Russian Journal of General Chemistry, Vol. 71, No. 10, 2001, pp. 1547–1549. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 10, 2001, pp. 1634–1636.
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New Data on the Reaction of Diethyl Hydrogen Phosphite with 3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde

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Received March 22, 2000

Abstract — 3,3',5,5'-Tetra-*tert*-butylstilbene quinone and 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,2-bis-(diethoxyphosphinoyl)-ethane were isolated from a mixture of products of the reaction of equivalent amounts of diethyl hydrogen phosphite and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde. A scheme of chemical transformations in this reaction system was offered.

It was previously shown that diethyl hydrogen phosphite reacts with 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde in different ways, depending on reactant ratio [1, 2].

In the present work we reacted equimolar amounts of diethyl hydrogen phosphite and 3,5-*tert*-butyl-4-hydroxybenzaldehyde. The reaction was carried out in boiling *p*-xylene for 6 h. The presence of the starting reagents in the final reaction mixture (3,5-di-*tert*-butyl-4-hydroxybenzaldehyde precipitates from the reaction mixture just after cooling, and diethyl hydrogen phosphite gives a signal at δ_P 6.4 ppm in the ^{31}P NMR spectrum of the reaction mixture) is indirect evidence showing that the reaction is slow and reversible.

3,3',5,5'-Tetra-*tert*-butylstilbene quinone (**I**) and 1,2-bis(diethoxyphosphinoyl)butyl-1,2-bis(3,5-di-*tert*-4-hydroxyphenyl)ethane (**II**) were isolated from the reaction mixture in low yields. Basing on published data on the properties of α-substituted derivatives of sterically hindered phenols [3, 4], phosphonate–phosphate rearrangement [5], and dimerization of methylenequinone structures [3, 4, 6], the formation of compounds **I** and **II** can be explained by a scheme including a number of parallel and consecutive stages.

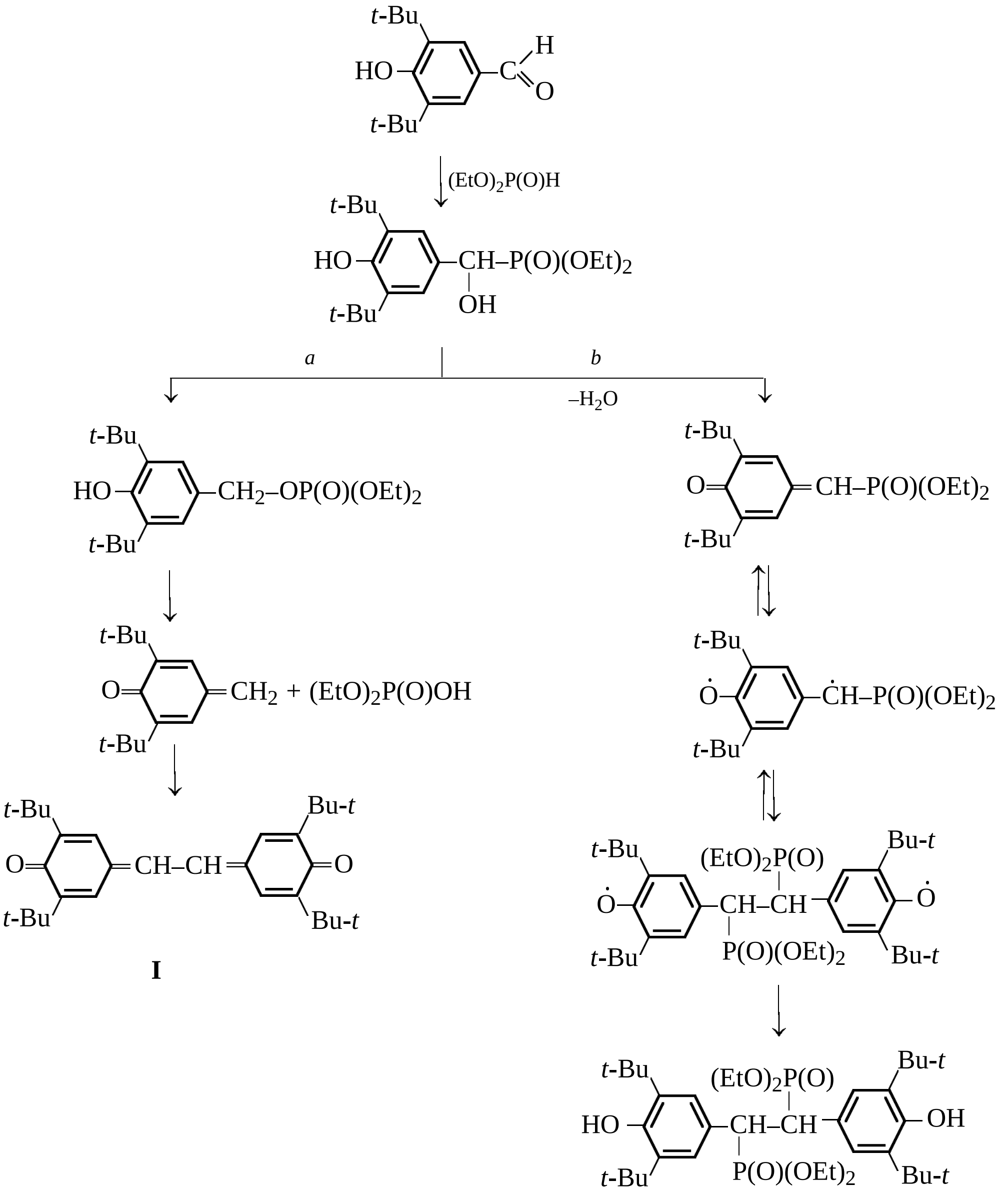
The Abramov addition of diethyl hydrogen phosphite to the starting aldehyde yields diethyl (3,5-di-*tert*-butyl-α,4-dihydroxybenzyl)phosphonate. The latter on heating may convert by two pathways. Pathway *a* involves the phosphonate–phosphate rearrangement leading to diethyl 3,5-di-*tert*-butyl-4-hydroxybenzyl phosphate which cleaves diethyl hydrogen phosphate to give 2,6-di-*tert*-butyl-4-methylene-2,5-cyclohexadienone. The latter in its turn dimerizes to 3,3',5,5'-tetra-*tert*-butylstilbene quinone (**I**). Pathway *b* includes intramolecular dehydration to form 2,6-di-*tert*-butyl-4-(diethoxyphosphinoyl)methylene-2,5-cyclohexadienone and dimerization of the latter to 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,2-bis(diethoxyphosphinoyl)ethane (**II**).

