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LETTERS TO THE EDITOR

Dimethyl [(3,5-Di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)-methyl]phosphonate in Reactions with Aliphatic Diols

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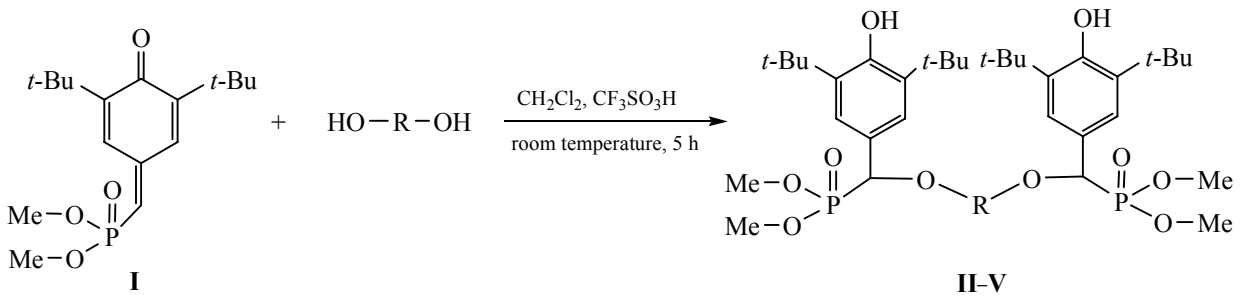
Cyclohexadienones (methylene quinones) are highly reactive compounds transformed into phenols via the reactions with proton-donor substrates [1]. The reactions of phosphorus-containing 2,6-di-*tert*-butyl-4-methylene-2,5-cyclohexadienones with nucleophiles has been recognized as a convenient approach to prepare spatially hindered phenols containing phosphoryl fragments [2, 3]. The stable dialkyl[(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)methyl]phosphonates readily react with nucleophiles to form the 1,6-addition products [2, 4, 5]. In particular, it has been shown that such phosphonates interact with aliphatic alcohols in the presence of inorganic acids as catalyst to yield dialkyl α-alkoxy-3,5-di-*tert*-butyl-4-hydroxybenzyl-phosphonates [6].

In this work we studied the interaction of dimethyl-[(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)-methyl]phosphonate (**I**) with aliphatic diols (1,3-propanediol, 2,2-dimethylpropane-1,3-diol, 1,3-butane-diol, and 1,4-butandiol). Earlier we have suggested the application of trifluoromethanesulfonic acid as a catalyst of the reaction between compound **I** and phenols [2]. Therefore, the addition of the diols to compound **I** (at the 1 : 2 ratio) was carried out in the presence of catalytic amounts of CF_3SO_3H in the CH_2Cl_2 medium at room temperature. The interaction gave compounds **II**–**V** in a high yield (Scheme 1).

The structure and composition of the products were elucidated using the ^1H, ^{13}C, and ^{31}P NMR data as well

Scheme 1.



R = $CH_2CH_2CH_2$ (**II**), $CH_2C(CH_3)_2CH_2$ (**III**), $CH_2CH_2CH(CH_3)$ (**IV**), $CH_2CH_2CH_2CH_2$ (**V**).

as IR spectroscopy, mass spectrometry (MALDI-TOF), and elemental analysis results. The prepared compounds were mixtures of the corresponding diastereomers, as confirmed by duplication of the signals in the ^{1}H and ^{13}C NMR spectra.

To summarize, the interaction of compound **I** with aliphatic diols is a convenient method to prepare the diesters containing phosphoryl and spatially hindered phenol structural fragments.

The starting compound **I** was prepared as described elsewhere [7].

Compounds II–V *(general procedure).* 1.5 mmol of the diol and 1–2 drops of trifluoromethanesulfonic acid were added to a solution of 1 g (3.0 mmol) of compound **I** in 2 mL of toluene. The reaction mixture was kept at room temperature during 5 h. The solvent was then removed, and the residue was dried in a vacuum (1 h, 40°C, 1 mmHg) to a constant mass. The products were yellow tar-like substances.

