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Dehydrogenation of 1-(Diphenylphosphinoyl)-2-(*N*'-phenylhydrazino)ethane and *N*-Butyl-*N*'-phenylhydrazine

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Abstract—Dehydrogenation of 1-(diphenylphosphinoyl)-2-hydrazino-substituted ethanes and *N*-butyl-*N*'-phenylhydrazine to the corresponding hydrazone derivatives is performed. Both reactions were established to involve predominantly, if not exclusively, an azo intermediate.

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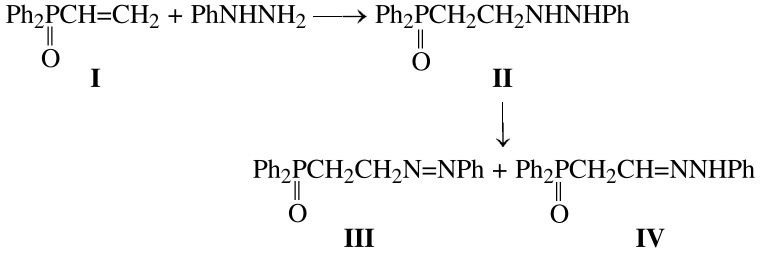
Recently we found [1, 2] that triphenyl- and tributylhydrazinoethylphosphonium salts, even under moderate heating in alcohol or acetonitrile, are dehydrogenated to afford the corresponding hydrazone derivatives or their further isomerization products, viz. α,β-unsaturated phosphonium salts.

To extend the field of application of this reaction and elucidate the feasibility of similar dehydrogenation of related tertiary hydrazino-substituted phosphine oxides and *N*-alkyl-*N*'-phenylhydrazines, we first of all performed synthesis of 1-(diphenylphosphinoyl)-2-(*N*'-phenylhydrazino)ethane (**II**) by the reaction of diphenyl(vinyl)phosphine oxide (**I**) with phenylhydrazine.

It was found that even when a mixture of phosphine oxide **I** with a double molar excess of phenylhydrazine was kept at room temperature, compound **II** was formed together with its dehydrogenation products 1-(diphenylphosphinoyl)-2-(phenylazo)ethane (**III**) and (diphenylphosphinoyl)acetaldehyde phenylhydrazone (**IV**). Unchanged compound **I** was recovered by 36.4%.



$$\underset{\mathbf{I}}{\mathrm{Ph_2}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{CH{=}CH_2}} + \mathrm{PhNHNH_2} \longrightarrow \underset{\mathbf{II}}{\mathrm{Ph_2}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{CH_2CH_2NHNHPh}}$$

$$\downarrow$$

$$\underset{\mathbf{III}}{\mathrm{Ph_2}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{CH_2CH_2N{=}NPh}} + \underset{\mathbf{IV}}{\mathrm{Ph_2}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{CH_2CH{=}NNHPh}}$$

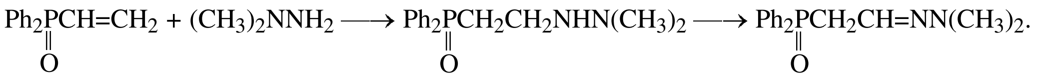
The resulting mixture was refluxed in anhydrous benzene for 4 h, which resulted in complete isomerization of the azo derivative to phenylhydrazone.

Similar results were obtained when the reaction was performed under heating, except that less diphenyl(vinyl)phosphine oxide was recovered.

It is interesting to note that the reaction of oxide **I** with a large excess of phenylhydrazine under the same conditions gave an isomeric product formed by alkylation by the substituted nitrogen atom of phenylhydrazine. The products were isolated by fractional crystallization and identified by ^{1}H and ^{31}P NMR spectroscopy.

The reaction of oxide **I** with *N,N*-dimethylhydrazine occurs much easier than with phenylhydrazine and results in quantitative formation of adduct **V**. However, unlike compound **II**, phosphine oxide **V** even under longer heating at a higher temperature gives only little dehydrogenation product (diphenylphosphinoyl)acetaldehyde dimethylhydrazone (**VI**).

