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## LETTERS TO THE EDITOR

# Unusual Course of Reaction of Buta-1,3-diene-1,4-diylbis(triphenylphosphonium Chloride) with Phenylhydrazine

**M. Zh. Ovakimyan, M. L. Movsisyan, G. A. Gasparyan, and M. G. Indzhikyan**

*Institute of Organic Chemistry, National Academy of Sciences of Armenia,*
*ul. Z. Kanakertsy 167a, Yerevan, 375091 Armenia*
*e-mail: ioc_phos@mail.ru*

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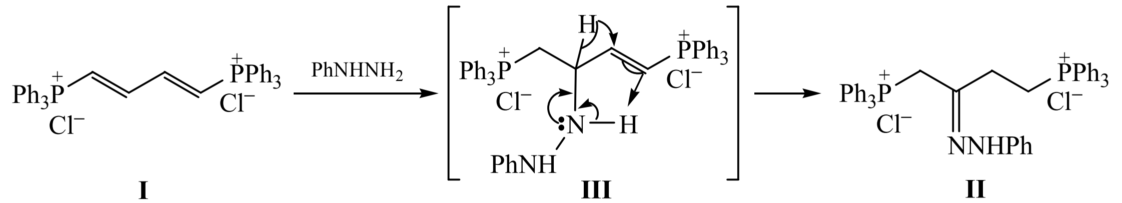
Previously we have found that triphenyl- and tributyl-2-phenylhydrazinoethylphosphonium salts when heated in ethanol or DMF are dehydrated to form phenylhydrazones of the corresponding phosphonium acetic aldehydes in high yields [1]. The same reaction occurred in the case of triphenyl- and tributylphosphonium salts with 4-*N*-phenylhydrazino-3-chlorobut-2-enyl group [2].

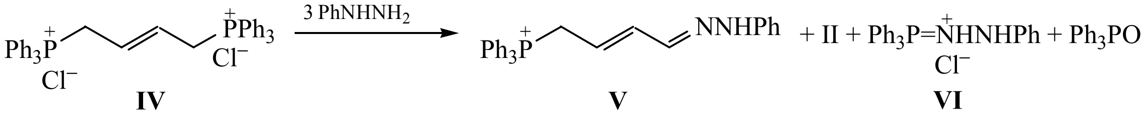
Based on the results of these studies we suggested that this reaction had a cyclic nature including the shift of a lone electron pair to the onium phosphorus atom and the hydride ion expulsion from the neighboring $sp^3$-carbon atom [3].

We found that buta-1,3-diene-1,4-diylbis(triphenylphosphonium chloride) **I** at reflux with 2 mol of phenylhydrazine in chloroform formed 2-phenylhydrazonobutane-1,4-diylbis(triphosphonium chloride) **II** in 85% yield. Yield of compound **II** decreased to 51% when the starting reagents were used in the equimolar ratio. The reaction was accompanied in both cases with the formation of phenylhydrazine hydrochloride in high amounts. The latter was established to form by the reaction of phenylhydrazine with chloroform. As expected, the reaction of salt **I** with equimolr amount of phenylhydrazine in acetonitrile affords compound **II** almost in the quantitative yield. Probably the formation of salt **II** occurs through initial addition of phenylhydrazine at one of multiple bonds of salt **I** to give intermediate **III** followed by hydrogenation of the multiple bond involving the transfer of a hydride ion by the cyclic mechanism:



