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LETTERS TO THE EDITOR

Synthesis and Oxidation of (4-Hydroxy-3,5-di-*tert*-butylphenyl)-methanebis[diethyl(diphenyl)phosphine Oxides]

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

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

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia*

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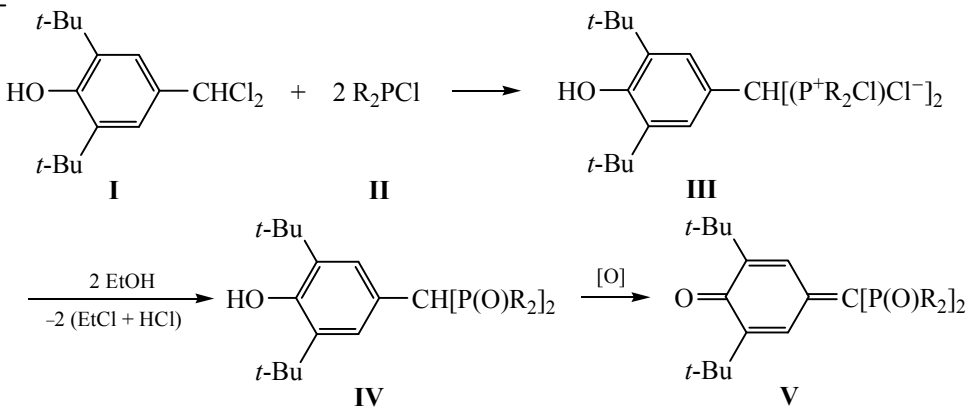
The phosphorylated sterically hindered phenols and methylenequinones are potential inhibitors of oxidation of organic materials like polymers, petrochemical products, and biological systems [1–2]. In extension of studying the reaction of geminal polyhalides with aprotic nucleophilic reagents [3–5] we studied the reaction of 4-hydroxy-3,5-di-*tert*-butylbenzal chloride **I** with diethyl and diphenyl chlorophosphines.

The reaction of dichloride **I** with diethyl chlorophosphine was found to proceed at keeping the hexane solution of reagents taken in the ratio 1:2 at room temperature for 24 h. The reaction of dichloride **I** with diphenyl chlorophosphine requires the heating of the reagents mixture at 100–110°C for 3 h. Adducts **III** form in high yields as colorless hygroscopic viscous products, weakly fuming in the air. According to the ^{31}P NMR spectra, compounds **IIIa** (δ_P 69.36 ppm) and **IIIb** (δ_P 71.02 ppm) have phosphonium structure in keeping with the literature data [6, 7]. The treatment of adducts **IIIa** and **IIIb** with anhydrous ethanol followed by evaporating of the solvents in a vacuum gives the corresponding bisphosphine oxides **IV**.

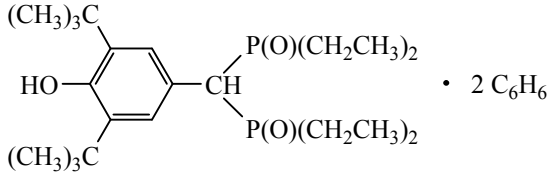


R = Et (**a**), Ph (**b**).

Several minutes after dissolving the crude product **IVa** in a large excess of benzene (~1:10) precipitates the crystalline solvate complex **A,** 4-hydroxy-3,5-di-*tert*-butylphenyl)methanebis(diethylphosphine oxide) with benzene. The complex was separated by filtration.

The solvate complex **A** melts with decomposing at the temperature close to the boiling temperature of benzene (78–83°C). On the following gradual heating for 30–60 min to 145–150°C, the abundant liberation of benzene bubbles was observed, and crystals of individual bisphosphine oxide **IVa** form in the melt

mass. The process completes by the total mass crystallization. Benzene mass loss corresponds to the components ratio in the solvate complex **A** which is approximately equal to 1:2.



A

In the mass spectrum (EI) of the complex **A** the ion peak with *m/z* 428 belongs to the molecular ion (M^+) of the molecule of **IVa** structure. The presence of two compounds in **A** is based on a comparison of the mass spectra (1) and (2) recorded at the various temperature of the sample admission into the ions source. The intensity peaks ratio of ions *m/z* 78 and 428 originating from M^+-ions of the molecule of benzene and **IVa** is 1.0:0.0 and 0.2:1.0 at the admission system temperature 40°C (1) and 90°C (2) respectively. The mass spectrum (1) coincided virtually with the mass spectrum of benzene from the instrument computer database. The mass spectra changes attest that on the mass spectral studying benzene fractionation occurs from the sample and the residue is enriched with the low-volatile compound **IVa**.

