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Reaction of Triphenyl(phenylethynyl)phosphonium Bromide with α-Aminoethers, Dipiperidinomethane, and Secondary Amines

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Abstract — The reactions of triphenyl(phenylethynyl)phosphonium bromide with α-aminoethers lead to formation of triphenyl(2-amino-2-phenylvinyl)phosphonium bromides. In the case of acyclic aminoethers, this reaction is accompanied by the formation of the corresponding amine hydrobromide and triphenylphosphine oxide by a scheme analogous to that of alkaline hydrolysis of phosphonium salts and involving attack of the amine on the phosphorus atom. The reaction of the same salt with diethyl- or dipropylamine affords hydrobromides of the latter, while with piperidine, together with salts, its adduct by the triple bond is formed. Piperidinomethane with the same salt forms triphenylphosphonium (2-phenyl-2-piperidinovinyl)phosphonium bromide.

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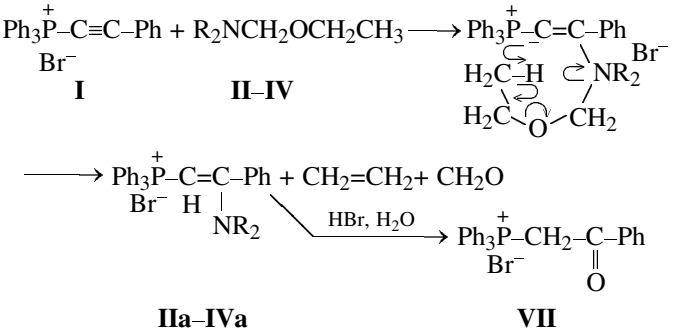
According to published data, triphenyl(phenylethynyl)phosphonium bromide (**I**) reacts with primary amines and azoles, affording vinyl-containing adducts [1–4]. Similar pathways are characteristic of the reactions of **I** with phenylhydrazine, hydroxylamine, and dialkyl phosphates, with the only difference that in these cases the resulting adducts enter further transformations: The adducts of phenylhydrazine and hydroxylamine undergo tautomerization into hydrazones and oximes, those of hydrazine hydrate undergo alkaline hydrolysis, and those of dialkyl phosphates are converted into *O*-betaines with the positively charged phosphonium center [5, 6].

We studied the reactions of salt **I** with α-aminoethers **II**–**V** and dipiperidinomethane (**VI**).

The presence of two centers of nucleophilic attack in compounds **II**–**V** did not allow us to predict the actual reaction pathway. It might be assumed that the greater mesomeric effect of the nitrogen atom can direct this reaction to the side of oxygen with a weak C–O bond.

The resulting data were rather unexpected. The reactions of compounds **II**–**IV** with salt **I** gave triphenyl[2-phenyl-2-(dialkylamino)vinyl]phosphonium bromides **IIa**–**IVa**.

We suggest that this reaction proceeds by the following scheme:

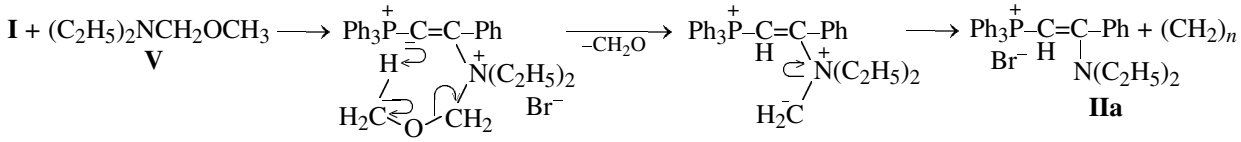


I **II–IV** **IIa–IVa** **VII**

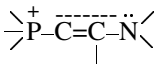
R^2 = $(C_2H_5)_2$ (**II, IIa**), $(C_3H_7)_2$ (**III, IIIa**), $(CH_2)_5$ (**IV, IVa**).

As seen, the ylide formed by the attack of the aminoether nitrogen on the triple bond is stabilized via elimination of ethylene and formaldehyde. Formaldehyde, indeed, was detected among the reaction products.

