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

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

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

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center,*
Russian Academy of Sciences, Kazan, Tatarstan, Russia

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Abstract—The main stable products of the reactions 4-chloromethylene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one with triethyl phosphite and ethyl diphenylphosphinite are the phosphorylated phosphorus ylides, 3,3',5,5'-tetra-*tert*-butylstilbenequinone, and biphosphorylated sterically hindered phenols.

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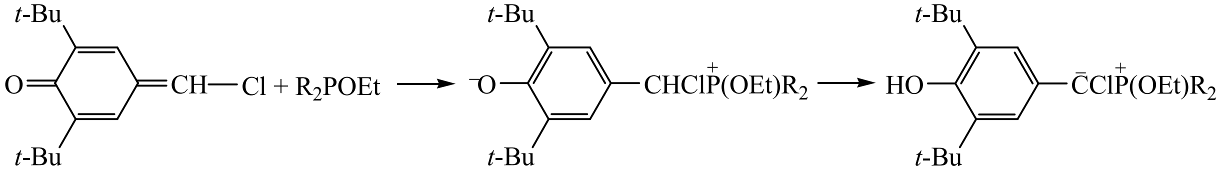
In extension of the research on the chemical behavior of organic halides in the reactions with aprotic reagents [1, 2] we studied the reaction of 4-chloromethylene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (**I**) with the esters of P(III) acids, triethyl phosphite (**IIa**), and ethyl diphenylphosphinite (**IIb**) in various molar ratios. We found that the main stable products in such reaction systems are phosphorylated phosphorus ylide (**VIII**), 3,3',5,5'-tetra-*tert*-butylstilbenequinone (**XII**), and bisphosphorylated sterically hindered phenols (**XIII**). To understand the formation of these compounds we suggest a scheme involving a series of parallel and consecutive reactions.

In the initial stage of the reaction ether **II** is added to the highly electrophilic chloromethylenequinone **I** to form an intermediate of a betaine structure **III** capable of transforming into ylide **IV**.



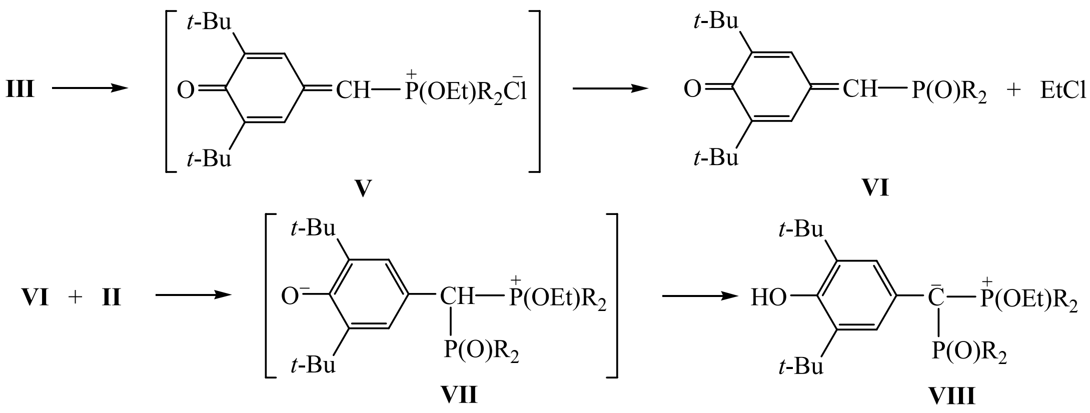
I **II** **III** **IV**

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

Intermediates **III** and **IV** are the key structures for understanding further course of these reactions.