The main processes of the molecule **IVa** decay at the electron impact, mass spectrum (2), are due to the hydrocarbon particles ejection from ethyl and *tert*-butyl groups. As a result of these processes the ions $[M - CH_3]^+$, $[M - C_2H_5]^+$, $[M - C_4H_8]^+$, $[M - C_4H_9]^+$ form.

The presence of ion peak *m/z* 324 owes to P–C bond cleavage and diethylphosphinyl group P(O)$(C_2H_5)_2$ release with the migration of the one hydrogen atom to the charged fragment. In the mass spectrum (2) of compound **IVa** the ion peak *m/z* 219, formed probably from the ion *m/z* 324 after release of one more diethylphosphinyl group, is maximal by intensity. The presence of other firagment ions with low values of *m/z* in the mass spectrum (2) is evidently determined by sequential decay of the mentioned ions at the electron impact.

After the mother liquor concentrating the viscous noncrystallizable mass remains. The heating of it to 150°C leads to bisphosphine oxide **IVa**.

The oxidation of benzene solution of bisphosphine oxides **IVa** and **IVb** with alkaline solution of potassium ferrocyanide over 3–6 h yields the corresponding bisphosphorylated methylenequinones **V**.

(4-Hydroxy-3,5-di-*tert*-butylphenyl)methanebis-(diethylphosphine oxide) (IVa). To a solution of 3.44 g of diethyl chlorophosphine in 10 ml of hexane was added a solution of 3.99 g of dichloride **I** in 25 ml of hexane. The mixture was kept for 24 h at room temperature. The formed viscous mass was twice washed with hexane and dissolved in 15 ml of ethanol. This solution was stirred at room temperature for 3 h. Then the solvent was removed and the residue was dissolved in 40 ml of cold benzene. The product precipitates from this solution after 5–10 min as solvate complex with benzene. Yield 0.63 g, mp 78–83°C (decomp.). Mass spectrum (1) for sample **A** (40°C), *m/z* (%): 79(6.7), 78(100.0) $[M_2^+]$, 77(22.6), 52(9,7), 51 (8.7), 50(7.3), 39(7.8); mass spectrum (2) for sample **A** (90°C): 429(4.7), 428(49.7), $[M^+_1]$, 413(2.3) $[M_1 - CH_3]^+$, 399(3.1) $[M_1 - C_2H_5]^+$, 372(17.6) $[M_1 - C_4H_8]^+$, 371 (69.5) $[M_1 - C_4H_9]^+$, 324 (79.0), 323(44.6), 278(56.5), 247(37.8), 219 (100.0), 78(10.9) $[C_6H_6]^+$, 77(16.5) $[C_6H_5]^+$, 57 (69.0) $[C_4H_9]^+$.

Benzene solution was concentrated in a vacuum. The product crystallizes gradually on slow heating of viscous residue to 150°C. Yield 2.81 g (47%), mp 168–173°C (isooctane–benzene, 10:1) (174–175°C [2]). ^{1}H NMR spectrum ($CDCI_3$), δ, ppm: 0.75–1.30 m (12H, CH_2CH_3), 1.40 s [18H, $C(CH_3)_3$], 1.60–2.38 m (8H, CH_2CH_3), 3.28 t (1H, PCHP, $^2J_{PH}$ 15 Hz), 5.38 s (1H, OH), 7.38 br. s (2H, C_6H_2). Found, %: P 14.30, 14.65. $C_{23}H_{42}O_3P_2$. Calculated, %: P 14.49.

(4-Hydroxy-3,5-di-*tert*-butylphenyl)methanebis-(diphenylphosphine oxide) (IVb). A mixture of 0.73 g of dichloride **I** and 1.11 g of diphenyl chlorophosphine was heated in a sealed ampule at 100–110°C for 3 h. The formed adduct was dissolved in 10 ml of ethanol. Then the volatile substances were evaporated. Yield 0.81 g (71%), mp 263.5–266°C (toluene) (262–264°C [2]). ^{1}H NMR spectrum ($CDCI_3$), δ, ppm: 1.10 s [18H, $C(CH_3)$], 4.63 t (1H, PCHP, $^2J_{PH}$ 16 Hz), 4.98 s (1H, OH), 6.88 s (2H, C_6H_2), 7.07–8.13 m (20 H, C_6H_5). Found, %: P 10.35, 10.41. $C_{39}H_{42}O_3P_2$. Calculated, %: P 10.00.

