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## LETTERS TO THE EDITOR

# Phosphorylated Formazans

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Formazans are known to be widely used in the chemistry of dyes, analytical chemistry, histo-, and cytochemistry. Recently formazans became relevant and promising targets for photochemistry. Due to the presence of labile *p*-electron system, ease of oxidation-reduction processes, ability to isomerization and prototropic tautomerism, high basicity and acidity (especially of hetarylformazans), and complex formation ability formazans are promising objects for pursuit and creation of photosensitive materials on their base [1–3].

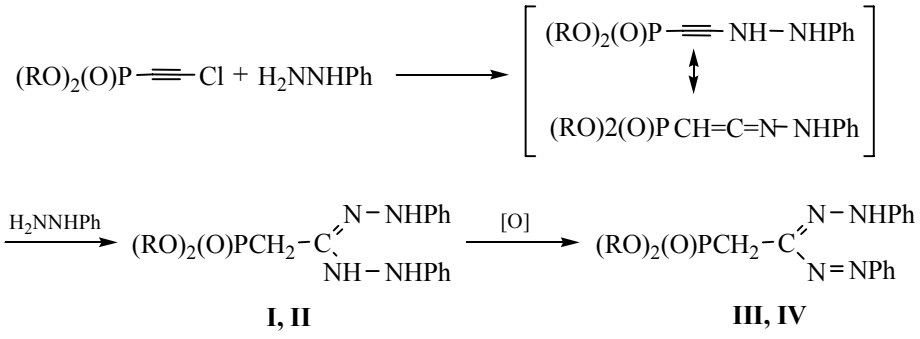
In continuation of our studies on interaction of chloroacetylenephosphonates with nucleophilic reagents, we performed the reactions of esters of 2-chloroacetylenephosphonic acid with phenylhydrazine.

The reaction proceeded with high chemo- and regioselectivity via substitution of the halogen atom followed by addition of the second molecule of phenylhydrazine to form hydrazide–hydrazones **I** and **II**. The latter were easily oxidized in air to give the previously undescribed phosphorylated formazans **III** and **IV**. The likely reaction pathway involves the formation of highly reactive ketene imine intermediate which attaches selectively the second nucleophile molecule through the primary attack at the digonal atom of ketene imine (Scheme 1).

Phosphorylated hydrazide-hydrazones **I** and **II** were yellow plate crystals. In the $^1$H NMR spectra of compounds **I** and **II** the protons of methylenephosphonate group were represented as a doublet signals at 2.80 ppm, $J \sim 20.0$ Hz. The $^{31}$P NMR spectra of hydrazide–hydrazones **I** and **II** contained the signals at 20.0 (**I**) and 20.4 ppm (**II**).

Phosphorylated formazans **III** and **IV** were red plate crystals. In the $^1$H NMR spectra of the obtained formazans there was downfield shifting of the signals compared to those of compounds **I** and **II**. The chemical shift of the phosphorus nuclei of formazans **III** and **IV** equaled 25 ppm.

**Scheme 1.**




R = Me (**I, III**), Et (**II, IV**).

**Dimethyl {[*N*',*N*-bis(phenylamino)carbamimidoyl]-methyl}phosphonate (I) and dimethyl {[*N*'-(phenyl-amino)-*N*-(phenylimino)carbamimidoyl]methyl}phos-phonate (III).** A solution of 3.8 g (0.035 mol) of phenylhydrazine in 10 mL of anhydrous diethyl ether was added to a solution of 1.68 g (0.01 mol) of dimethyl chloroacetylenephosphonate in 50 mL of anhydrous diethyl ether at vigorous stirring under inert atmosphere. The reaction mixture was refluxed for 2 h and then treated with gaseous ammonia. The precipitate was filtered off, washed with 5 mL of water, and dried over $P_2O_5$ in a desiccator under inert atmosphere to give 2.5 g (73%) of **I** as yellow crystals. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.78 d (2H, $PCH_2$, $^2J_{HP}$ 20.8.0 Hz), 3.71 d (6H, $OCH_3$, $^3J_{HP}$ 12.0 Hz), 7.0 br.s (3H, NH), 6.8–7.4 m (10H, Ph).

The resulting crystals were rapidly oxidized in air to form formazan **III**. Red crystals, mp 119–120°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 3.02 d (2H, $PCH_2$, $^2J_{HP}$ 20.8 Hz), 3.72 d (6H, $OCH_3$, $^3J_{HP}$ 12.0 Hz), 7.00 br.s (1H, NH), 6.8–7.4 m (10H, Ph). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 28.68 d ($CH_2$, $^1J_{CP}$ 139.3 Hz), 52.85 d ($OCH_3$, $^2J_{CP}$ 6.5 Hz), 120–145 (Ph), 133.81 d (C=N, $^2J_{CP}$ 10.5 Hz). $^{31}$P NMR spectrum: $\delta_P$ 25.0 ppm.

**Diethyl {[*N*',*N*-bis(phenylamino)carbamimidoyl]-methyl}phosphonate (II) and diethyl {[*N*'-(phenyl-amino)-*N*-(phenylimino)carbamimidoyl]methyl}phos-phonate (IV)** were prepared similarly. Compound **II**, yellow crystals. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 t (6H, $CH_3$, $^3J_{HH}$ 7.5 Hz), 2.73 d (2H, $PCH_2$, $^2J_{HP}$ 20.6 Hz), 3.61 d.q (4H, $OCH_2$, $^3J_{HH}$ 7.5, $^3J_{HP}$ 11.5 Hz), 6.7 br.s (3H, NH), 6.8–7.4 m (10H, Ph).

Formazan **IV**, red crystals, mp 104–105°C. Yield 75%. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 t (6H, $CH_3$, $^3J_{HH}$ 7.5 Hz), 3.72 d.q (2H, $PCH_2$, $^2J_{HP}$ 21.0 Hz), 3.75 d (4H, $OCH_2$, $^3J_{HH}$ 7.5, $^3J_{HP}$ 11.5 Hz), 6.7 br.s (H, NH), 6.8–7.4 m (10H, Ph). $^{31}$P NMR spectrum: $\delta_P$ 25.3 ppm.

The $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on a Bruker Avance 400 spectrometer [400.13 ($^1$H), 100.61 ($^{13}$C), 161.98 MHz ($^{31}$P)].

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## REFERENCES

1. Tkachenko, L.I., Semenov, Yu.E., Smirnov, V.A., Aldoshin, S.M., Lipunova, G.N., and Sigeikin, G.I., *Russ. Chem. Bull*., 2002, no. 5, p. 839. DOI: 10.1023/A:1016093019344.
2. Sigeikin, G.I., Lipunova, G.N., and Pervova, I.G., *Russ. Chem. Rev*., 2006, vol. 75, no. 10, p. 885. DOI: 10.1070/RC2006v075n10ABEH003612.
3. Sigeikin, G.I., Lipunova, G.N., and Pervova, I.G., *Ross. Khim. Zh*., 2006, vol. 50, no. 5, p. 64.