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LETTERS TO THE EDITOR

Synthesis and Properties of [(4-Hydroxy-3,5-di-*tert*-butylphenyl)-chloromethanediphenylphosphine Oxide

M. B. Gazizov[a], R. K. Ismagilov[a], L. P. Shamsutdinova[a], R. F. Karimova[a], R. Z. Musin[b], K. A. Nikitina[b], A. A. Bashkirtsev[a], and O. G. Sinyashin[b]

[a] *Kazan State Technological University, ul. Marksa 68, Kazan, Tatarstan, 420015 Russia*
e-mail: mukattisg@mail.ru

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia*

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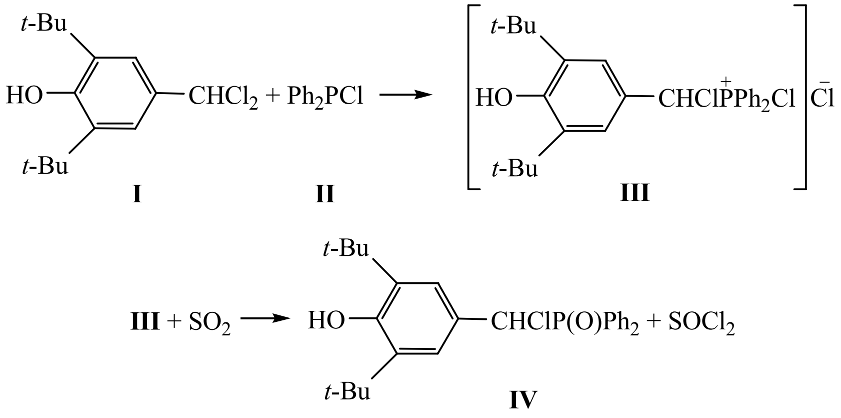
Previously, 4-hydroxy-3,5-di-*tert*-butylbenzylidene-chloride (*gem*-dichloride) **I** has been found to react with esters of P(III)-acids in molar ratios of 1:2 and 1:1 and secondary chlorophosphines in the ratio of 1:2 by the scheme of the exhaustive dechlorophosphorylation to form (4-hydroxy-3,5-di-*tert*-butylphenyl)methanediphosphonates and -diphosphine oxides [1, 2].

The reaction of *gem*-dichloride **I** with diphenylchlorophosphine **II** in a 1:1 ratio occurs at room temperature over 24–48 h to give adduct **III** of the equimolar amounts of the reactants. Adduct **III** is a colorless crystalline solid. The ^{31}P NMR spectral data (δ_P 36.31 ppm) confirm the phosphonium structure.

At treating with sulfur dioxide adduct **III** transforms into [(4-hydroxy-3,5-di-*tert*-butylphenyl)chloromethanediphenylphosphine oxide **IV**.

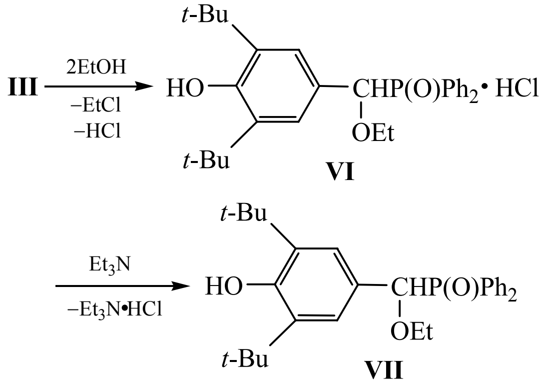


Adduct **III** also decomposes when exposed to moisture in air over 10–15 days. The process takes place with the release of hydrogen chloride and the formation of phosphine oxide **IV**.

Compound **IV** was also obtained via the reaction of hydrogen chloride with 4-(diphenylphosphinyl-methylene)-2,6-di-*tert*-butylcyclo-hexadien-2,5-one **V**. The melting points and the ^{1}H, ^{31}P NMR and IR spectra of both products **IV** synthesized are identical.

The structure of **IV** was confirmed by the EI mass spectrometry. The main decay processes of compound **IV** are associated with the primary release of hydrogen chloride, and then of diphenylphosphinyl groups and hydrocarbon radicals. In the mass spectrum (EI) of **IV** the most intensive peak with *m*/*z* 418 belongs to the ion formed by the release of hydrogen chloride from the molecular ion. The ion peak with *m*/*z* 217 is the result of releasing diphenylphosphinyl group from the ion with *m*/*z* 418. Also in the spectra the following peaks, *m*/*z*, were observed: 403 $[418 - \text{Me}]^+$, 361 $[418 - t\text{-Bu}]^+$, 201 $[\text{Ph}_2\text{P=O}]^+$.

The reaction of adduct **III** with an excess of anhydrous ethanol results in hydrochloric salt **VI.** Treating salt **VI** with triethylamine provides phosphine oxide **VI** .