Diethyl(methoxymethyl)amine (**V**) reacted in a similar way. In this case, the intermediate ylide is most probably stabilized by a scheme involving elimination of a proton from the methoxy group, expulsion of formaldehyde, and elimination of a methylene group as a carbene which then converts into polymethylene. Analogous behavior of methylammonium ylides has been described earlier [7].

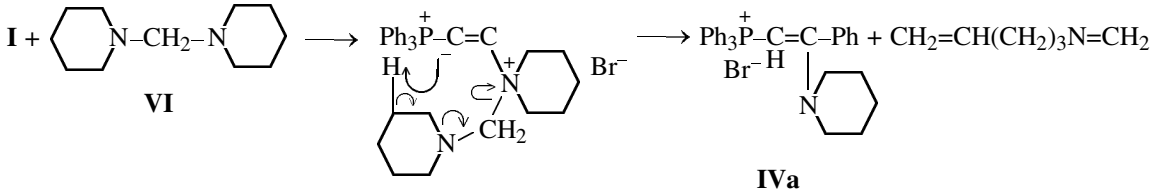


The structure of the obtained adducts was established by their acid hydrolysis into phenacyltriphenylphosphonium bromide (**VII**) and by NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra of these compounds show that two alkyl groups at the nitrogen atom are nonequivalent, implying a high barrier to rotation about the C–N bond, and, consequently, a considerable shift of the the nitrogen lone electron pair toward the C=C bond.

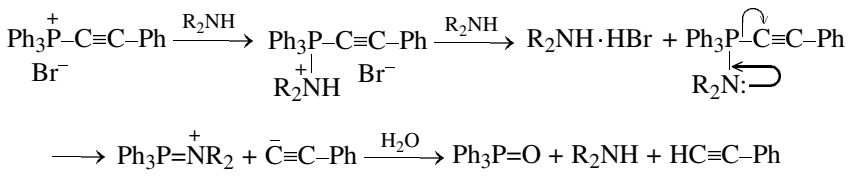


Furthermore, in the ^{13}C NMR spectrum of compound **IIa**, the signal of the α-carbon atom appears fairly upfield (δ_C 59.9 ppm), which is absolutely atypical of sp^2-carbon atoms. At the same time, the signal of the α-carbon atom is shifted downfield to δ_C 164.4 ppm. The difference of the chemical shifts of more than 100 ppm provides evidence showing that the C=C bond in these compounds is strongly polarized.

The reaction of salt **I** with dipiperidinomethane (**VI**) gave adduct **IVa** by the following scheme:

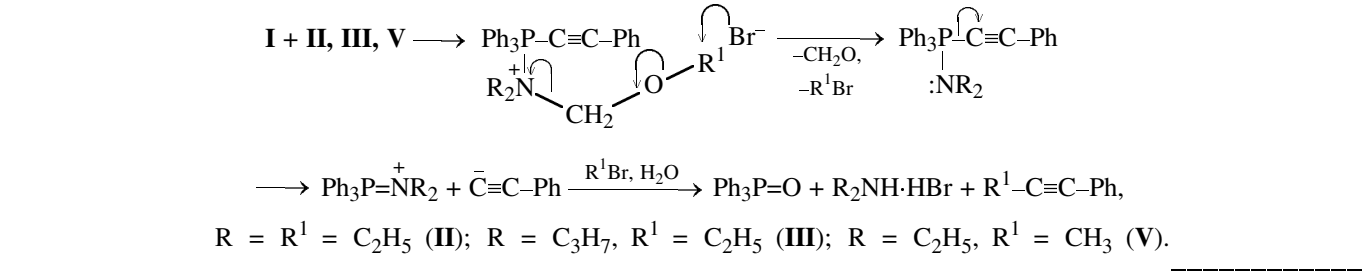


Conclusive evidence for the structure of the products was provided by the results of the reactions of salt **I** with diethylmine, dipropylamine, and piperidine under the same conditions as in the reactions with aminoethers. In the two first cases we unexpectedly isolated the corresponding amine hydrobromides, and in the third case we obtained a mixture of adduct **IVa** and piperidine hydrobromide. We suggest that the hydrobromide is formed by a scheme analogous to alkaline hydrolysis or the so-called paraffin cleavage of phosphonium salts.



