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LETTERS TO THE EDITOR

On the Reaction of 4-Chloromethylene-2,6-di-*tert*-buthylcyclohexa-2,5-dien-1-one with P(III) Acids Esters

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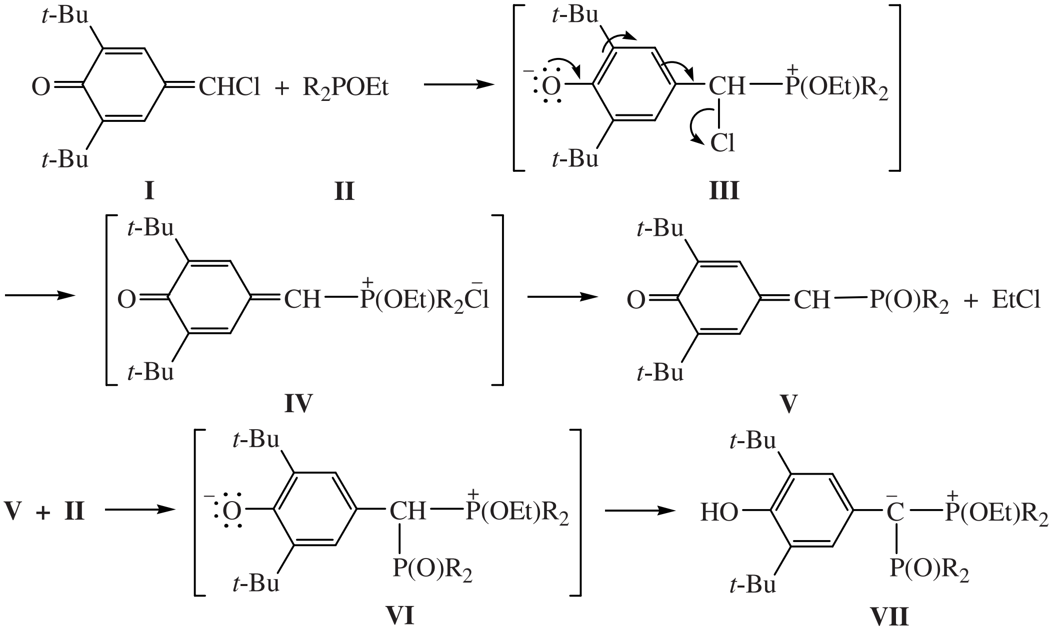
Proceeding with investigations on reactions of organic halides with aprotic reagents [1, 2], we pioneered in studying reactions of 4-chloromethylene-2,6-di-*tert*-butylcyclohexa-2,6-dien-1-one **I** (chloromethylenequinone) with P(III) acids esters, such as triethyl phosphite **IIa** and ethyl diphenylphosphinite **IIb**. Phosphorylated ylides **VII** were established to be the main products of the reaction of chloromethylenequinone **I** with esters **II** in a 1:2 ratio. We suppose that ylide **VII** is formed by the following two-stage scheme:



II–VII: R = EtO (**a**), Ph (**b**).

In the first stage of the reaction, ester **II** adds to a highly electrophilic chloromethylenequinone **I** to form betaine intermediate **III** which eliminates chloride anion through intramolecular nucleophilic substitution and transforms into quasiphosphonium compound **IV**. The latter is stabilized into phosphorylated methylenequinone **V** in accordance with the scheme of the second stage of the Arbuzov reaction.

At the second stage of the reaction, ester **II** adds to methylenequinone **V** to form bisphosphorylated betaine **VI** which transforms into phos-phorylated ylide **VII** through 1,6-proton shift [3–5].

Ylide **VIIa** was earlier prepared [5] by boiling compounds **Va** and **IIa** in benzene for 1.5 h. Our studied reactions proceed under milder conditions (20–25°C), and, therefore, we reproduced the second stage of the proposed scheme as a model experiment. A few minutes after mixing hexane solutions of equimolar amounts of compounds **Va** and **IIa** or **Vb** and **IIb**, crystallization of products **VIIa** or **VIIb**, respectively, occurred at room temperature.

