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LETTERS TO THE EDITOR

Addition of *O*,*O*-Dialkyldithiophosphoric Acid to Phosphorylated Methylenequinones

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It is known that addition hydrophosphoryl compounds to phosphorylated methylenequinones **Ia** and **Ib** occurs in the presence of sodium ethylate to form diphosphorus-containing hindered phenols [1, 2]. However, in the literature there have been no information on the reaction of phosphorylated methylenequinones **Ia** and **Ib** with thiophosphoryl compounds, in particular, with *O*,*O*-dialkyldithiophosphoric acids **IIa** and **IIb**.

We found that 4-[diphenyl(diethyl)phosphinylmethylene]-2,6-di-*tert*-butylcyclohexadiene-2,5-ones **Ia** and **Ib** reacted with *O*,*O*-dialkyldithiophosphoric acids **IIa** and **IIb** in the absence of any catalyst to form 1,6-adducts: *O*,*O*-dialkyldithiophosphato(4-hydroxy-3,5-di-*tert*-butylphenyl)methanediphenyl(diethyl)phosphine oxides **IIIa**–**IIId** (Scheme 1).

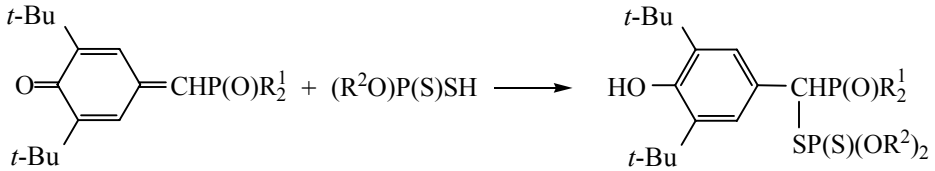
The reaction occurred under mild conditions (benzene, 20°C, 24 h) to afford the final adducts with high yields. That pointed at high nucleophilicity of dialkyldithiophosphoric acids **IIa** and **IIb** towards phosphorylated methylenequinones **Ia** and **Ib**.

Composition and structure of compounds **IIIa**–**IIId** were confirmed by elemental analysis as well as ^{1}H and ^{31}P NMR spectroscopy.

4-(Diphenylphosphinylmethylene)-2,6-di-*tert*-butylcyclohexadiene-2,5-one **Ia** was prepared according to the procedure described elsewhere [3, 4].

4-(Diethylphosphinyl)methylene-2,6-di-*tert*-butylcyclohexadiene-2,5-one (Ib). A solution of 7.82 g (0.027 mol) of 4-hydroxy-3,5-di-*tert*-butylbenzylidene chloride in 25 mL of hexane was added dropwise to a solution of 3.37 g (0.027 mol) of diethylchlorophosphine in 25 mL of *n*-hexane. The mixture was refluxed during 30 min. The resulting viscous mixture was twice washed with hexane and treated with 11.45 g (0.11 mol) of trimethyl orthoformate. The reaction was exothermic. The reaction mixture was refluxed during 1 h until methyl chloride evolution ceased. After distilling off the volatile products, the solid residue was recrystallized from a 10 : 1 heptane–toluene mixture. Yield 6.57 g (76%), mp 170–172°C (173–175°C

Scheme 1.



Ia, Ib **IIa, IIb** **IIIa–IIId**

R^1 = Ph (**Ia**), Et (**Ib**); R^2 = Et (**IIa**), *i*-Pr (**IIb**); R^1 = Ph, R^2 = Et (**IIIa**); R^1 = Ph, R^2 = *i*-Pr (**IIIb**); R^1 = Et, R^2 = Et (**IIIc**); R^1 = Et, R^2 = *i*-Pr (**IIId**).

[5]). ^{1}H NMR spectrum, δ, ppm: 1.20 s (18H, CMe_3), 1.2 t (6H, $CH_2\underline{Me}$, $^3J_{HH}$ 7.5 Hz), 1.7 d.q (4H, $\underline{CH_2}Me$, $^3J_{HH}$ 7.5, $^2J_{PH}$ 22.5 Hz), 5.09 br.s (1H, OH), 5.90 d (1H, CHP, $^2J_{PH}$ 22.5 Hz), 6.65 s and 8.30 s (2H, C_6H_2). Found P, %: 9.30, 9.60. $C_{19}H_{31}O_2P$. Calculated P, %: 9.62.

***O*,*O*-Diethyldithiophosphato(4-hydroxy-3,5-di-*tert*-butylphenyl)methanediphenylphosphine oxide (IIIa).** A mixture of 0.63 g (0.0015 mol) of quinone **Ia** and 0.29 g (0.0016 mol) of *O*,*O*-diethyldithiophosphoric acid **IIa** in 12 mL of benzene was allowed to stand at room temperature during 24 h. After removal of the solvent, the residue was treated with hexane and recrystallized. Yield 0.86 g (89%), mp 165–166°C (toluene–heptane). ^{1}H NMR spectrum, δ, ppm: 0.80 t and 0.92 t (6H, $OCH_2\underline{Me}$, $^3J_{HH}$ 7.2 Hz), 1.17 s (18H, CMe_3); 3.29 d.q, 3.41 d.q, 3.52 d.q and 3.73 d.q (4H, $O\underline{CH_2}Me$, $^3J_{HH}$ 7.2, $^3J_{PH}$ 14.4 Hz), 4.74 d.d (1H, CH, $^3J_{PH}$ 19.6, $^2J_{PH}$ 9.2 Hz), 4.91 br.s (1H, OH), 6.86 s (2H, C_6H_2), 7.06–7.83 m (10H, Ph). ^{31}P NMR spectrum, δ_P, ppm: 28. 97 d (P^1, $^3J_{PP}$ 38.07 Hz), 96.38 d (P^2, $^3J_{PP}$ 38.07 Hz). Found P, %: 10.24, 10.65. $C_{31}H_{42}O_4P_2S_2$. Calculated P, %: 10.26.