The possibility of such cleavage was established earlier in our study of the reaction of a phosphonium salt containing a 3,4-dichlorobut-2-enyl group with hydrazine [8].

Note that the formation of amine hydrohalides was also observed in the reactions of salt **I** with aminoethers **II**, **III**, and **V**. These reactions are likely to proceed by a scheme analogous to shown above, but the intermediate phosphinoammonium compound is stabilized by nucleophlic substitution at the oxygen atom, anionization of the phenylethynyl goup, and alkylation with the liberated alkyl halide.



EXPERIMENTAL

The NMR spectra were registered on a Varian Mercury-300 spectrometer at 300.08 (^{1}H), 121.75 (^{31}P), and 75.46 MHz (^{13}C), respectively, at 303 K. The chemical shifts were measured relative to internal TMS (^{1}H, ^{13}C) and external H_3PO_4 (31P). The DEPT procedure was used for assignment of the ^{13}C NMR spectra. The IR spectra are registered on UR-20 and Specord IR-75 instruments.

(1) **Reaction of triphenyl(phenylethynyl)phosphonium bromide (I) with (ethoxymethyl)diethylamine (II).** A solution of 3.0 g of salt **I** and 0.88 g of aminoether **II** in 13 ml of anhydrous acetonitrile was heated on a water bath at 80°C for 16 h. After cooling, acetonitrile was removed in a vacuum, the precipitate formed was washed with absolute benzene and absolute ether, and dried to obtain 2.64 g of a mixture of [2-(diethylamino)-2-phenylvinyl]triphenylphosphonium bromide (**IIa**) and diethylamine hydrobromide in a 4.6 : 1 ratio (by ^{1}H NMR). IR spectrum of the mixture, ν, cm^{-1}: 1635 (P^+–CH=C). ^{1}H NMR spectrum of salt **IIa** (DMSO-d_6/CCl_4, 1 : 3), δ, ppm (*J*, Hz): 0.99 t (3H, $^3J_{HH}$ 7.1 Hz, CH_3), 1.51 t (3H, $^3J_{HH}$ 7.1 Hz, CH_3), 2.97 q (2H, $^3J_{HH}$ 7.1, NCH_2), 3.82 q (2H, $^3J_{HH}$ 7.1, NCH_2), 4.50 d (1H, $^2J_{PH}$ 12.5, PCH), 6.71 m (2H, *ortho*-HPh), 6.90 m (2H, *meta*-HPh), 7.14 t.t (1H, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.4 *para*-HPh), 7.42–7.70 m (15H, PPh_3). ^{13}C NMR spectrum (DMSO-d_6/CCl_4, 1 : 3), δ_C, ppm: 10.9 (CH_3), 13.8 (CH_3), 43.5 (NCH_2), 45.4 (NCH_2), 59.9 d ($^1J_{PC}$ 123.0, PCH), 123.4 d (3C, $^1J_{PC}$ 90.6, C_{ipso}, PPh_3), 129.1 d (6C, $^2J_{PC}$ 12.1, PPh_3), 132.0 d (6C, $^3J_{PC}$ 10.6, PPh_3), 132.8 d (3C, $^4J_{PC}$ 2.7, PPh_3), 166.4 d ($^2J_{PC}$ 15.1, N=C). ^{31}P NMR spectrum ($CDCl_3$): δ_P 22.2 ppm. ^{1}H NMR spectrum of diethylamine hydrobromide (DMSO-d_6/CCl_4, 1 : 3), δ, ppm, (*J*, Hz): 1.3 t (6H, CH_3), 2.95 q (4H, NCH_2), 8.85 br (2H, $^+NH_2$).

After washing with water and drying, 2.4 g (68.65%) of mixture **IIa** was obtained. Found, %: Br^- 16.2. $C_{30}H_{31}BrNP$. Calculated, %: Br^- 15.50.