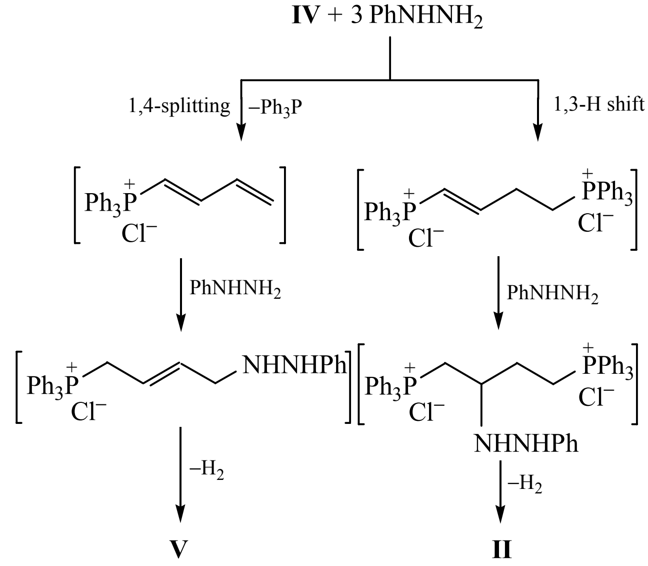
**I** **III** **II**

Compound **II** was found to form also from 2-butene-1,4-diylbis(triphenylphosphonium chloride) **IV** via the reaction with threefold excess of phenylhydrazine in chloroform, but its yield was 7% only. At the same time among the reaction products were also triphenyl(4-phenylhydrazonobut-2-enyl)phosphonium chloride **V** (46%), triphenylphosphine oxide (34%), and *N*-phenyltriphenylphosphine imine hydrochloride **VI** (19%), identified by the $^1$H NMR and elemental analysis data, and phenylhydrazine hydrochloride.



**IV** **V** **VI**

The formation of phenylhydrazone derivatives **II** and **V** can be represented as follows:



Triphenylphosphine was not detected in the reaction product. We found that triphenylphosphine reacts with phenylhydrazine to afford compound **VI**. It is possible that the triphenylphosphine oxide is a product of partial hydrolysis of **VI**.

The $^1$H, $^{13}$C and $^{31}$P NMR spectra were registered on a Varian Mercury-300 spectrometer operating at 300.077 ($^1$H), 75.46 ($^{13}$C) and 121.47 MHz ($^{31}$P), respectively, at 303 K, internal reference TMS. The starting salts **I** and **IV** were obtained by procedures [4, 5].

**2-Phenylhydrazonobutane-1,4-diylbis(triphenylphosphonium chloride) (II).** A mixture of 2 g of salt **I** and 0.67 g of phenylhydrazine in chloroform was stirred at 60°C, then treated with water and chloroform to obtain 0.5 g of phenylhydrazine hydrochloride and 2 g of **II**. Yield 85%, mp 215–220°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm ($J$, Hz.): 2.85 m (2H, $\mathrm{C}C\mathit{H}_2\mathrm{CH_2}$), 4.52 m (2H, $\mathrm{CCH_2}C\mathit{H}_2$), 5.60 d (2H, $\mathrm{P^+CH_2C}$, $J$ 14.2), 6.19 m (2H, 2,6-H Ph), 6.58 m (1H, 4-H Ph), 6.84 m (2H, 3,5-H Ph), 7.64-8.04 m (30H, $\mathrm{P^+Ph_3}$), 9.45 br.s (1H, NH). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm ($J$, Hz): 17.9 d ($\mathrm{P^+}\mathit{C}\mathrm{H_2CH_2}$, $J$ 50.7), 23.2 d ($\mathrm{P^+CH_2}\mathit{C}\mathrm{H_2}$, $J$ 8.9), 29.7 d ($\mathrm{P^+}\mathit{C}\mathrm{H_2C{=}}$, $J$55.9), 112.5 (2,6-C, NHPh), 118.0 d (1-C, $\mathrm{P^+Ph_3}$, $J$85.9), 118.5 (4-C, NHPh), 120.2 d (1-C, $\mathrm{P^+Ph_3}$, $J$88.6), 127.7 (3,5-C, NHPh), 129.2 d (2,6-C, $\mathrm{P^+Ph_3}$, $J$12.7), 129.8 d (2,6-C, $\mathrm{Ph_3P^+}$, $J$12.6), 133.5 d (4-C, $\mathrm{P^+Ph_3}$, $J$2.8), 133.6 d (3,5-C, $\mathrm{P^+Ph_3}$, $J$10.3), 134.0 d (3,5-C, $\mathrm{P^+Ph_3}$, $J$10.4), 134.3 d (4-C, $\mathrm{P^+Ph_3}$, $J$2.8), 137.2 d.d (N=C, $J_1$ 17.8, $J_2$ 8.8), 145.1 (NPh). $^{31}$P NMR spectrum (DMSO-$d_6$), $\delta_P$, ppm ($J$, Hz): 28.12, 30.64. Found, %: C 73.06; H 5.59; Cl 9.44; N 3.71; P 8.02. $\mathrm{C_{46}H_{42}Cl_2N_2P_2}$. Calculated, %: C 73.11; H 5.56; Cl 9.40; N 3.71; P 8.21.

