Synthesis and dimerization of dibutyl (3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidenemethyl)phosphonate

T. R. Shaekhov, E. M. Gibadullina,* Yu. K. Voronina, A. R. Burilov, and M. A. Pudovik

A. E. Arbuzov Institute of Organic and Physical Chemistry Kazan Scientific Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843) 275 2253. E-mail: elmirak@iopc.ru

While studing the synthesis and properties of phosphorylated methylenequinones,[1—5] we have accessed dibutyl (3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidenemethyl)phosphonate (**1**) by oxidation of dibutyl (3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphonate (**2**) with alkaline potassium ferrihexacyanide (Scheme 1).

The structure and composition of compound **1** were established based on the ^{1}H, ^{31}P NMR and IR spectroscopic data, mass spectrometric (MALDI) data, and elemental analysis. We found that with time compound **1** undergoes dimerization leading to 1,2-bis(dibutoxyphosphoryl)-1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethane (**3**). The process reached completion within 10 days, which was indicated by the disappearance in the ^{31}P NMR spectrum of the signal for the starting compound **1** (δ_P 15.0) and the presence of the only singlet for the dimerization product **3** (δ_P 27.5). The structure and composition of compound **3** were confirmed by the ^{1}H, ^{31}P NMR and IR spectroscopic data, mass spectrometric (MALDI) data, elemental analysis, and X-ray diffraction studies (Fig. 1).

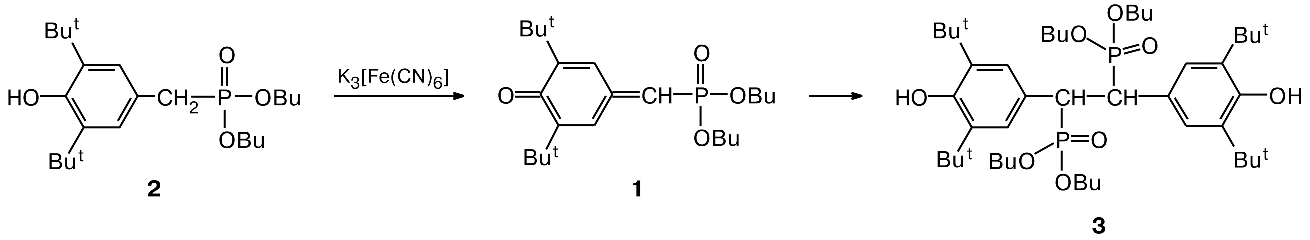
It should be noted that in the solution in benzene, methylenequinone **1** did not undergo visible changes over prolonged period of time.

^{1}H NMR spectra were recorded on a Bruker Avance-600 spectrometer (600 MHz) relative to the signals of residual protons of the deuterated solvent (DMSO-d$_6$), ^{31}P NMR spectra were recorded on a Bruker MSL-400 spectrometer (166.93 MHz) relative to the 85% aqueous H_3PO_4 as an external standard. IR spectra were recorded on a Bruker Vector 22 Fourier-spectrometer (in KBr pellets for crystalline samples) in the range of 400—4000 cm^{-1}. Mass spectra of the matrix-activated laser desorption/ionization (MALDI) were obtained on a Bruker Daltonics MALDI TOF/TOF time-of-flight mass spectrometer. Elemental analysis was performed on a Carlo-Erba EA 1108 elemental analyzer. A crystal of compound **3** ($C_{46}H_{78}O_8P_2$, M = 821.02) is orthorhombic, space group *Pbcn*, at 296 K $a = 17.521(5)$, $b = 14.434(4)$, $c = 19.997(6)$ Å, $V = 5057(3)$ Å^3, $Z = 4$, $F(000) = 1792$, $d_{calc} = 1.078$ g cm^{-3}, $\mu = 0.131$ mm^{-1}. Parameters of the unit cell and intensities of 36391 reflections were measured on a Smart Apex II CCD diffractometer (296 K, λMo-Kα irradiation, graphite monochromator, φ- and ω-scan technique, $\theta_{max} = 26.0°$). The structure was solved by direct method using the SIR program[6] and refined first in isotropic and then in anisotropic approximation using the SHELXL-97 program.[7] Positions of hydrogen atoms were calculated geometrically and refined in isotropic approximation. The final *R*-factors: $R_1 = 0.0775$ for 2105 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.2860$ for 4972 independent reflections. All the calculations were carried out using the WinGX[8] and APEX2 programs.[9] The figures of the molecules were performed using the ORTEP3 and PLATON programs.[10—11] The hydrogen atom of the hydroxy group containing atom O(12) was not found in the differential Fourier-synthesis because of the low reflecting ability of the crystal and the high degree of disorder in it. Thus, both *n*-butyl groups are disordered over two positions with the populations of 0.68 : 0.32 and 0.78 : 0.22, respectively. The crystallographic data were deposited with the Cambridge Structural Database CCDC (the structure number 884917).

