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LETTERS TO THE EDITOR

Dehydrogenation of 1-(Diphenylphosphinyl)-2-(hydroxylamino)ethane and Phosphonium Salts Containing 2-(Hydroxylamino)propyl Group

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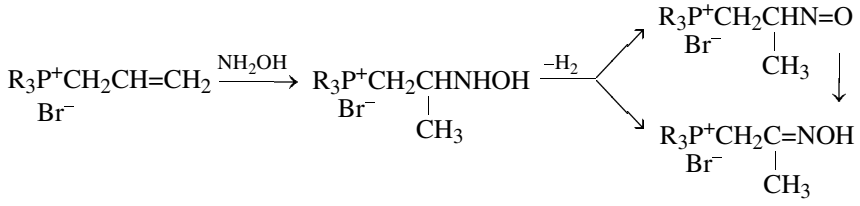
Recently we established that hydrazine derivatives of quaternary phosphonium salts, diphenylphosphinoyl compounds, and alkanes form hydrazones on heating in the absence of oxidizers [1–4]. In this work we revealed the possibility of dehydration reactions both in hydroxylaminoalkylphosphonium salts and in phosphine oxides.

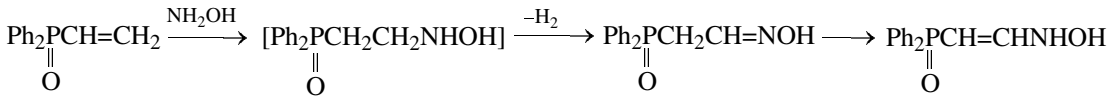
We found that tributyl- and triphenyl[2-(hydroxylamino)propyl]phosphonium bromides already during their synthesis from tributyl- and triphenylallylphosphonium salts and hydroxylamine by heating in DMF at 80°C undergo partial (33%), in the first case, or complete, in the second, dehydration to afford a mixture of the *cis* and *trans* isomers of tributyl (**I**) or triphenylacetonylphosphonium bromide oximes (**II**). ^{1}H NMR spectrum of **I**, DMSO, δ, ppm: 1.0 m [9H, $(CH_2)_3CH_3$]; 1.5 m [12H, $CH_2(CH_2)_2CH_3$]; 1.9 s (3H, CCH_3); 2.35 m [6H, $P^+CH_2(CH_2)_2CH_3$]; 3.45 d (2H, P^+CH_2, J_{PH} 14 Hz) and 3.55 d (2H, P^+CH_2, J_{PH} 14 Hz); 10.92 s (1H, OH) and 11.15 s (1H, OH) for the *cis* and *trans* isomers, respectively. ^{1}H NMR spectrum of **II**, DMSO, δ, ppm: 1.90 s and 1.95 s (3H, CH_3); 4.9 d and 5.05 d (2H, P^+CH_2, J_{PH} 14 Hz); 7.63–8.0 m (15H, P^+Ph_3), 10.9 s and 11.2 s (1H, OH) for the *cis* and *trans* isomers, respectively. Found, %: Br^- 19.0. $C_{21}H_{21}BrNOP$. Calculated, %: Br^- 19.32. This reaction is likely to proceed by one of the schemes below:



I, II

I, R = Bu; **II**, R = Ph.

The reaction of (diphenylphosphinoyl)ethene with hydroxylamine was studied to show that already in the cold dehydration in the intermediate 1-(diphenylphosphinoyl)-2-(hydroxylamino)ethane occurs, affording the *cis* and *trans* isomers of (diphenylphinoyl)-acetaldehyde oxime. ^{1}H NMR spectrum, $CDCl_3$, δ, ppm: *cis* isomer, 3.3 d.d, *trans* isomer, 3.6 d.d [2H, $P(O)CH_2$, $^2J_{PH}$ 14.8 Hz, $^3J_{HH}$ 6.6 Hz]; 7.35–7.8 m [11H, $Ph_2P(O)$, CH=N]. When heated in toluene, this compound converted partially into an α,β-unsaturated



isomer. ^{1}H NMR spectrum, $CDCl_3$, δ, ppm: 4.3 d.d [1H, P(O)CH, $^2J_{PH}$ 17.6, $^3J_{HH}$ 15.4]; 6.7 d.d (H, C=CHN, $^3J_{PH}$ 15.4 Hz, $^3J_{HH}$ 15.4 Hz); 7.36–7.8 m [10H, $Ph_2P(O)$].

The ^{1}H NMR spectra were registered on a Varian Mercury-300 spectrometer (300 MHz).

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