Tetramethyl {[(propane-1,3-duylbis(oxy)]bis-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)methylene]}bisphosphonate (II). Yield 0.86 g (78 %). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.42 s [36H, C(CH$_3$)$_3$], 1.89 m (2H, CH$_2$), 3.53 m (4H, OCH$_2$), 3.59–3.67 m (12H, OCH$_3$); 4.44 d, 4.48 d, 4.53 d, and 4.54 d (2H, CH, J_{PH} 12), 5.27 br.s (2H, OH), 7.16 s, 7.18 s and 7.20 s (4H, CH$_{Ar}$). ^{13}C NMR spectrum, δ$_C$, ppm (*J*, Hz): 30.3 [C(<u>C</u>H$_3$)$_3$], 32.2 (CH$_2$), 34.3 [<u>C</u>(CH$_3$)$_3$], 53.3–53.8 (OCH$_3$), 68.94 (OCH$_2$, J_{PC} 15.0), 78.1 (CH, J_{PC} 210.0), 124.6 (CH$_{Ar}$), 125.0 (<u>C</u>$_{Ar}$CH), 135.9 and 136.0 [<u>C</u>$_{Ar}$C(CH$_3$)$_3$], 154.02, 154.09 (C$_{Ar}$OH). ^{31}P NMR spectrum, δ$_P$, ppm: 21.9, 22.1, 22.2. Mass spectrum (MALDI), *m*/*z* (I_{rel}, %): 751.1 [*M* + Na]$^+$, 767.0 [*M* + K]$^+$. Found, %: C 60.46; H 8.62; P 8.15. $C_{37}H_{62}O_{10}P_2$. Calculated, %: C 60.97; H 8.57; P 8.50.

Tetramethyl {[(2,2-dimethylpropane-1,3-diyl)bis-(oxy)]bis[(3,5-di-*tert*-butyl-4-hydroxyphenyl)methylene]}bisphosphonate (III). Yield 0.92 g (80%). ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 1.02 s and 0.99 s (6H, CH$_3$), 1.44 s [36H, C(CH$_3$)$_3$], 3.19 d and 3.33 d (4H, OCH$_2$, $^3J_{HH}$ 8.0), 3.64 m (12H, OCH$_3$), 4.35 m and 4.58 m (2H, CH), 5.23 br.s (2H, OH), 7.18 s (4H, CH$_{Ar}$). ^{13}C NMR spectrum, δ$_C$, ppm (*J*, Hz): 21.2, 21.5, 21.6 [C(<u>C</u>H$_3$)$_2$]; 29.8 [C(<u>C</u>H$_3$)$_3$], 34.3 [<u>C</u>(CH$_3$)$_3$]; 36.2, 36.3, 36.4 [<u>C</u>(CH$_3$)$_2$]; 52.3–52.9 (OCH$_3$), 76.2–76.9 (OCH$_2$); 68.3, 77.0, 78.1, 79.8 (CH, J_{PC} 210.0); 124.3, 124.4, 124.5, 124.6 (CH$_{Ar}$); 125.8, 125.9 (<u>C</u>$_{Ar}$CH); 137.0, 137.1 [<u>C</u>$_{Ar}$C(CH$_3$)$_3$], 153.7, 153.9 (C$_{Ar}$OH). ^{31}P NMR spectrum: δ$_P$ 21.9 ppm. Mass spectrum (MALDI), *m*/*z* (I_{rel}, %): 757.5 [*M*]$^+$, 779.6 [*M* + Na]$^+$, 795.7 [*M* + K]$^+$. Found, %: C 60.53; H 8.73; P 8.00. $C_{39}H_{66}O_{10}P_2$. Calculated, %: C 61.89; H 8.79; P 8.18.