(2) **Acid hydrolysis of [2-(diethylamino)-2-phenylvinyl] triphenylphosphonium bromide (IIa).** To a solution of 0.75 g of salt **IIa** in 7.0 ml of alcohol, 0.5 ml of 40.5% HBr was added dropwise with stirring. The mixture was refluxed for 1 h with stirring. The precipitate formed after most alcohol had been removed by distillation was washed with water and dried to obtain 0.35 g (54.28%) of phenacyltriphenylphosphonium bromide (**VII**), mp 272–273°C, which showed no melting point depression in mixture with an authentic sample. IR spectrum, ν, cm^{-1}: 1673 (PhC=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, (*J*, Hz): 6.4 d (2H, CH_2, $^2J_{PH}$ 11.3), 7.4–8.0 m (15H, PPh_3 and 3H, *meta*,*para* PhC=O), 8.35–8.45 m (2H, *ortho*,*ortho* PhC=O). ^{31}P NMR spectrum ($CDCl_3$): δ_P 22.55 ppm. Found, %: Br^- 16.45. $C_{26}H_{22}BrOP$. Calculated, %: Br^- 17.35.

Acid hydrolysis of compounds **IIIa**–**IVa** was performed similarly.

(3) **Reaction of salt I with (ethoxymethyl)dipropylamine (III).** A mixture of 0.8 g of salt **I** and 0.34 g of compound **III** in acetonitrile was heated for 20 h and then treated as in the preceeding experiment to obtain 0.5 g of a mixture of triphenyl[2-(dipropylamino)-2-phenylvinyl]phosphonium bromide (**IIIa**) and dipropylamine hydrobromide in a 1 : 2 ratio (by ^{1}H NMR) as an oily substance. IR spectrum of the mixture, ν, cm^{-1}: 1635 (P^+–CH=C). ^{1}H NMR spec-

trum of salt **IIIa** (DMSO-d_6/CCl_4, 1 : 3), δ, ppm, (*J*, Hz): 0.61 t (3H, $^3J_{HH}$ 7.2, CH_3), 1.10 t (3H, $^3J_{HH}$ 7.2, CH_3), 1.45 m (2H, CH2), 1.93 m (2H, CH2), 2.94 br (2H, NCH_2), 3.68 br (2H, NCH_2), 4.71 d (1H, $^2J_{PH}$ 11.8, PCH), 6.71 m (2H, *ortho*-HPh), 6.88 m (2H, *meta*-HPh), 7.13 t.t (1H, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.1, *para*-HPh), 7.45–7.72 m (15H, PPh_3). ^{31}P NMR spectrum (DMSO-d_6/CCl_4, 1 : 3), δ_P, ppm: 19.4. ^{1}H NMR spectrum of dipropylamine hydrobromide (DMSO-d_6/CCl_4, 1 : 3), δ, ppm, (*J*, Hz): 1.02 t (6H, CH_3), 1.79 m (4H, CH_2), 2.82 t (4H, NCH_2), 8.87 br (2H, $^+NH_2$).

(4) **Acid hydrolysis of triphenyl[2-dipropyl-2-(phenylamino)vinyl]phosphonium bromide (IIIa).** From 1.5 g of compound **IIIa** under conditions of exp. no. 2 we obtained 0.66 g (53.22%) of ketophosphonium salt **VII**, mp 272–273°C, which showed no melting point depression in mixture with an authentic sample. The IR and ^{1}H and ^{31}P NMR spectra coincide with those in exp. no. 2. Found, %: Br^- 16.95. $C_{26}H_{22}BrOP$. Calculated, %: Br^- 17.35.

(5) **Reaction of salt I with 1-(ethoxymethyl)piperidine (IV).** A mixture of 3.5 g of salt **I** and 1.13 g of compound **IV** was heated for 18 h in acetonitrile and then treated with a minimum quantity of water followed by absolute benzene and absolute ether to obtain 3.0 g (70.88%) of triphenyl(2-phenyl-2-piperidinovinyl)phosphonium bromide (**IVa**), mp 119–121°C, which showed no melting point depression in mixture with an authentic sample. IR spectrum, ν, cm^{-1}: 1640 (P^+–CH=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, (*J*, Hz): 1.62–1.86 m (6H, CH_2) and 2.84–3.0 m (4H, NCH_2 piperidine), 5.0 d (1H, $^2J_{PH}$ 12.3, PCH), 6.75–7.15 m (5H, PhC=C), 7.5–7.77 m (15H, PPh_3). ^{31}P NMR spectra (DMSO-d_6), δ, ppm: 19.64. Found, %: Br^- 15.35. $C_{31}H_{31}BrNP$. Calculated, %: Br^- 15.15.