Solvents were purified and dried according to the known procedures.[12] Dibutyl (3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphonate (**2**) was synthesized using procedure described earlier.[13]

Dibutyl (3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidenemethyl)phosphonate (1). A solution of dibutyl (3,5-di-*tert*-butyl-

Scheme 1



Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2344—2346, December, 2012.

1066-5285/12/6112-2367 © 2012 Springer Science+Business Media, Inc.

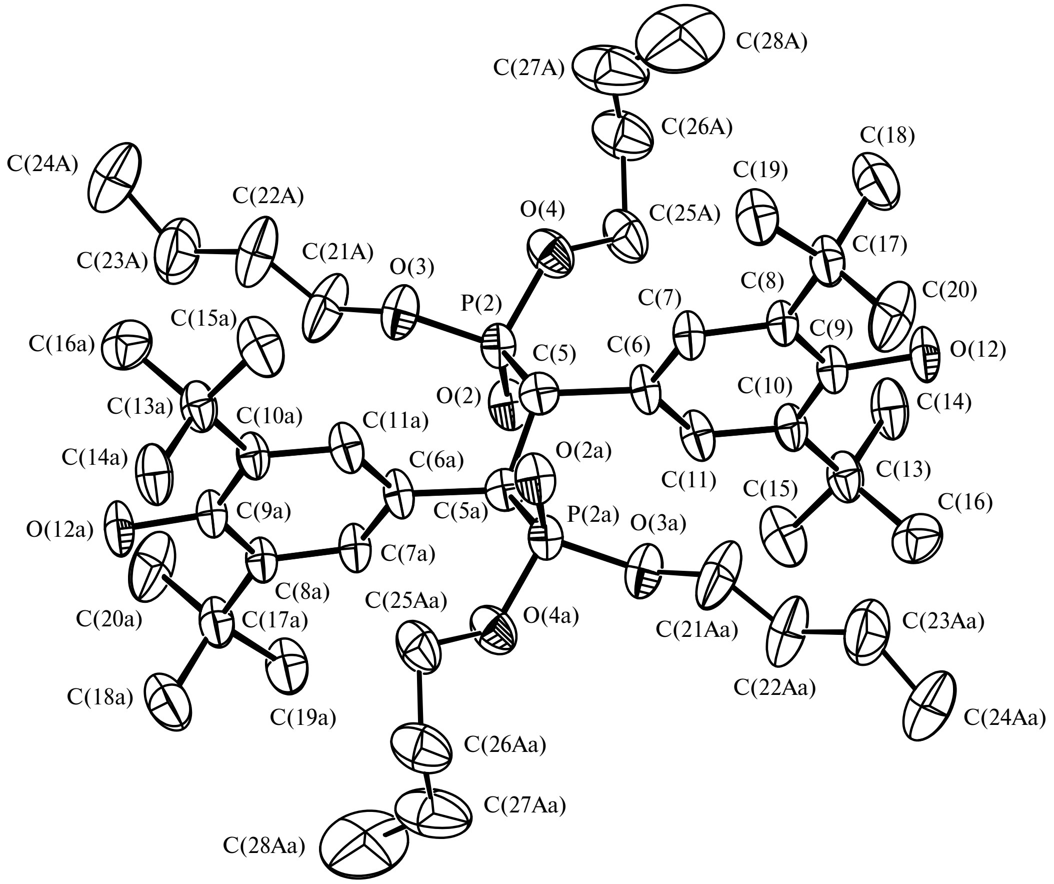


Fig. 1. Molecular structure of compound **3**. The hydrogen atoms and the disorder of the C(21)—C(22)—C(23)—C(24) and C(25)—C(26)—C(27)—C(28) chains are not shown. Ellipsoids of anisotropic thermal vibrations are given with 20% probability.

4-hydroxybenzyl)phosphonate (**2**) (4.1 g, 10 mmol) in benzene (160 mL) was stirred with a solution of $K_3Fe(CN)_6$ (24.6 g, 60 mmol) in 2 *M* KOH (180 mL) for 3 h at 20 °C. The colored benzene solution was separated, washed with water to neutrality, and dried with anhydrous Na_2SO_4. Benzene was evaporated *in vacuo* using a water-jet pump, the residue was washed with pentane and dried *in vacuo* to obtain reddish brown tar-like product **1** (3.9 g, 97%). Found (%): C, 66.84; H, 9.47; P, 7.26. $C_{23}H_{39}O_4P$. Calculated (%): C, 67.29; H, 9.58; P, 7.54. ^{1}H NMR ($CDCl_3$), δ: 0.72 (m, 6 H, $C\underline{H}_3(CH_2)_2$); 1.07 (m, 18 H, $(C\underline{H}_3)_3C$); 1.22 (m, 4 H, $-CH_3C\underline{H}_2-$); 1.46 (m, 4 H, $-C\underline{H}_2CH_2O$); 3.80 (br.s, 4 H, $-CH_2C\underline{H}_2O$); 5.80 (d, 1 H, $PC\underline{H}$, $J_{P,H}$ = 14.0 Hz); 6.06 (s, 1 H, H_{arom}); 7.79 (s, 1 H, H_{arom}). ^{31}P NMR ($CDCl_3$), δ: 15.4. IR (neat), ν/cm^{-1}: 1634 (C=O), 1596 (C=CH), 1251 (P=O), 934 (POC). MS, *m/z*: 410.50 $[M]^+$.