Comparison of the results of dehydrogenation of



$$Ph_2\underset{\underset{O}{\|}}{P}CH{=}CH_2 + (CH_3)_2NNH_2 \longrightarrow Ph_2\underset{\underset{O}{\|}}{P}CH_2CH_2NHN(CH_3)_2 \longrightarrow Ph_2\underset{\underset{O}{\|}}{P}CH_2CH{=}NN(CH_3)_2.$$

V **VI**

hydrazino-substituted phosphonium salts and phosphine oxides shows that the most essential difference is the absence of azo intermediates in the first case. Previously we proposed an ionic mechanism for the dehydrogenation of the salts, involving expulsion of hydride ion from the carbon atom neighboring to the hydrazino group [2]. The absence of azo derivative in this case might be explained by its easier isomerization into hydrazone derivative. However, this explanation is ruled out by the absence of this possibility with *N*',*N*'-dimethylhydrazino-substituted phosphonium salts. On the other hand, two alternative mechanisms of dehydrogenation can be assumed for different cases.

We obtained interesting data with *N*-butyl-*N*'-phenylhydrazine, a phosphorus-free analog of the compounds studied. It is known from the literature that *N*-alkyl-*N*'-phenylhydrazines in the presence of mercury oxide are smoothly dehydrogenated to form the corresponding azo compounds [3]. We found that *N*-butyl-*N*'-phenylhydrazine on 4-h heating at 150°C both in an inert atmosphere and in air converts to a mixture of phenylazobutane and butyraldehyde phenylhydrazone, and further 10-h heating leads to complete conversion of the azo isomer to phenylhydrazone.

Thus, the resulting data allow us to conclude that the tendency for dehydrogenation is a general property of hydrazino derivatives, and it can proceed by different schemes, depending on the structures of the latter.

EXPERIMENTAL

The ^1H and ^{31}P NMR spectra were registered on a Varian Mercury-300 spectrometer (300 MHz), in $CDCl_3$.

Reaction of diphenyl(vinyl)phosphine oxide (I) with phenylhydrazine. Diphenylvinylphosphine oxide was prepared according to [4]. *a*. Phenylhydrazine, 0.95 g, was added to 1 g of oxide **I** in 6 ml of anhydrous benzene, and the mixture was kept at room temperature for 4 days. Excess phenylhydrazine was then filtered off to obtain 1.4 g of a substance which, according to the ^1H NMR spectrum, contained 36.4% of diphenyl(vinyl)phosphine oxide, 27.3% of 1-(diphenylphosphinoyl)-2-(*N*'-phenylhydrazino)ethane (**II**), ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.60 d.t (2H, PCH_2, $^2J_{PH}$ 11.0, J_{HH} 7.0), 2.90 d.t (2H, CH_2N, $^3J_{PH}$ 11.50, J_{HH} 7.0), 6.20–6.80 and 7.40–7.80 m [15H, $(C_6H_5)_2P$, NC_6H_5], 22.7% of 1-(diphenylphosphinoyl)-2-(phenylazo)ethane (**III**), ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.20 d.t (2H, PCH_2, $^2J_{PH}$ 13.80, J_{HH} 7.0), 4.40 d.t (2H, CH_2N, $^3J_{PH}$ 8.0, J_{HH} 7.0) 6.20–6.80 and 7.40–7.80 m [15H, $(C_6H_5)_2P$, NC_6H_5], and 13.6% of a mixture of *cis*- and *trans*-(diphenylphosphinoyl)acetaldehyde phenylhydrazone (**IV**) whose ^1H and ^{31}P NMR data correspond to those in [5].