Formaldehyde, 0.057 g (24%), was also isolated. Its 2,4-dinitrophenylhydrazone melted at 166°C and showed no melting point depression in mixture with an authentic sample.

(6) **Acid hydrolysis of triphenyl(2-phenyl-2-piperidinovinyl)phosphonium bromide (IVa).** By heating 1.8 g of compound **IVa** under conditions of exp. no. 2 we obtained 0.8 g (50%) of ketophosphonium salt **VII**, mp 272–273°C, which showed no melting point depression in mixture with an authentic sample. The IR and ^{1}H and ^{31}P NMR spectra coincide with those in exp. no. 2. Found, %: Br^- 16.6. $C_{26}H_{22}$·BrOP. Calculated, %: Br^- 17.35.

(7) **Reaction of salt I with diethyl(methoxymethyl)amine (V).** A mixture of 2.0 g of salt **I** and 0.63 g of compound **V** was heated for 18 h in acetonitrile and then treated with absolute benzene and absolute ether to obtain 1.5 g of a mixture of **IIa** and diethylamine hydrobromide (by ^{1}H NMR). The mixture was washed with water to isolate 1.25 g (53.3%) of compound **IIa**. The IR and ^{1}H NMR spectra coincide with those in exp. no. 1. Found, %: Br^- 16.05. $C_{30}H_{31}BrNP$. Calculated, %: Br^- 15.5.

(8) **Reaction of salt I with dipiperidinomethane (VI).** A mixture of 1.4 g of salt **I** and 0.57 g of compound **VI** was heated for 16 h at 80°C in 25 ml of anhydrous acetonitrile and then treated with absolute ether and benzene to obtain 1.2 g (72.2%) of mixture **IVa**. The IR and ^{1}H and ^{31}P NMR spectra coincide with those in exp. no. 5. Found, %: Br^- 15.09. $C_{31}H_{31}BrNP$. Calculated, %: Br^- 15.15.

(9) **Reaction of salt I with piperidine.** A mixture of 0.8 g of salt **I** and 0.18 g of piperidine was heated for 9.5 h in acetonitrile to obtain 0.5 g of mixture **IVa** and piperidine hydrobromide (by ^{1}H NMR) and then trated with water, absolute ether, and absolute benzene to isolate 0.3 g (31.5%) of phosphonium salt **IVa**, mp 120–121°C, which showed no melting point depression in mixture with an authentic sample.

(10) **Reaction of salt I with diethylamine.** A mixture of 0.7 g of salt **I** and 0.14 g of diethylamine was heated for 17 h in anhydrous acetonitrile and then treated with absolute ether and recrystallized (absolute benzene : absolute alcohol, 5 : 1) to obtain 0.164 g (67.08%) of diethylamine hydrobromide, mp 210–210.5°C, which showed no melting point depression in mixture with an authentic sample. Found, %: Br^- 52.6. $C_4H_{12}BrN$. Calculated, %: Br^- 51.94.

After removal of the solvent from the ethereal extracts we isolated 0.154 g (35.2%) triphenylphosphine oxide, mp 153–154°C, which showed no melting point depression in mixture with an authentic sample.

(11) **Reaction of of salt I with dipropylamine.** From 0.45 g of salt **I** and 0.12 g of dipropylamine under conditions of exp. no. 10 we obtained 0.0673 g (37%) of dipropylamine hydrobromide, mp 268°C, which showed no melting point depression in mixture with an authentic sample. Found, %: Br^- 43.8. $C_6H_{15}BrN$. Calculated, %: Br^- 43.95. Triphenylphosphine oxide, 0.1158 g (41.65%), was also obtained.

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