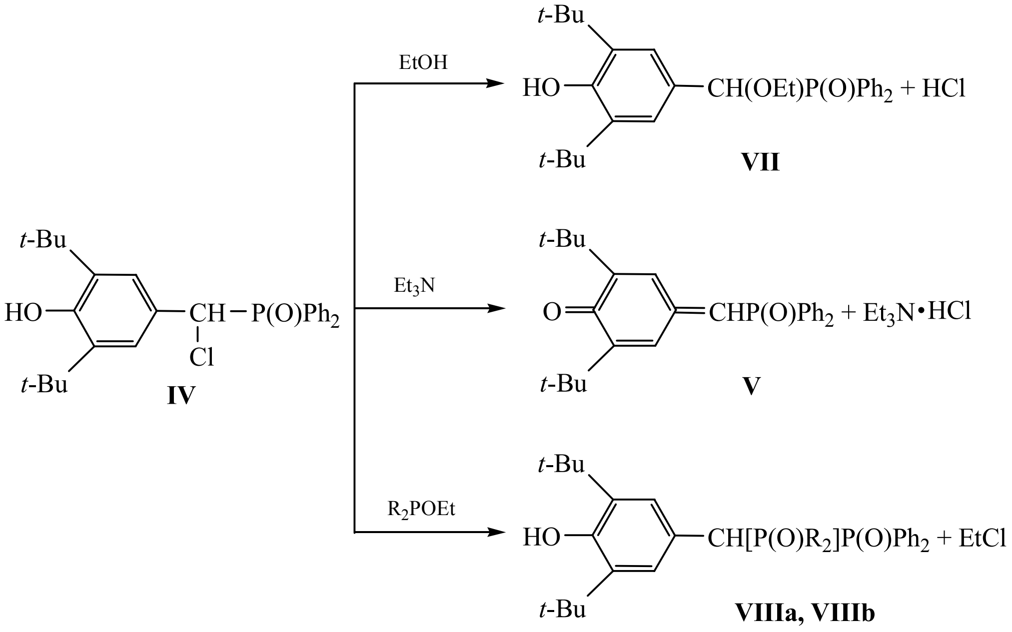


[(4-Hydroxy-3,5-di-*tert*-butylphenyl)chloromethane-diphenylphosphine oxide **IV** corresponds to the poorly studied class of the phosphorylated halogen derivatives of the sterically hindered phenols. We showed the high reactivity of this compound with respect to the reagents of basic and nucleophilic character.

The reactions of compound **IV** with anhydrous ethanol, triethylamine, and esters of P(III)-acids proceed in high yields.

[(4-Hydroxy-3,5-di-*tert*-butyl)chloromethane-diphenylchlorophosphonium chloride (III). A mixture of a solution of 2.89 g (0.01 mol) of *gem*-dichloride **I** in 30 ml of hexane and 2.20 g (0.01 mol) of diphenylchlorophosphine **II** in 10 ml of hexane was kept for 48 h at room temperature. After removing of the solvent the solid residue was ground to a fine powder. A sample of the product (0.25 g) was washed with a small amount of cold benzene to yield 0.18 g of a colorless crystalline adduct **III**, mp 175–180°C. ^{31}P NMR spectrum: δ_P 36.31 ppm. Found P, %: 5.95, 5.80. $C_{27}H_{32}OPCl_3$. Calculated P, %: 6.08.

[(4-Hydroxy-3,5-di-*tert*-butyl)chloromethane-diphenylphosphine oxide (IV). *a*. Through a suspension of 4.89 g of the adduct **III** in 60 ml of benzene was passed dry sulfur dioxide for 1 h until complete disappearance of the solid phase. Volatile components were removed in vacuo, the residue was triturated with hexane to complete solidification. Yield 2.46 g (57%), mp 183–187°C (toluene). ^{1}H NMR spectrum (CCl_4 + $CDCl_3$), δ, ppm: 1.48 s [18H, $C(CH_3)_3$], 5.45 d (1H, CHP, $^2J_{PH}$ 6.5 Hz), 7.12 d (2H, C_6H_2, $^3J_{HH}$ 2 Hz), 7.40–8.2 m (10H, C_6H_5). ^{31}P NMR spectrum: δ_P 26.55 ppm. Found, %: Cl 7.60; P 7.18. $C_{27}H_{32}O_2PCl$. Calculated, %: Cl 7.81; P 6.82.



R=OEt (**a**), Et (**b**).

b. Through a solution of 2.9 g (0.005 mol) of the phosphorylated methylenequinone **V** in 30 ml of benzene was passed dry hydrogen chloride for 15–20 min. After removing of the volatile components in vacuo the residue was treated with hexane to yield 2.18 g (96%) of compound **IV**, mp 185–187°C (toluene).