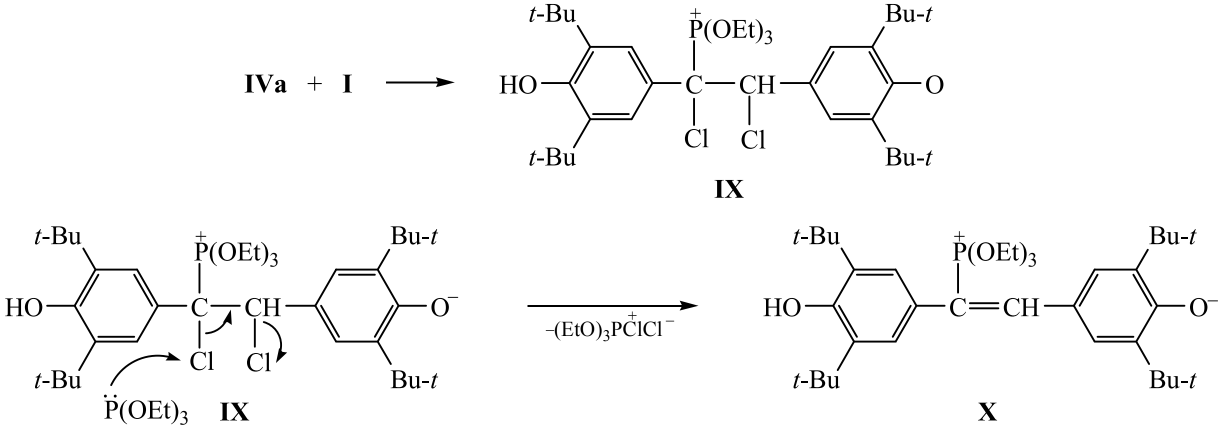
The intermediate of betaine structure (**III**) through intramolecular nucleophilic substitution eliminates the chloride anion and is transformed into quasiphosphonium compound **V** which is stabilized along the scheme of the second stage of Arbuzov reaction affording phosphorylated methylenequinone **VI**. The addition to the latter of ester **II** leads to bisphosphorylated betaine **VII**. The latter is converted into the phosphorylated ylide **VIII** through 1,6 proton shift [3, 4].

In a parallel route ylide **IVa** is added to the second molecule of chloromethylenequinone **I** with the formation of intermediate **IX** containing two chlorine atoms in the vicinal position. The presence of electron-



V **VI** **VII** **VIII**

acceptor quasiphosphonium group promotes the attack of triethyl phosphite **IIa** on the positively polarized chlorine atom which leads to the appearance of intermediate **X**.

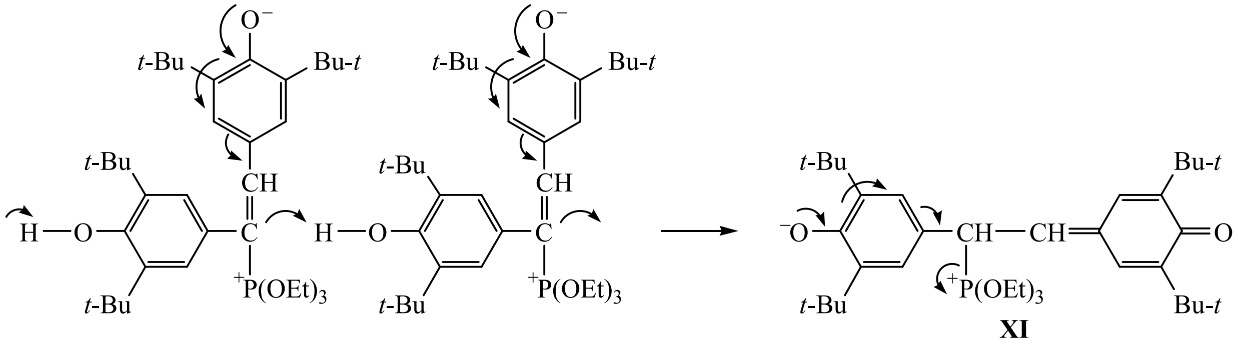


IX **X**

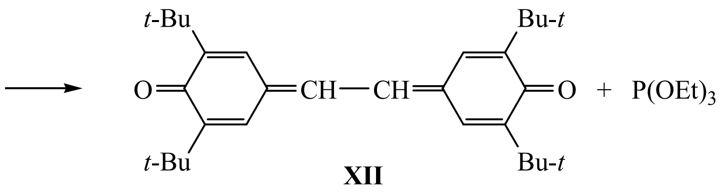
$[(EtO)_3\overset{+}{P}Cl\overset{-}{Cl}] \longrightarrow (EtO)_2P(O)Cl + EtCl$

An argument in favor of the proposed scheme is the presence in the ^{31}P NMR spectrum of the reaction mixture of a singlet resonance signal $\delta_P = -1.37$ ppm corresponding to the phosphorus atom in diethyl chlorophosphate.

As a result of the transfer of the negative charge from the phenolate oxygen, the double bond of the intermediate **X** becomes capable to deprotonate phenolic hydroxy group of similar intermediate **X**. Betaine **XI** is stabilized by the elimination of triethyl phosphite (**IIa**) to form a stable stilbenequinoid system **XII**.

