH_2$) and 3.0–3.1 t (4H, $NCH_2$), 9.1 w (2H, $^+NH_2$).

**Reaction of triphenylpropargylphosphonium bromide (I) with triethylamine.** A heterogeneous mixture of 1 g of salt **I**, 0.3 g of triethylamine, and 10 ml of acetonitrile was allowed to stand at room temperature for 24 h. Acetonitrile was removed under a vacuum. The precipitate was washed with several portions of absolute ether and dried to obtain 0.95 g of a mixture of triphenylphosphine oxide and triethylamine hydrobromide. $^1$H NMR spectrum of the mixture ($CDCl_3$), δ, ppm, (*J*, Hz): 1.42 t (9H, $NCH_2CH_3$), 3.19 m (6H, $NCH_2$), 7.41–7.88 m (15H, $C_6H_5$ of oxide), 11.25 br (1H, $N^+H$). $^{31}$P NMR spectrum ($CDCl_3$), δ, ppm: 33.2 (oxide). Chloroform and water were added to the mixture, and the layers were separated. Triethylamine hydrobromide, 0.23 g (48.9%), mp 245°C, was isolated from the aqueous layer after evaporation on a water bath. The product gave no melting point depression in a mixture with an authentic sample. From the chloroform layer, 0.4 g (55.5 %) of triphenylphosphine oxide was isolated, mp 152–154°C. The product gave no melting point depression in a mixture with an authentic sample.

**Reaction of triphenyl(phenylethynyl)phosphonium bromide with triethylamine.** Triethylamine, 0.34 g, was added dropwise to a solution of 1.5 g of the salt in 7 ml of acetonitrile. After 2 h, crystal formation was observed. At the next day, the solvent was removed by vacuum distillation. The precipitate was washed with several portions of absolute ether and dried to obtain 0.9 g of a mixture of the starting salt and triethylamine hydrobromide in a 44.5 : 55.5 ($^1$H NMR spectrum). IR spectrum of the mixture, ν, $cm^{-1}$: 2200 (–C≡C–). $^1$H NMR spectrum of the mixture ($CDCl_3$), δ, ppm, (*J*, Hz): 1.42 t (9H, $NCH_2CH_3$), 3.21 m (6H, $NCH_2$), 7.41–7.65 m (5H, $P^+$–C≡C–$C_6H_5$ ), 7.8–7.98 m (15H, $C_6H_5$), 10.4 br (1H, $N^+H$). $^{31}$P spectrum ($CDCl_3$), δ, ppm: 11.9 (salt). Triphenylphosphine oxide, 0.37 g (40%), was also obtained, mp 154ºC. The product gave no melting point depression in a mixture with an authentic sample. $^{31}$P NMR spectrum ($CDCl_3$), δ, ppm: 33.3.

**Isomerization of triphenylpropargylphosphonium bromide (I) in various solvents.** *a. In water.* Salt **I,** 1 g, was refluxed in 15 ml of water for 5 h. The solvent was removed by distillation. The residue was washed with benzene and ether and dried to obtain 1 g of a mixture of salts **V** and **III**. IR spectrum of the mixture, ν, $cm^{-1}$: 2215 (–C≡C–) and 1700 (C=O).

*b. In dry acetonitrile*. Salt **I,** 1 g, was refluxed in 15 ml of acetonitrile for 17 h. The solvent was removed under a vacuum. The residue was washed with absolute ether and dried to obtain 0.9 g of a mixture of salts **V** and **I**. IR spectrum of the mixture, ν, $cm^{-1}$: 2200 (–C≡C–) and 2100 (–C≡CH), 3150 (≡CH ).

*c. In chloroform*. : Salt **I,** 1 g, was refluxed in 8 ml of chloroform for 21 h and then treated as above to obtain 1 g of a mixture of salts **V** and **II**. IR spectrum of the mixture, ν, $cm^{-1}$: 2200 (–C≡C–) and 1940 (allene).

**[2-(Hydroxylimino)propyl]triphenylacetonylphosphonium bromide.** A mixture of 2 g of salt **III**, 0.7 g of hydroxylamine hydrochloride, 4.1 ml of ethanol, and 4.0 g of pyridine was heated on a water bath with stirring for 2 h. Water was partially removed by distillation, the residue was filtered off, and dried to obtain 1.78 g (85.9%) of the oxime as a mixture of two stereoisomers, mp 177–179°C. IR spectrum, ν, $cm^{-1}$: 1670 (C=N). $^1$H NMR spectrum (DMSO), δ, ppm, (*J*, Hz): 1.96 s (3H, $CH_3$), 4.88 d (2H, $^2J_{PH}$ 16.9, $PCH_2$) and 5.08 d (2H, $^2J_{PH}$ 14.2, $PCH_2$), 7.3–7.95 m (15H, $C_6H_5$), 10.87 s (1H, OH) and 11.19 s (1H, OH). Found, %: Br 19.88, $C_{21}H_{21}BrNOP$. Calculated, %: Br 19.32.

**Attempted cyclization of [2-(hydroxylimino)-propyl]triphenylacetonylphosphonium bromide.** According to [11], a mixture of 1.3 g of the oxime in a minimum of methanol and 3.6 ml of 1 N aqueous NaOH was allowed to stand at room temperature to obatin 0.8 g (95.9%) of triphenylphosphine oxide, mp 150–152ºC. The product gave no melting point depression in a mixture with an authentic sample.

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