[(4-Hydroxy-3,5-di-*tert*-butyl)ethoxymethanediphenylphosphine oxide (VII). *a*. Adduct **III**, prepared from 1.45 g (0.005 mol) of *gem*-dichloride **I** and 1.10 g (0.005 mol) of diphenylchlorophosphine, was boiled with 15 ml of anhydrous ethanol for 1 h. After removing of the volatile components in vacuo the residue was dissolved in 30 ml of toluene and treated with 0.50 g of triethylamine. The resulting triethylamine hydrochloride was filtered off. The residue was concentrated. Yield 1.40 g (60%), mp 170–173°C (heptane–toluene) (170–172°C [3]). IR spectrum, ν, cm^{-1}: 3350 br. (OH, as), 1595 (C_6H_5), 1150 (P=O). ^{1}H NMR spectrum(CCl_4 + *d*-acetone), δ, ppm: 1.15 t (3H, CH_3, $^3J_{HH}$ 6 Hz), 1.35 s [18H, $C(CH_3)_3$], 3.35–3.70 m (2H, OCH_2), 5.00 d (1H, PCH, $^2J_{PH}$ 10 Hz), 5.60 br.s (1H, OH), 6.75 d (2H, C_6H_2, $^4J_{HH}$ 2 Hz), 7.30–8.10 m (10H, C_6H_5). Found P, %: 6.35, 6.43. $C_{29}H_{37}O_3P$. Calculated P, %: 6.68.

b. A solution of 0.91 g (0.002 mol) of compound **IV** in 5 ml of anhydrous ethanol was refluxed for 30 min. After distilling off the volatile components in a vacuum the residue was treated with hexane to yield 0.60 g (65%) of the product **VII**, mp 170–172°C (heptane–toluene).

4-(Diphenylphosphinylmethylene)-2,6-di-*tert*-butylcyclohexadien-2,5-one (V). Adding a solution of 0.11 g (0.001 mol) of triethylamine in 3 ml of benzene to a solution of 0.45 g (0.001 mol) of compound **IV** in 20 ml of benzene at stirring resulted in a colorless precipitate. The reaction mixture was kept for 6 h at room temperature. Then triethylamine hydrochloride (0.11 g, 80.3%) was filtered off. The residue was concentrated in a vacuum. Yield 0.37 g (88%), mp 216–219°C (toluene) (219–221°C [4]).

[(4-Hydroxy-3,5-di-*tert*-butylphenyl)(diethoxyphosphoryl)methanediphenylphosphine oxide (VIIIa). A mixture of 0.91 g (0.002 mol) of compound **IV** and 0.37 g (0.0022 mol) of triethyl phosphite was kept at 120–130°C for 40 min to complete the active release of ethyl chloride. The crystallized reaction mixture was treated with hexane. Yield 1.10 g (98%), mp 162–163°C (toluene) (160°C [5]). ^{1}H NMR spectrum (CCl_4 + $CDCl_3$), δ, ppm: 1.12 t (3H, CH_3, $^3J_{HH}$ 6 Hz), 1.20 t (3H, CH_3, $^3J_{HH}$ 6 Hz), 1.42 s [18H, $C(CH_3)_3$], 3.85–4.25 m (5H, OCH_2, PCHP), 5.18 s (OH), 7.10 br.s (2H, C_6H_2), 7.20–8.20 m (10H, C_6H_5). ^{31}P NMR spectrum, δ_P, ppm: 19.32 (phosphine oxide), 26.12 (phosphonate). Found P, %: 10.50, 10.55. $C_{31}H_{42}O_5P_2$. Calculated P, %: 11.13.

[(4-Hydroxy-3,5-di-*tert*-butylphenyl)(diethylphosphinyl)methanediphenylphosphine oxide (VIIIb). To 1.59 g (0.0035 mol) of compound **IV** was added dropwise 0.47 g (0.0035 mol) of ethyldiethylphosphinite. The mixture self-heated to 70°C. Ethyl chloride release and the crystal mixture restructuring occur. After 3 h the reaction mixture was treated with toluene. Yield 1.53 (84%), mp 222–224°C (toluene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.95–1.40 m (6H, CH_3), 1.45 s [18H, $C(CH_3)_3$], 1.70–2.40 m (4H, CH_2), 4.04 t (1H, PCHP, $^2J_{PH}$ 16 Hz), 5.25 s (1H, OH), 7.10 br. s (2H, C_6H_2), 7.35–8.05 m (10H, C_6H_5). Found P, %: 11.45, 11.65. $C_{31}H_{42}O_3P$. Calculated P, %: 11.83.

The ^{1}H NMR spectra were recorded on a Tesla BS-567A (100 MHz) spectrometer relative to internal TMS. The ^{31}P NMR spectra were registered on a CXP-100 instrument (36.5 MHz) relative to external 85% H_3PO_4. The mass spectra were obtained by electron impact on a TRACE MS Finnigan MAT instrument (70 eV, 200°C) at a direct input of the substance into the ion source. The processing of mass spectral data was performed using a Xcalibur software. The peaks of the ions containing the most common isotopes are given.

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