The resulting mixture was refluxed in anhydrous benzene for 4 h, after which the percentages of compounds **I**, **II** and **IV** in it became 28.6, 23.8, and 47.6%, respectively.

b. Phenylhydrazine, 2 g, was added to 1 g of oxide **I**. The reaction mixture was kept at room temperature for 5 days, diluted with anhydrous diethyl ether, and left to stand for 2 days to precipitate 0.25 g (17%) of *N*-phenyl-*N*-[2-(diphenylphosphinoyl)ethyl]hydrazine (**VII**), mp 151–152°C, yellow crystals. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.70 d.t (2H, PCH_2, $^2J_{PH}$ 5.50, J_{HH} 7.60), 3.80 d.t (2H, CH_2N, $^3J_{PH}$ 6.50, J_{HH} 7.60), 4.0–4.20 m (2H, NHNH), 6.80–7.20 m (5H, NC_6H_5), 7.40–7.80 m [10H, $(C_6H_5)_2P$]. ^{31}P NMR spectrum: δ_P 31.36 ppm. The ether solution was evaporated to isolate a mixture of compounds **I, II, III, IV**, and **VII** in yields of 46.6, 21.6, 8.3, 11.7, and 11.7%, respectively.

Reaction of diphenyl(vinyl)phosphine oxide (I) with *N*,*N*-dimethylhydrazine. A mixture of 1 g of oxide **I** and 1 g of *N*,*N*-dimethylhydrazine was left at room temperature for 4 days. Excess *N*,*N*-dimethylhydrazine was distilled off to obtain 1.25 g (98%) of 1-(diphenylphosphinoyl)-2-(*N*',*N*'-dimethylhydrazino)ethane (**VI**). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.20 s [6H, $(CH_3)_2N$], 2.45 d.t (2H, PCH2, $^2J_{PH}$ 9.90, J_{HH} 6.60), 2.60 d.t (2H, NCH2, $^3J_{PH}$ 11.60, J_{HH} 6.60), 7.40–7.70 m [10H, $(C_6H_5)_2P$]. ^{31}P NMR spectrum: δ_P 31.60 ppm. Compound **V**, 1 g, was dissolved in 10 ml of acetonitrile (or benzene), the solution was heated at 80°C for 24 h, and the solvent was removed to obtain of 1 g of a mixture of compound **VI** and (diphenylphosphinoyl)acetaldehyde dimethylhydrazone (**VII**), ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.62 s [6H, $(CH_3)_2N$], 3.38 d.d (2H, PCH_2, $^2J_{PH}$ 17.30, J_{HH} 8.0), 6.40 d.t (1H, CH=N), 7.40–7.80 m [10H, $(C_6H_5)_2P$], in yields of 92 and 8%, respectively.

Dehydrogenation of *N*-butyl-*N*'-phenylhydrazine prepared by hydrogenation of butyraldehyde phenylhydrazone according to [3]. *N*-Butyl-*N*'-phenylhydrazine, 0.3 g, was heated in Wood's alloy at 150°C for 2 h to obtain 0.3 g of a mixture containing, according to the ^{1}H NMR spectrum, butyraldehyde phenylhydrazone, ^{1}H NMR spectrum, δ, ppm: 1.0 m (3H, CH_3), 1.60 m (2H, $CH_3C\mathit{H}_2$), 2.20–2.40 m (2H, $CH_3CH_2 \cdot C\mathit{H}_2$), 7.0–7.30 m (6H, C_6H_5NH), and phenylazobutane, ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.0 m (3H, CH_3), 1.60 m (2H, $CH_3C\mathit{H}_2$), 1.90 m (2H, $CH_3CH_2 \cdot C\mathit{H}_2$), 4.10 t (2H, $CH_2N{=}N$, J_{HH} 6.60), 7.40–7.60 m (5H, $C_6H_5N{=}N$), in a 3 : 2 ratio. A 0.3-g portion of the resulting mixture was heated at the same temperature for 10 h to obtain ca. 100% of butyraldehyde phenylhydrazone identified by the ^{1}H NMR spectrum of an authentic sample.

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