The structure of the synthesized compounds was proved by ^{31}P NMR spectroscopy. The ^{31}P NMR spectra of compounds **VIIa** and **VIIb** contain two doublet signals from nonequivalent phosphorus atoms: **VIIa**: $\delta_{P(1)}$ 29.20 ppm ($^2J_{PP}$ 91.25 Hz) (phosphonate P); $\delta_{P(2)}$ 50.13 ppm ($^2J_{PP}$ 91.25 Hz) (ylide P); **VIIb**: $\delta_{P(1)}$ 27.82 ppm ($^2J_{PP}$ 49.4 Hz) (phosphine oxide P), $\delta_{P(2)}$ 50.49 ppm ($^2J_{PP}$ 49.4 Hz) (ylide P).

Ylides **VIIa** and **VIIb** are colorless crystalline substances; when they melted or dissolved in heptane, benzene, toluene, or chlorofom, a red-purple color appeared.

4-Chloromethylene-2,6-di-*tert*-butylcyclohexa-2-dien-1-one was prepared by the procedure in [6], mp 59–61°C. ^{1}H NMR spectra (CCl_4 + $CDCl_3$), δ, ppm: 1.25 s, 1.30 s [18 H, $C(CH_3)_3$], 6.85 s [1H, CHCl], 6.88 d (1H, CH, $^4J_{HH}$ 2 Hz), 7.45 d (1H, CH, $^4J_{HH}$ 2 Hz).

[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(diethoxyphosphinoyl)methylene]triethoxy-λ^5-phosphorane (VIIa). *a*. A mixture of solutions of 1.01 g of compound **I** in 7 ml of hexane and 1.33 g of triethylphosphite in 3 ml of hexane was kept at 20–25°C for 24 h. The product crystallized and was washed with hexane. Yield 1.08 g (51.9%), mp 131–133°C (heptane) (published data [5]: mp 133–135°C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t (6H, $POCH_2CH_3$, $^3J_{HH}$ 7.5 Hz), 1.40 t (9 H, $P^+OCH_2CH_3$, $^3J_{HH}$ 7.5 Hz), 1.55 s [18H, $C(CH_3)_3$], 4.08 q (4H, $POCH_2$, $^3J_{PH}$ = $^3J_{HH}$ 7.5 Hz), 4.32 q (6H, P^+OCH_2, $^3J_{PH}$ = $^3J_{HH}$ 7.5 Hz), 5.08 s (1H, OH), 7.18 s (2H, C_6H_2). Found, %: P 11.80, 11.50. $C_{25}H_{46}O_7P_2$. Calculated, %: P 11.92.

b. After mixing solutions of 1.06 g of **Va** in 3 ml of hexane and 0.5 g of triethylphosphite in 3 ml of hexane abundant product crystallization occurred. After 24 h, the product was filtered off. Yield 1.32 g (84.6%), mp 135–136°C (heptane).

[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(diethoxyphosphinoyl)methylene](ethoxy)diphenyl-λ^5-phosphorane (VIIb). *a*. From a mixture of solutions of 0.51 g of compound **I** in 3 ml of toluene and 0.92 g of ethyl diphenylphosphinite (20–25°C, 24 h). Yield 0.73 g (57.0%), mp 210–212°C (toluene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 s [18H, $C(CH_3)_3$], 1.70 t (3H, CH_3, $^3J_{HH}$ 7 Hz), 4.80 q (2H, CH_2, $^3J_{PH}$ = $^3J_{HH}$ 7 Hz), 4.95 s (1H, OH), 6.92 d (2H, C_6H_2, $^2J_{HH}$ 2 Hz), 7.40–8.10 m (20H, C_6H_5). Found, %: P 9.45, 9.30. $C_{41}H_{46}O_3P_2$. Calculated, %: P 9.57.

b. From a mixture of 0.84 g of compound **Vb** in 10 ml of toluene and 0.46 g of ethyl diphenylphosphinite in 5 ml of toluene. Yield 1.06 g (81.5%), mp 213–214°C (toluene).

The ^{1}H NMR spectra were recorded on a Tesla BS-567A spectrometer (100 MHz, TMS). The ^{31}P NMR spectrum was registered on a CXP-100 instrument (36.5 MHz, 85% H_3PO_4).

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