ДОПОВІДІ
НАЦІОНАЛЬНОЇ
АКАДЕМІЇ НАУК
УКРАЇНИ

ХІМІЯ

doi: https://doi.org/10.15407/dopovidi2018.05.067
UDC 547.241

**A.O. Kolodiazhna, E.V. Grishkun, A.O. Gudyma,
O.O. Kolodiazhna, S.Yu. Sheiko, O. I. Kolodiazhnyi**

Institute of Bioorganic Chemistry and Petrochemistry of the NAS of Ukraine, Kiev
E-mail: olegkol321@gmail.com

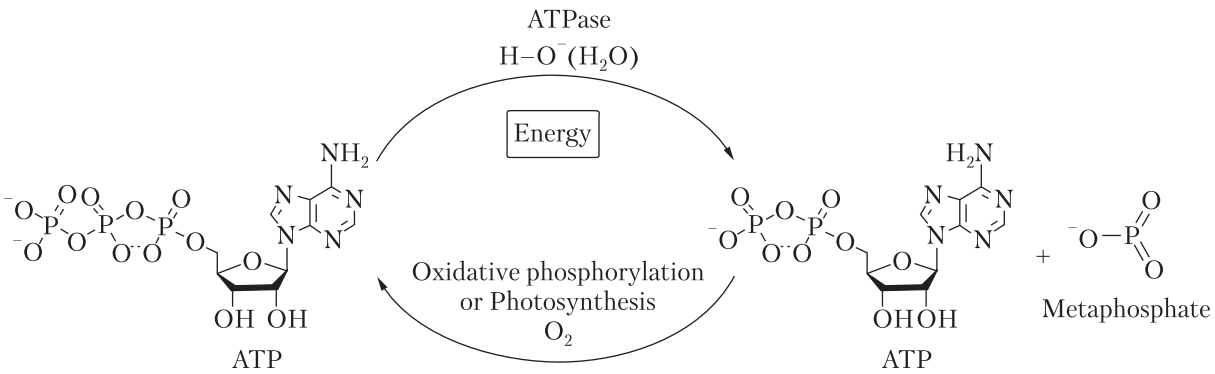
Tert-butyldioxophosphorane as metaphosphate analog

Presented by Corresponding Member of the NAS of Ukraine O.I. Kolodiazhnyi

The flash-vacuum thermolysis (FVT) of trimethylsilyl tert-butylhalogenophosphonates is performed in an attempt to generate tert-butyldioxophosphorane. The FVT proceeds with elimination of halogenotrimethylsilane to give unstable tert-butyldioxophosphorane readily transforming into a trimer. Tert-butylhalogenophoshonic acids form rather stable salts with trimethylamine, which eliminate triethytamine hydrohalohenide on the heating to afford a trimer.

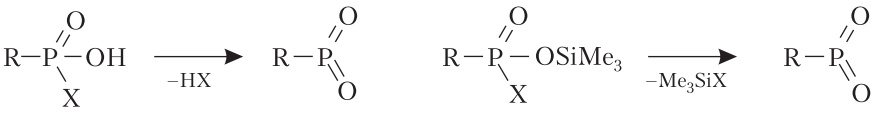
Keywords: *tert-butyldioxophosphorane, trimer of tert-butyldioxophosphorane, flesh-vacuum thermolysis.*

The study of transfer reactions of the phosphoryl group is important for biological and molecular chemistries [1, 2]. For example, it was reported recently that the hydrolysis of ATP takes place in ATPase enzymes through an intermediate, in which ATP phosphate is connected to the protein as metaphosphate (PO_3^-). We have also reported that the reactions of phosphorylation—dephosphorylation of natural phosphates, for example, adenosine triphosphate, which is the most important energy-generating molecule that provides the vital activity of living organisms, proceed by the monomolecular mechanism with the formation of a metaphosphate anion [1—4].



The molecules containing the fragment P (= O)$_2$ are highly reactive and extremely unstable. The only two observable, although unstable, inorganic molecules with the dioxophosphorane structure were detected by physicochemical methods, and only under extreme conditions. The metaphosphate anion (O =)$_2$PO$^-$ and chloro derivative ClP(= O)$_2$ were generated in the gas phase, preserved in an argon matrix, and detected by physicochemical methods. The IR spectrum of ClPO$_2$ had a peak for the P—O stretching at 1443 cm^{-1}. The photoelectron spectrum was recorded at 450 ^{0}K.