**Reaction of salt IV with phenylhydrazine.** A mixture of 0.7443 g of **IV** and 0.35 g of phenylhydrazine in 15 ml of chloroform was heated for 10 h at 55–57°C. The reaction mixture was treated with water and extracted with chloroform. After chloroform removal the residue was subjected to fractional recrystallization (acetone, isopropanol). Compounds **V** (0.23 g, mp 162–164°C), **II** (0.058 g, mp 215–220°C), **VI** (0.085 g, mp 240–245°C), triphenylphosphine oxide (0.1025 g, mp 154°C) and phenylhydrazine hydrochloride (0.37 g) were otained. **Compound V.** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm ($J$, Hz.): 4.55 d.d (2H, $\mathrm{P^+CH_2}$, $^2J_{PH}$ 16.2, $^3J$ 7.5), 5.49 d. t. d (1H, $\mathrm{CH_2C}\mathit{H}$, $^3J$ 15.4, $^3J$ 7.5, $^3J_{PH}$ 6.6), 6.39 d.d.d (1H, $\mathrm{CH_2CH{=}C}\mathit{H}$, $^3J$ 15.4, $^3J$ 9.1, $^4J_{PH}$ 5.2), 6.65 m (1H, 4-H Ph), 6.94 m (2H, 2,6-H Ph), 7.05 m (2H, 3,5-H Ph), 7.54 d (1H, N=CH, $^3J$ 9.1), 7.60–7.84 m (15H, $\mathrm{Ph_3P^+}$) 10.34 br. s (1H, NH). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm ($J$, Hz.): 23.7 d ($\mathrm{CH_2}$, $^1J_{PC}$ 49.4), 112.0 (2,6-C, NHPh), 115.2 d $\mathrm{CH_2}\mathit{C}\mathrm{H}$, $^2J_{PC}$ 11.5), 117.5 d (1-C, $\mathrm{P^+Ph_3}$, $^1J_{PC}$ 85.3), 118.6 d (4-C, NHPh), 128.2 (3,5-C, NHPh), 129.7 d (2,6-C, $\mathrm{Ph_3P^+}$, $^2J_{PC}$ 12.5), 133.3 d (3,5-C, $\mathrm{Ph_3P^+}$, $^3J_{PC}$ 9.7), 134.6 d (4-C, $\mathrm{Ph_3P^+}$, $^4J_{PC}$ 2.8), 135.8 d (1C, N=CH, $^4J_{PC}$ 5.2), 137.7 d (=$\mathrm{CH}\mathit{C}\mathrm{HN}$, $^3J_{PC}$ 13.8), 144.3 (1-C, NHPh). $^{31}$P NMR spectrum (DMSO-$d_6$), $\delta_P$, ppm ($J$, Hz): 25.7. Found, %: C 73.64; H 5.67; Cl 7.73; N 6.15; P 6.81. $\mathrm{C_{28}H_{26}ClN_2P}$. Calculated, %: C 73.60; H 5.69; Cl 7.77; N 6.13; P 6.79. **Compound VI.** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm ($J$, Hz.): 6.69 t. t (1H, 4-H NHPh, $J$ 3.1), 6.83 m (2H, 2,6-H NHPh), 7.03 m (2H, 3,5-H NHPh), 7.63–7.70 m (6H, 2,6-H $\mathrm{Ph_3P^+}$), 7.79-7.92 m (9H, 3,5-H, 4-H $\mathrm{Ph_3P^+}$), 8.46 s (1H, N$\mathit{H}$Ph), 10.51 d (1H, =NH, $J_{PC}$ 31.3). $^{31}$P NMR spectrum (DMSO-$d_6$), $\delta_P$, ppm ($J$, Hz): 43.1. Found, %: C 71.02; H 5.35; Cl 8.52; N 6.80; P 7.53. $\mathrm{C_{24}H_{22}ClN_2P}$. Calculated, %: C 71.19; H 5.44; Cl 8.78; N 6.92; P 7.66.

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