1,2-Bis(dibutoxyphosphoryl)-1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethane (3). Compound **1** (0.8 g) was allowed to stand at room temperature for 10 days. A crystalline product formed was washed with pentane several times and dried *in vacuo* using a water-jet pump to obtain light yellow product **3** (0.6 g, 74%). M.p. 223—226 °C (pentane). Found (%): C, 67.38; H, 10.20; P, 7.64. $C_{46}H_{80}O_8P_2$ Calculated (%): C, 67.13; H, 9.80; P, 7.53. ^{1}H NMR (DMSO-d_6), δ: 0.69 (t, 6 H, $C\underline{H}_3CH_2$, J = 7 Hz); 0.76 (t, 6 H, $C\underline{H}_3CH_2$, J = 7 Hz); 0.94—1.14 (m, 16 H, $CH_3(C\underline{H}_2)_2$); 1.46 (s, 36 H, $(C\underline{H}_3)_3C$); 2.86 (m, 2 H, $-CH_2C\underline{H}_2O$); 2.98 (m, 4 H, $-CH_2C\underline{H}_2O$); 3.44 (m, 2 H, $-CH_2C\underline{H}_2O$); 3.53 (m, 2 H, $-CH_2C\underline{H}_2O$); 3.73 (d, 1 H, $-C\underline{H}-CH-$, J = 7 Hz); 3.74 (d, 1 H, $-CH-C\underline{H}-$, J = 7 Hz); 5.13 (s, 2 H, $O\underline{H}$); 7.36 (br.s, 4 H, H_{arom}). ^{31}P NMR (DMSO-d_6), δ: 27.57. IR, ν/cm^{-1}: 1648 (C_{arom}), 1251 (P=O), 934 (POC). MS, *m/z*: 824.13 $[M]^+$.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 12-03-97041) and the Ministry of Education and Science of the Russian Federation (Federal Target Program "Scientific and Scientific-Pedagogical Specialists of the Innovative Russia, GK No. P837).

References

1. H. Gross, S. Ozegowski, B. Costisela, *Phosphorus, Sulfur, Silicon Relat. Elem.*, 1990, **47**, 7.
2. H. Gross, I. Keitel, B. Costisela, *Phosphorus, Sulfur, Silicon Relat. Elem.*, 1991, **62**, 35.
3. R. K. Ismagilov, V. V. Moskva, L. Yu. Mosunova, V. P. Arkhipov, *Zh. Obshch. Khim.*, 2000, 70, 49 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2000, **70**, 46].

4. Yu. V. Bakhtiyarova, M. S. Bondar, V. V. Andriyashin, O. N. Kataeva, I. V. Galkina, V. I. Galkin, *Mendeleev Commun.*, 2009, **19**, 37.
5. T. R. Shaekhov, E. M. Gibadullina, Yu. K. Voronina, V. V. Syakaev, D. R. Sharafutdinova, A. R. Burilov, M. A. Pudovik, *Russ. Chem. Bull.* (*Int. Ed.*), 2011, **60**, 1999 [*Izv. Akad. Nauk, Ser. Khim.*, 2011, 1964].
6. A. Altomar, G. Cascarano, C Giacovazz, D Viterbo, *Acta Crystallogr. Sec. A.*, 1991, **47**, 744.
7. M. Sheldrick, SHELXL-97 *Program for Crystal Structure Refinement*, University of Goettingen, Germany, 1997.
8. L. J. Farrugia, *WinGX 1.64.05, An Integrated System of Windows Programs for the solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data. J. Appl. Cryst.*, 1999, **32**, 837.
9. *APEX2 (Version 2.1), SAINTPlus, Data Reduction and Correction Program (Version 7.31A, Bruker Advansed X-ray Solutions)*, BrukerAXS Inc., Madison, Wisconsin, USA, 2006.
10. L. J. Farrugia, *J. Appl. Cryst.*, 1997, **30**, P. 565.
11. A. L. Spek, *Acta Crystallogr. Sect. A.*,1990, **46**, 34.
12. A. Vaisberger, E. Proskauer, D. Riddik, E. Tunis, *Organicheskie rastvoriteli* [*Organic Solvents*], Moscow, Inostr. Lit. Publ., 1959, 518 pp. [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 1992, **62**].
13. N. A. Mukmeneva, V. Kh. Kadyrova, V. M. Zharkova, *Zh. Obshch. Khim.*, 1992, **62**, 1620 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 1992, **62**].

Received June 27, 2011;
in revised form December 4, 2012