Dimethyl {(3,5-di-*tert*-butyl-4-hydroxyphenyl)[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)(dimethoxyphosphoryl)methoxybutoxy]methyl}phosphonate (IV). Yield 0.83 g (74%). ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 1.07 d, 1.08 s, 1.11 d, and 1.15 d (1.5H, CH$_3$, $^3J_{HH}$ 6.0); 1.46 m [36H, C(CH$_3$)$_3$], 1.69 m (2H, C<u>H</u>$_2$CH); 3.58 d, 3.59 d, 3.67 d, and 3.68 d (12H, OCH$_3$, J_{PH} 10.0); 4.67 d, 4.68 d, 4.83 d, and 4.84 d (2H, CH, J_{PH} 11.5); 7.30 d, 7.31 d, 7.32 d, and 7.33 d (4H, CH$_{Ar}$, J_{PH} 2.0). ^{13}C NMR spectrum, δ$_C$, ppm (*J*, Hz): 21.9, 23.1, 23.3 (CH<u>C</u>H$_3$); 29.9 [C(<u>C</u>H$_3$)$_3$], 34.4 [<u>C</u>(CH$_3$)$_3$]; 39.0, 39.1 (<u>C</u>H$_2$CH); 52.7, 52.8, 52.9, 53.0 (OCH$_3$, J_{PC} 150.0); 64.1, 64.6 (<u>C</u>HCH$_3$); 67.8, 67.9 (OCH$_2$); 74.3, 76.1 77.7, 77.8 (CH, J_{PC} 210.0); 124.5, 124.6, 124.7, 124.8 (CH$_{Ar}$); 125.2, 125.5, 125.6, 125.7, 125.8 (<u>C</u>$_{Ar}$CH); 137.1, 137.4 [<u>C</u>$_{Ar}$C(CH$_3$)$_3$]; 153.7, 154.0 (C$_{Ar}$OH). ^{31}P NMR spectrum, δ$_P$, ppm: 21.7, 22.1, 22.5. Mass spectrum (MALDI), *m*/*z* (I_{rel}, %): 765.1 [*M* + Na]$^+$. Found, %: C 61.19; H 8.78; P 8.67. $C_{38}H_{64}O_{10}P_2$. Calculated, %: C 61.44; H 8.68; P 8.34.

Tetramethyl {[butane-1,4-diylbis(oxy)]bis[(3,5-di-*tert*-butyl-4-hysroxyphenyl)methylene]}bisphosphonate (V). Yield 0.97 g (86%). ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 1.47 m [36H, C(<u>C</u>H$_3$)$_3$], 1.66 m (4H, C<u>H</u>$_2$CH$_2$O), 3.47 m (12H, OCH$_2$); 3.56 d, 3.57 d, 3.67 d, and 3.69 d (12H, OCH$_3$, J_{PH} 10.0); 4.63 d, 4.65 d, and 4.67 d (2H, CH, J_{PH} 12.0); 7.30 d and 7.32 d (4H, CH$_{Ar}$, J_{PH} 2.0). ^{13}C NMR spectrum, δ$_C$, ppm (*J*, Hz): 26.1 (OCH$_2$<u>C</u>H$_2$), 29.8 [C(<u>C</u>H$_3$)$_3$], 34.2 [<u>C</u>(CH$_3$)$_3$]; 51.9, 52.5, 52.6 (OCH$_3$, J_{PC} 150.0); 68.8, 69.9, 70.4 (OCH$_2$); 68.3, 71.1 77.5, 79.1 (CH, J_{PC} 210.0); 124.2, 124.7, 124.8 (CH$_{Ar}$); 125.8 (<u>C</u>$_{Ar}$CH); 137.0, 136.9 [<u>C</u>$_{Ar}$C(CH$_3$)$_3$]; 153.5, 153.8 (C$_{Ar}$OH). ^{31}P NMR spectrum: δ$_P$ 21.5 ppm. Mass spectrum (MALDI), *m*/*z* (I_{rel}, %): 743.4 [*M*]$^+$, 765.4 [*M* + Na]$^+$, 781.4 [*M* + K]$^+$. Found, %: C 60.6; H 8.62; P 8.15. $C_{38}H_{64}O_{10}P_2$. Calculated, %: C 61.44; H 8.68; P 8.34.

^{13}C NMR spectra were recorded using a Bruker Avance-600 instrument at 150 MHz using as internal reference the signals of residual protons of the solvent [$CDCl_3$ in the case of compounds **II** and **III**; $(CD_3)_2CO$ in the case of compounds **IV** and **V**]. ^{1}H and ^{31}P NMR spectra were recorded using a Bruker MSL-400 spectrometer at 400.13 and 161.94 MHz, respectively. MALDI-TOF mass spectra were registered using an

ULTRAFLEX III TOF/TOF Bruker instrument (*p*-nitroaniline as matrix). Elemental analysis was performed using an EA 1108 (Carlo-Erba) instrument.

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