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LETTERS TO THE EDITOR

Unusual Transformations of Phosphoryl Compounds in the Kishner Reduction

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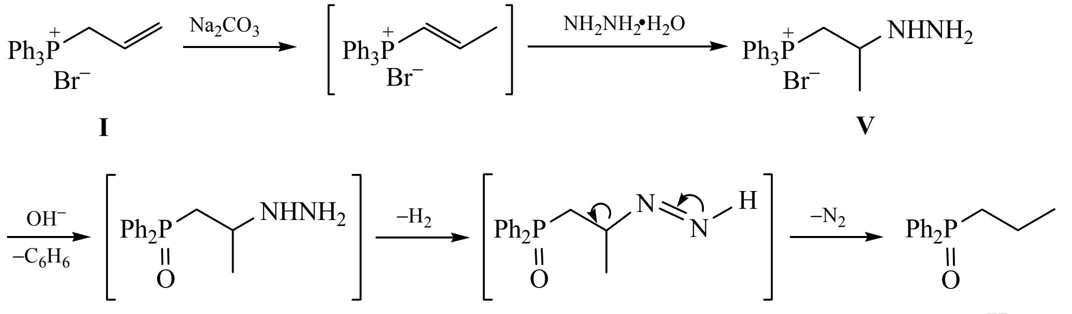
Recently we found that triphenyl-2-methyl-2-phenylhydrazinoethylphosphonium bromide formed in the reaction of triphenylprop-2-enylphosphonium bromide **I** [1] with phenylhydrazine was dehydrogenated in the presence of sodium carbonate under stirring for 6 h in chloroform at room temperature to give triphenyl-2-oxopropylphosphonium bromide phenylhydrazone in a 50% yield [2].

Aiming to obtain the similar unsubstituted hydrazone analog of the same phosphonium salt we studied the reaction of salt **I** with an aqueous hydrazine in the presence of sodium carbonate in chloroform at 30°C. Unexpectedly, propyldiphenylphosphine oxide **II** was obtained in 50% yield as the reaction product along with the doubly *N*-alkylated adduct. Probably the formation of **II** occurs through an intermediate diphenyl-2-methyl-2-hydrazinoethylphosphine oxide **III**. The latter undergoes successive dehydrogenation and denitrogenation as follows:



I **V** **III** **IV** **II**

Theoretically, there is a possibility of the intermediate formation of compound **IV** via the alkaline hydrolysis of azophosphonium salt derived through the direct dehydrogenation of salt **V**.

The phosphine oxide **II** was obtained with almost the same yield by the reaction of the phosphonium salt **I** with ethylhydrazine in an aqueous medium in the presence of acetic acid at 50°C. The reaction probably proceeds according to the same scheme, however in this case the reaction is accompanied by the ethylene formation.

We found that diphenylprop-1-enylphosphine oxide does not react with aqueous hydrazine at 30°C, but at reflux in acetonitrile it also transforms into propyldiphenylphosphine oxide in a low yield (30%). The residual phosphine oxide was recovered. Obviously, the low product yield is caused by the difficult addition of hydrazine to diphenylvinylphosphine oxide.

According to the experimental results, the elimination of the molecular nitrogen occurs in the phosphoryl intermediate **IV**.

The studied reaction is actually related to the Kishner reaction with the only difference that the latter usually proceeds at high temperatures. It can be assumed that the presence of the phosphoryl group in the substrate favors significantly the denitrogenation reaction, due likely to the formation of the hydrogen bonds between the phosphoryl oxygen and the hydrogen atom of the azo-groups.

Reaction of salt I with aqueous hydrazine. A mixture of 5.2 mmol of salt **I**, 0.28 g (5.2 mmol) of 60% aqueous hydrazine, and 5.2 mmol of dry sodium carbonate in 15 ml of chloroform was stirred for 6 h at 30°C and then diluted with water. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated. The residue was washed with anhydrous benzene, dried in a vacuum, and recrystallized from an ethyl acetate–isopropanol mixture to afford *N*,*N*-bis-(triphenylisopropylphosphoniodibromido)hydrazine. Yield 1.2 g (30%), mp 220°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.28 d (6 H, CH_3, $^3J_{HH}$ 6.3), 3.45 d.q.t [2H, $C\underline{H}(CH_3)N$, $^3J_{HH}$ 6.3, $^3J_{HH}$ 6.2, $^3J_{PH}$ 9.5), 3.82 d.d.d [2H, $P^+(H_a)H_b$, $^2J_{HH}$ 15.6, $^3J_{HH}$ 6.2, $^2J_{PH}$ 11.6], 4.17 d.d.d [2H, $P^+H_a(H_b)$, $^2J_{HH}$ 15.6, $^3J_{HH}$ 6.2, $^2J_{PH}$ 13.5], 7.6–8.0 m (30 H, P^+Ph_3), 9.15 br.s (2H, NH_2). ^{31}P NMR spectrum (DMSO-d_6): δ_P 28.50 ppm. Found, %: P 7.05; Br 19.98. $C_{42}H_{44}N_2P_2Br_2$. Calculated, %: P 7.77; Br 20.05.

The benzene extract was concentrated, and the residue was recrystallized from a benzene–petroleum ether mixture to afford propyldiphenylphosphine oxide [3]. Yield 0.62 g (49.3%), mp 99–100°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.15 t (3H, CH_3, $^3J_{HH}$ 7), 1.42–1.68 m (2H, $C\underline{H_2}CH_3$), 2.20–2.43 m (2H, PCH_2), 7.4–7.7 m (10H, PPh_2). ^{31}P NMR spectrum (DMSO-d_6): δ_P 30.77 ppm.

Reaction of salt I with ethylhydrazine. A mixture of 2.6 mmol of salt **I**, 2.6 mmol of acetic acid, and 2.6 mmol of ethylhydrazine in 10 ml of water was heated for 8 h at 55–57°C and extracted with chloroform. The chloroform extract was dried over $MgSO_4$, filtered, and concentrated. The residue was washed with anhydrous benzene and dried in a vacuum to afford triphenylprop-1-enylphosphonium bromide [1]. Yield 0.35 g (35%), mp 213–214°C. The benzene extract was concentrated, and the residue was recrystallized to afford propyldiphenylphosphine oxide. Yield 0.3 g (47.3%), mp 99–100°C. The NMR spectral parameters are completely consistent with the known data.

Reaction of diphenylprop-1-enylphosphine oxide with aqueous hydrazine. A mixture of 4.5 mmol of diphenylprop-1-enylphosphine oxide [4] and 0.35 g (6 mmol) of 60% aqueous hydrazine in 15 ml of acetonitrile was heated for 6 h at 75°C. Then the solvent was removed, and the residue was extracted with water and benzene. The benzene layer was dried over $MgSO_4$ and concentrated. The fractional recrystallization of the residue from benzene–petroleum ether results in propyldiphenylphosphine oxide. Yield 0.33 g (30%), mp 99–100°C. The NMR spectral parameters are completely consistent with the known data.

Also diphenylprop-1-enylphosphine oxide was isolated. Yield 0.7 g (64%), mp 127–128°C.

The ^1H and ^{31}P NMR spectra were recorded on a Varian Mercury-300 spectrometer [300.077 MHz (^1H), 121.47 MHz (^{31}P)] at 303 K relative to internal TMS and external 85% H_3PO_4, respectively.

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