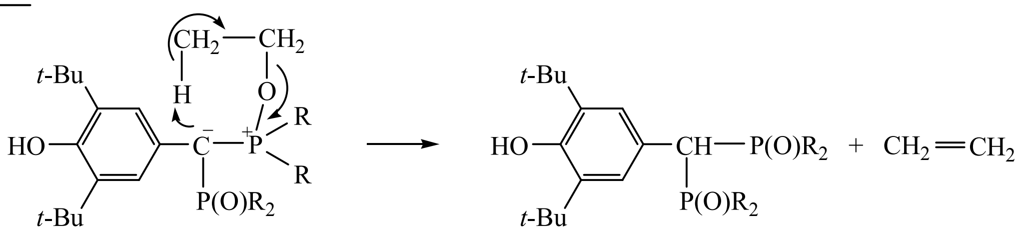


XI



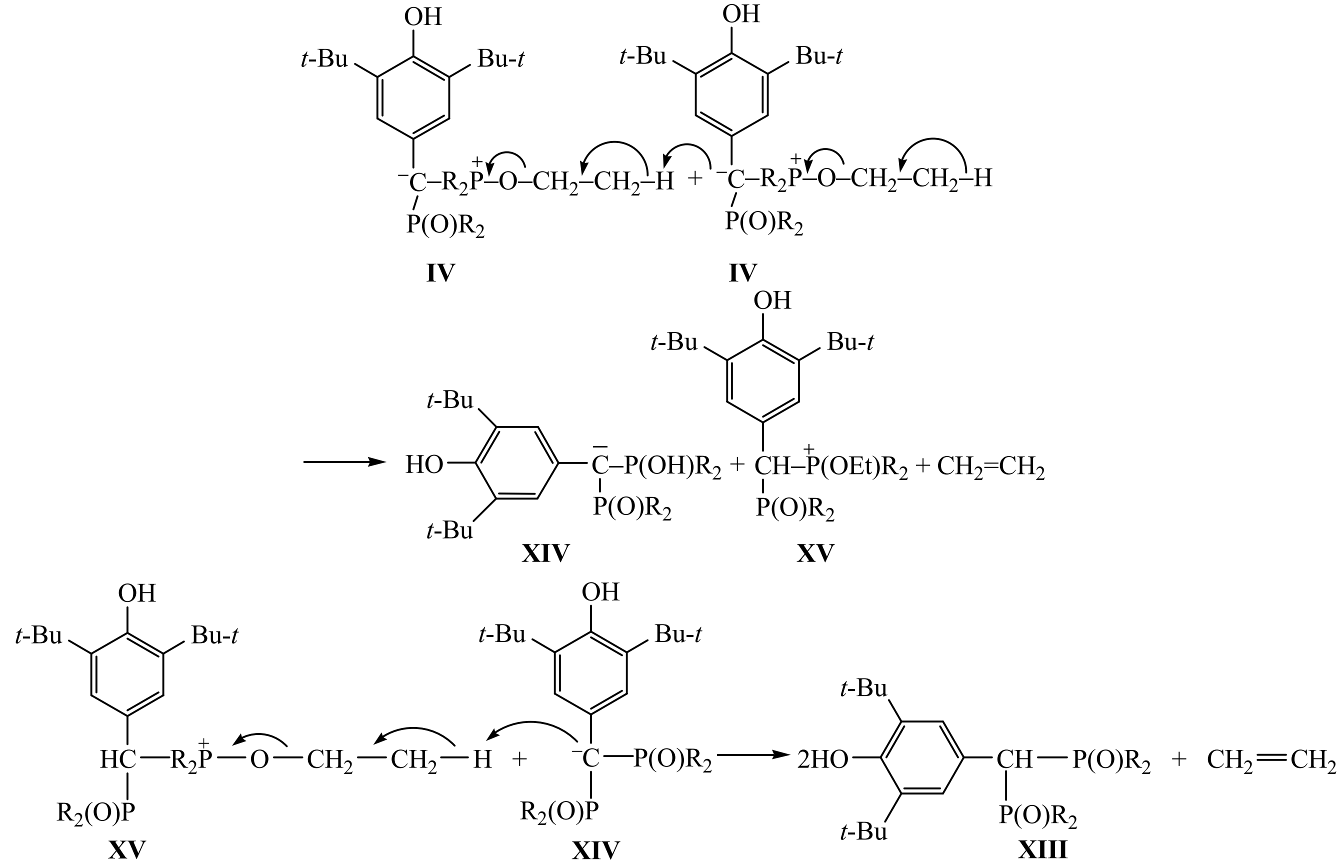
XII

The noted formation of biphosphorylated sterically hindered phenols **XIII** may be caused by intramolecular deprotonation of the ethoxy group in the quasiphosphonium moiety with the simultaneous removal of ethylene and generation of a stable phosphoryl group.