***O*,*O*-Diisopropyldithiophosphato(4-hydroxy-3,5-di-*tert*-butylphenyl)methanediphenylphosphine oxide (IIIb)** was prepared similarly from 0.42 g (0.001 mol) of quinone **Ia** and 0.23 g (0.0011 mol) of *O*,*O*-diisopropyldithiophosphoric acid **IIb**. Yield 0.52 g (83%), mp 169–173°C (toluene–heptane). ^{1}H NMR spectrum, δ, ppm: 0.68 d, 0.88 d, 0.93 d and 1.17 d (12H, $\underline{Me_2}CHO$, $^3J_{HH}$ 6.2 Hz), 1.25 s (18H, CMe_3), 4.29 d. septets, 4.02 d. septets (2H, $Me_2\underline{CH}O$, $^3J_{HH}$ 6.2, $^3J_{PH}$ 12.1 Hz), 4.97 d.d. d (1H, CH, $^3J_{PH}$ 20.6, $^2J_{PH}$ 8.8, $^4J_{HH}$ 4.0 Hz), 4.81 br.s (1H, OH), 7.14 d (2H, C_6H_2, $^4J_{HH}$ 4.0 Hz), 7.21–7.95 m (10H, Ph). ^{31}P NMR spectrum, δ_P, ppm: 30. 51 d (P^1, $^3J_{PP}$ 42.12 Hz), 95.45 d (P^2, $^3J_{PP}$ 42.12 Hz). Found P, %: 9.45, 9.47. $C_{33}H_{46}O_4P_2S_2$. Calculated P, %: 9.81.

***O*,*O*-Diethyldithiophosphato(4-hydroxy-3,5-di-*tert*-butylphenyl)methanediethylphosphine oxide (IIIc)** was prepared similarly from 0.97 g (0.003 mol) of quinone **Ib** and 0.586 g (0.0031 mol) of *O*,*O*-diethyldithiophosphoric acid **IIa**. Yield 1.32 g (87%), mp 117–118°C (isooctane). ^{1}H NMR spectrum, δ, ppm: 0.75 t and 0.99 t (6H, $OCH_2\underline{Me}$, $^3J_{HH}$ 7.2 Hz), 0.78–0.82 m and 1.01–1.06 m (6H, $PCH_2\underline{Me}$), 1.57–1.83 m (4H, PCH_2), 1.28 s (18H, CMe_3); 3.92 d.q, 3.71 d.q, 3.50 d.q and 3.39 d.q (4H, $O\underline{CH_2}Me$, $^3J_{HH}$ 7.2, $^3J_{PH}$ 19.2 Hz), 4.08 d.d (1H, CH, $^3J_{PH}$ 19.2, $^2J_{PH}$ 9.2 Hz), 5.19 br.s (1H, OH), 7.04 s (2H, C_6H_2). ^{31}P NMR spectrum, δ_P, ppm: 49.91 d (P^1, $^3J_{PP}$ 32.4 Hz), 95.86 d (P^2, $^3J_{PP}$ 32.4 Hz). Found P, %: 11.50, 12.05. $C_{23}H_{42}O_4P_2S_2$. Calculated P, %: 12.20.

***O*,*O*-Diisopropyldithiophosphato(4-hydroxy-3,5-di-*tert*-butylphenyl)methanediethylphosphineoxide (IIId)** was prepared similarly from 0.97 g (0.003 mol) of quinone **Ib** and 0.67 g (0.0031 mol) of *O*,*O*-diisopropyldithiophosphoric acid **IIb**. Yield 1.36 g (84%), mp 142–145°C (isooctane). ^{1}H NMR spectrum, δ, ppm: 0.93 d and 1.25 d (6H, $OCH\underline{Me_2}$, $^3J_{HH}$ 6.4 Hz), 0.96 d and 1.35 d (6H, $OCH\underline{Me}$, $^3J_{HH}$ 6.0 Hz), 1.01 t and 1.24 t (6H, $PCH_2\underline{Me}$, $^3J_{HH}$ 7.6 Hz), 1.43 s (18H, CMe_3), 1.53–2.14 m (4H, PCH_2), 4.28 septet and 4.78 septet (2H, $O\underline{CH}Me_2$, $^3J_{HH}$ 6.4 Hz), 4.78 d.d (1H, PCH, $^3J_{PH}$ 20.0, $^2J_{PH}$ 9.2 Hz), 5.10 br.s (1H, OH), 7.29 s (2H, C_6H_2). ^{31}P NMR spectrum, δ_P, ppm: 50.65 d (P^1, $^3J_{PP}$ 36.5 Hz), 94.61 d (P^2, $^3J_{PP}$ 36.5 Hz). Found P, %: 10.90, 11.18. $C_{25}H_{46}O_4P_2S_2$. Calculated P, %: P 9.81.

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