The proposed scheme is supported by the obsevation of a signal assignable to diethyl hydrogen phosphate (δ_P 2 ppm) in the ^{31}P NMR spectrum of the reaction mixture. Dimerization of 2,6-di-*tert*-butyl-4-(diethoxyphosphinoylmethylene)-2,5-cyclohexadienone was carried out separately. The low yield of product **II** may be explained by the fact that separate stages of the reaction in question are only slightly shifted to the side of the dimeric compound.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer for suspensions in Vaseline oil. The ^{1}H NMR spectra were obtained on a Bruker WP-80 s pectrometer (32.38 MHz). The phosphorus chemical shift was measured against 85% phosphoric acid. The yields of the products (in per cent) are not presented since the reaction is incoplete and occurs by several pathways.

3,3',5,5'-Tetra-*tert*-butylstilbene quinone (I) and 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,2-bis-(diethoxyphosphinoyl)ethane (II). A solution of 1.38 g of diethyl hydrogen phosphite and 2.34 g of di-*tert*-butyl-4-hydroxybenzaldehyde in 15 ml of *p*-xylene was refluxed for 6 h. After cooling of the dark claret reaction mixture, 0.14 g of the starting aldehyde was isolated. Most *p*-xylene was removed in a vacuum at a temperature below 60°C. The residue was



I

II

mixed with 5 ml of acetone and left at room temperature for crystallization with simultaneuos evaporation of the solvents. After two days, crystals formed and were washed with a small amount of acetone to give 0.11 g of a reddish orange product **I**, mp 305–308°C (from acetone). Published data [4]: mp 310–311°C. Found, %: C 83.25, 83.40; H 9.70, 9.95. $C_{30}H_{42}O_2$. Calculated, %: C 82.95; H 9.72.

The acetone was evaporated, and the residue was washed with water (3 × 5 ml) and dissolved in 10 ml of ethanol. Two days later, crystals formed and were filtered off to obtain 0.06 g of a colorless compound **II**, mp 246–250°C (from toluene). Published data [7]: mp 257°C. Found, %: P 8.85, 9.07. $C_{38}H_{64}O_8P_2$. Calculated, %: P 8.73

1,2-Bis(2,5-di-*tert*-butyl-4-hydroxyphenyl)-1,2-bis(diethoxyphosphinoyl)ethane (II). A solution of 1.06 g of 2,6-di-*tert*-butyl-4-(diethoxyphosphinoyl)-methylene-2,5-cyclohexadienone, 0.4 g of water, and 2 drops of sulfuric acid in 10 ml of acetone were refluxed for 1 h and left to stand uncovered at room temperature for 15 days. The residue after evaporation of volatile products was washed with water (2 × 5 ml) and treated with hexane to obtain 0.07 g of a colorless product **II**, mp 248–252°C (from toluene). Found, %: P 8.81, 8.95.

The IR spectra of compounds **I** and **II** are identical to the spectra of authentic samples, and mixed samples give no melting point depression.

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