IV **XIII**

An alternative route of transformation **IV** to **VIII** can be suggested as a two-stage intermolecular interacttion. The carbanion center of ylide **IV** deprotonates the ethoxy group of another similar ylide **IV** to form bisphosphorylated carbanion **XIV** and quasiphosphonium intermediate **XV**. The ethoxy group of intermediate **XV** is deprotonated under the influence of the carbanion **XIV**. In both these stages ethylene is released and a stable phosphoryl group is generated.



IV **IV** **XIV** **XV** **XV** **XIV** **XIII**

The results of the study show that at the conservation of the general trend of the reactions occurring along the above routes, the use of an excess of ester **II** with respect to chloromethylenequinone **I** shifts the chemical transformations to the formation of ylides **VIII**.

In the case of the two-fold excess of chloromethylenequinone **I** with respect to ester **IIa**, the main direction, in accordance with the above scheme, is the formation of stilbenequinone **XII**. Using a double excess of chloromethylenequinone **I** to ester **IIb** does not shift the process to the formation of stilbenequinone, and the main reaction product of the reaction becomes bisphosphorylated sterically hindered phenol **XIIIb**, and a significant portion of the original chloromethylenequinone **I** remains unchanged in the reaction medium. This fact suggests that the tendency of betain **IIIb** to the transformation into the quasi-phosphonium compound **Vb** and the subsequent transformation into the phosphorylated methylenequinone **VIb**, ylide **VIIIb,** and bisphosphorylated sterically hindered phenol **XIIIb** is preferred over the transition to the ylide **IVb**. Probably, in this case there is an analogy with the higher activity of phosphinous esters as compared to phosphorous esters in the Arbuzov reaction.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Tesla BS-567A instrument (100 MHz), ^{31}P NMR spectra were recorded on a CXP-100 instrument (operating frequency 36.5 MHz). The chemical shifts of hydrogen nuclei are given relative to TMS, phosphorus, relative to 85% H_3PO_4.

Reaction of 4-chloromethylene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (I) with triethyl phosphite (IIa). *a*. At 1:1 ratio. Adding 0.83 g (0.005 mol) of ester **IIa** to 1.26 g (0.005 mol) of chloromethylenequinone **I** causes warming and formation of a wine-red solution. In a few minutes, a crystalline product begins to precipitate from the reaction mixture. The mixture was kept at room temperature for 6 h, then treated with hexane (2×10 ml). 0.83 g (63%) of **VIIIa** contaminated, according to ^{1}H NMR spectroscopy, with compounds **XII** and **XIIIa**, was isolated, mp 122–125ºC (heptane) (published data [4]: mp 131–133ºC). ^{31}P NMR spectrum: $\delta_{P(1)}$ 29.20 ppm ($^2J_{PP}$ 91.25 Hz) (phosphonate), $\delta_{P(2)}$ 50.13 ppm (^2J 91.25 Hz) (ylide). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.32 t (6H, POCH$_2$C$\underline{H}_3$, $^3J_{HH}$ 7.5 Hz), 1.40 t (9H, P$^+$OCH$_2$C$\underline{H}_3$, $^3J_{HH}$ 7.5 Hz), 1.55 s [18H, C(CH$_3$)$_3$], 8.4 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$_6$H$_2$). Found, %: P 11.72, 11.56. $C_{25}H_{46}O_7P_2$. Calculated, %: P 11.92.

The product **VIIIa** shows the characteristic of ylides the red-purple coloration at melting or dissolving in organic solvents (heptane, benzene, chloroform).