4-Bis(diethylphosphinyl)methylene-2,6-di-*tert*-butylcyclohexadien-2,5-one (Va). To a solution of 2.14 g of bisphosphine oxide **IVa** in 20 ml of benzene was added a solution of 9.87 g of potassium ferricyanide in 90 ml of 2N KOH under stirring for 3 h. The colored benzene solution was separated, washed

with water to neutral reaction, and dried with sodium sulfate. Then benzene was evaporated in a vacuum. Yield 1.32 g (62%), orange crystalline substance, mp 183–185°C (heptane). ^{1}H NMR spectrum (CCl_4 + $CDCI_3$), δ, ppm: 1.65 d. q (12H, CH_2CH_3, $^3J_{PH}$ 17.6 Hz, $^3J_{HH}$ 7.6 Hz), 1.20 s [18H, $C(CH_3)_3$], 2.03–2.14 m (8H, CH_2CH_3), 8.04 br. s (2H, C_6H_2). Found, %: P 14.30, 14.35. $C_{23}H_{40}O_3P_2$. Calculated, %: P 14.78.

4-Bis(diphenylphosphinyl)methylene-2,6-di-*tert*-butylcyclohexadien-2,5-one (Vb) was prepared similarly. Yield 67.7%, mp 224–226°C (hexane–benzene, 5:1), (225–228°C [8]). ^{1}H NMR spectrum (CCl_4 + $CDCI_3$), δ, ppm: 1.08 s [18H, $C(CH_3)_3$], 7.25–7.95 m (22H, C_6H_5, C_6H_2). Found, %: P 10.05, 9.75. $C_{33}H_{40}O_3P_2$. Calculated, %: P 10.03.

The ^{1}H NMR spectra were registered on a Tesla BS-567A spectrometer (100 MHz), ^{31}P NMR spectra, on a CXP-100 instrument (36.5 MHz). Chemical shifts for the hydrogen and phosphorus nuclei were determined relative to TMS and 85% H_3PO_4 respectively.

The mass spectra (electron impact) were obtained on a TRACE MS Finnigan MAT instrument (70 eV, 200°C). The system of direct admission of substance into the ions source was used. The processing of the mass spectral data was made using a Xcalibur program. The ions peaks containing the more abundant isotopes are given.

REFERENCES

1. Antonova, N.A., Kolyada, M.N., Osipova, V.P., Pimenov, Yu.T., Berberova, N.T., Tyurin, V.Yu., Gracheva, Yu.A., and Milayeva, E.R., *Dokl. Acad. Nauk*, 2008, vol. 419, no. 3, p. 342.
2. Tyurin, V.Yu., Gracheva, Yu.A., Milayeva, E.R., Prishchenko, A.A., Livantsov, M.V., Novikova, O.P., Livantseva, L.I., Maryashina, A.V., Bubnov, M.P., Kozhanov, K.A., and Cherkasov, V.K., *Izv. Akad. Nauk Ser. Khim*., 2007, no. 4, p. 744.
3. Gazizov, M.B., Ismagilov, R.K., Karimova, R.F., Shamsutdinova, L.P., and Sinyashin, O.G., *Dokl. Akad. Nauk*, 2005, vol. 400, no. 2, p. 204.
4. Gazizov, M.B., Ismagilov, R.K., Shamsutdinova, L.P., Karimova, R.F., and Sinyashin, O.G., *Zh. Obshch. Khim*., 2005, vol. 75, no.12, p. 2061.
5. Gazizov, M.B., Ismagilov, R.K., Shamsutdinova, L.P., Karimova, R.F., and Sinyashin, O.G., *Zh. Obshch. Khim*., 2006, vol. 76, no. 7, p.1224.
6. Nifantyev, E.E. and Vasyanina, L.K., *Spektroskopiya YaMR ^{31}P* (^{31}P NMR Spectroscopy), Moscow: MGPI imeni V.I. Lenina, 1986, p. 55.
7. Tsivunin, V.S., Gil'm Kamai, Shagidullin, R.R., and Khisamutdinova, R.Sh., *Zh. Obshch. Khim*., 1965, vol. 35, no. 7, p. 1234.
8. Gross, H., Keitel, I., and Costisella, B., *Phosph. Sulf. and Silicon*, 1991, vol. 62, p. 35.