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## LETTERS TO THE EDITOR

# Ethoxydeamination of α-Phenylaminobenzylphosphonate Derivatives

**R. K. Ismagilov, V. V. Moskva, E. N. Ofitserov, and L. P. Shamsutdinova**

*Kazan State Technological University, Kazan, Tatarstan, Russia*

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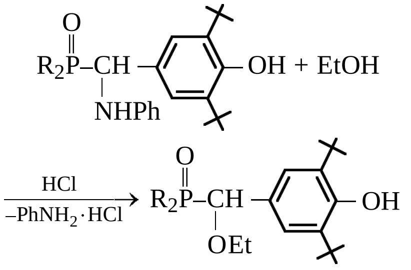
α-Substituted phosphonates are being intensively studied [1–3]. We showed that the reactions of diethyl (α-phenylamino-3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphonate and diphenyl(α-phenylamino-3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphine oxide with ethanol in the presence of hydrochloric acid involve substitution of the phenylamino group by ethoxyl. This finding is at variance with what has been reported in [1, 2].



**I, II**

R = OEt (**I**), Ph (**II**).

The presence in the reaction mixture of only traces of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde suggests an inconsiderable contribution of full hydrolysis which is characteristic of unsubstituted α-phenylaminobenzylphosphonates in acid media [4, 5].

The effect of structural factors on the above reaction pathway can be explained by a scheme involving protonation of the nitrogen atom, elimination of aniline hydrochloride, and formation of intermediate α-phosphorylated 2,6-di-*tert*-butyl-4-methylene-2,5-cyclohexadienone.

Compound **II** was obtained by independent synthesis. The reaction of ethanol with α-diphenylphosphinoyl-2,6-di-*tert*-butyl-4-methylene-2,5-cyclohexadienone in the presence of catalytic amounts of sulfuric acid occurs by the 1,6-addition scheme.

**Diethyl (α-ethoxy-3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphonate (I).** A solution of 0.55 g of diethyl (α-phenylamino-3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphonate in 10 ml of ethanol and 3 ml of concentrated hydrochloric acid was refluxed for 1 h and then allowed to reduce by half at room temperature (24 h). 3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde, 0.05 g, precipitated, mp 188–189°C (from alcohol) {mp 188–189°C [6]}. The coarse crystals that formed after volatile components had been almost completely removed were washed on a filter with aqueous alcohol (1 : 1) to obtain 0.22 g (37%) of compound **I**, mp 135–138°C (heptane) (mp 137–138°C [7]).

The IR and $^1$H NMR spectra of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde and compound **I** are identical to those of authentic samples, and mixed samples give no melting point depression.

**Diphenyl(α-ethoxy-3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphine oxide (II).** *a*. A solution of 0.47 g of diphenyl(α-phenylamino-3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphine oxide in a mixture of 5 ml of ethanol and 2 ml of concentrated hydrochloric acid was refluxed for 1.5 h and then treated as described above to obtain 0.03 g of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, mp 184–186°C (alcohol), and 0.31 g (62%) of compound **II**, mp 145–149°C (hexane). IR spectrum, ν, cm$^{-1}$: 3350 sh (OH$_{ass}$), 1595 ($C_6H_5$), 1190 (COC), 1150 (P=O). $^1$H NMR spectrum ($CCl_4$ + acetone-$d_6$), δ, ppm: 1.1 t (3H, $CH_3$), 1.21 s [18H, $C(CH_3)_3$], 3.42 m (2H, $OCH_2$), 4.85 d (1H, PCH, $^2J_{PH}$ 12.5 Hz), 5.31 s (1H, OH), 6.8 d (2H, $C_6H_2$, $^4J_{HH}$ 2 Hz), 7.45 m (5H, $C_6H_5$), 7.82 m (5H, $C_6H_5$). Found, %: P 6.95, 6.80. $C_{29}H_{37}O_3P$. Calculated, %: P 6.68.

*b*. To a solution of 0.42 g of α-diphenylphosphinoyl-2,6-di-*tert*-butyl-4-methylene-2,5-cyclohexadienone in 10 ml of ethanol we added 2 drops of sulfuric acid, and the mixture was refluxed for 1 h, after which the alcohol was removed by vacuum distillation, and the residue was treated with hexane to obtain 0.20 g (47%) of compound **II**, mp 149–150°C (heptane).

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The IR and $^1$H NMR spectra of compound **II** obtained by procedures *a* and *b* are identical to each other and the mixed sample gives no melting point depression.

The IR spectra for Njol suspensions in Vaseline oil were recorded on a Specord M-80 spectrometer. The $^1$H NMR spectrum were obtained on a Tesla BS-567A (100 MHz) spectrometer against TMS.

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