The colored hexane solution after distilling off volatiles in vacuo gave 0.18 g of product **XII**, orange, mp 298–302ºC (toluene) (published data [5]: mp 305–308ºC). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.2 d [36H, C(CH$_3$)$_3$, $^3J_{HH}$ 2 Hz], 6.97 d [1H, CH, $^3J_{HH}$ 2 Hz], 7.22 s (4H, C$_6$H$_2$), 7.47 d (1H, CH, $^3J_{HH}$ 2 Hz).

b. At 1:1 ratio in hexane. A mixture of the solutions of 1.26 g (0.005 mol) of **I** in 15 ml of hexane and 0.83 g (0.005 mole) of ester **IIa** in 5 ml of hexane was kept at room temperature for 48 h, therewith occurred a gradual precipitation of crystalline product. Compound **VIIIa,** 0.84 g (64%), was obtained, mp 125–129ºC (heptane) containing a little bisphosphonate **XIIIa**. After heating the above mixture of solutions of compounds **I** and **IIa** at 50–60ºC for 1 h and removing the solvent in a vacuum 0.51 g (58%) of compound **VIIIa** was isolated, mp 129–135ºC (heptane).

c. At 1:2 a ratio in hexane. A mixture of solutions of 1.01 g (0.004 mol) of **I** in 7 ml of hexane and 1.33 g (0.008 mol) of **IIa** in 3 ml of hexane was kept at 25ºC for 24 h. The resulting crystalline product was washed on the filter with hexane. 8.1 g (51.9%) of compound **VIIIa** was obtained, mp 131–133ºC (heptane).

d. At 1:3 ratio. A mixture of 0.85 g (0.0033 mol) of compound **I** and 1.66 g (0.01 mol) of ester **IIa** was heated at 40ºC for 1 h. The crystals precipitated on cooling were treated with hexane, 1.10 g (62%) of compound (**VIIIa**), mp 121–125ºC (heptane).

e. At 2:1 ratio. A mixture of 2.52 g (0.01 mol) of chloromethylenequinone **I** and 0.83 g (0.005 mol) of ester **IIa** was heated at 60–80ºC for 2h. After 48 h, 0.83 g (38%) of stilbenequinone **XII** was filtered off, mp 287–290ºC (toluene) with an admixture of **VIIIa**, which was removed after several recrystallizations from toluene.

Reaction of 4-chloromethylene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (I) with ethyl diphenylphosphinite (IIb). *a*. At 1:2 ratio in hexane. The addition of 0.63 g (0.0025 mol) of compound **I** to a solution of 1.15 g (0.005 mol) of ester **IIb** in 3 ml of hexane causes warming and deepening of the color. At triturating the reaction mixture the crystals restructured. The reaction mixture was kept at 20–25ºC for 24 h. 0.95 g (59%) of compound **VIIIb** was obtained, mp 212–215ºC (toluene–heptane, 4:1) (published data [4]: mp 210–212ºC). ^{31}P NMR spectrum: $\delta_{P(1)}$ 27.82 ppm ($^2J_{PP}$ 49.40 Hz) (phosphine oxide), $\delta_{P(2)}$ 50.49 ppm ($^2J_{PP}$ 49.4 Hz) (ylide). ^{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), s 4.95 (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.

Evaporation of the mother toluene–heptane solution gave 0.26 g of compound **XIIIb**, mp 258–260ºC (toluene) (published data [1]: mp 262–264ºC). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.25 s [18H, $C(CH_3)_3$], 4.72 m (1H, CH, $^3J_{PH}$ 12 Hz), 5.10 s (1H, OH), 6.95 s (2H, C_6H_2), 7.20–8.30 m (20H, C_6H_5).

b. At 1:2 and 1:3 ratio in toluene. From a mixture of solutions of 0.51 g (0.002 mol) of compound **I** in 3 ml of toluene and 0.92 g of compound **IIb** in 5 ml of toluene (25ºC, 24 h) 0.73 g (57%) of compound **VIIIb** was obtained, mp 210–212ºC (toluene).

Similarly, from a mixture of solutions of 0.39 g (0.0015 mol) of compound **I** in 3 ml of toluene and 1.15 g (0.005 mole) of ester **IIb** in 3 ml of toluene (20–25ºC, 48 h) 0.81 g (78%) of **VIIIb** was obtained, mp 209–211ºC (toluene).

c. At 2:1 ratio in hexane. A mixture of solutions of 1.26 g (0.005 mol) of **I** in 5 ml of hexane and 0.58 g (0.0025 mol) of ether **IIb** in 5 ml of hexane was refluxed for 1 h. The resulting colorless crystalline product was filtered off from the hot solution, and 0.53 g (68%) of compound **XIIIb** was isolated, mp 253–256ºC (toluene–heptane, 10:1). From the hexane reaction solution after cooling 0.21 g of the initial chloromethylenequinone **I** was isolated, mp 56–59ºC (published data [4]: mp 59–61ºC).

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