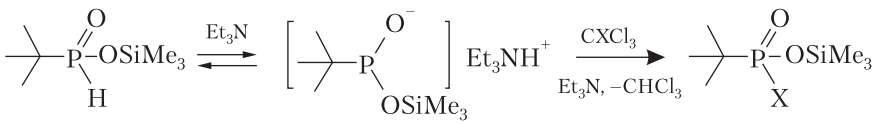
Organic dioxaphosphoranes up to now were not registered. Therefore, it seems interesting to carry out a research in this direction. Various precursors and methods for generating dioxophosphoranes were proposed [4—6]. In our opinion, chloro- and bromophosphonic acids **(1)**, as well as trimethylsilyl esters of these acids (3), are prospective precursors of highly reactive dioxophosphoranes **(2)**. It should be noted that the compounds of type (1), X = Br, Cl, are poorly explored, though derivatives of fluorophosphonic acids were described [7]



1a, b **2** **3a, b** **2**

X = Cl (a), Br (b); R = t-Bu

Results and discussion. The most convenient method for the preparation of the initial chloro- and bromophosphonic acids is the hydrolysis of trimethylsilyl tert-butylhalogenophosphonate **4**. In a previous publication, we have briefly described trimethylsilyl tert-butylchlorophosphonates, which are the first stable representative of trimethylsilyl esters of chlorophosphonic acids [8]. Now, we have also synthesized stable trimethylsilyl tertbutyl-bromophosphonate. Trimethylsilyl tert-butyl-halogenophosphonates may be easily obtained by the treatment of trimethylsilyl tert-butylphosphinic acids with carbon tetrachloride. The reaction proceeded slowly at reflux and only in the presence of triethylamine, which displaces the tautomeric equilibrium of phosphinic acid to the side of the tricoordinated form. With more active bromotrichloromethane and carbon tetrabromide, the reaction of trimethylsilyl tert-butylphosphinate **4** readily proceeded in the absence of triethylamine with the formation of the trimethylsilyl tert-butylbromophosphonate **3a, b** in a very good yield



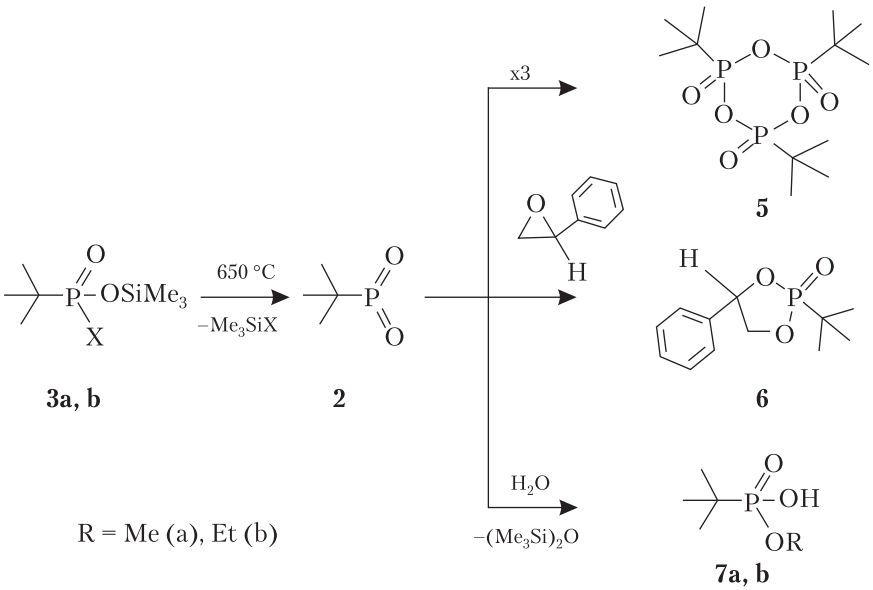
4 **3a, b**

X = Cl (a), Br (b)

Halogenophosphonic acids **(3a, b)** are stable colorless liquids at room temperature. These compounds are distilled without decomposition at a reduced pressure and can be preserved for a long time below 0 °C, when carefully protected from the moisture of air. Upon the heating above

120 °C, halogenophosphonates **(3a, b)** eliminate chloro- or bromotrimethylsilane to form a mixture of compounds containing a dimer (δ_P +30 ppm) and a trimer (δ_P +24 ppm) of tert-butyldioxophosphorane. Trimer **(5)** was isolated by the distillation in vacuum and purified by the crystallization in a moderate yield. The trimer of tert-butyldioxophosphorane **(5)** was isolated in the form of a stable colorless crystalline compound reactive to moisture. The structure of trimer **(5)** was shown by spectroscopic methods, elemental analysis, determination of molecular mass, and mass-spectrum. The NMR ^{31}P spectrum of **(5)** shows a single signal δ_P 24.5 ppm. The NMR ^1H spectrum contains a double doublet of signals corresponding to tert-butyl groups in a different position of the six-membered ring. The flash-vacuum thermolysis (FVT) is the most effective for the generation of dioxophosphorane **(2)** from halogenophosphonates **(3)**. The FVT (650°, δ_P = 0.01 mm Hg) of trimethylsilyl tert-butylchlorophosphonates proceeds with the elimination of chlorotrimethylsilane to give an unstable product, which was collected in a trap cooled with liquid nitrogen.

In all attempts made so far to generate an organic dioxophosphorane, only intermolecular condensation products of the monomer have been observed. Cases are known, however, in which the powerfully electrophilic dioxophosphorane (and oxothiophosphorane) group is trapped on the generation in a solution (usually at low temperatures) by the formation of a Lewis salt with aprotic amines or ethers. These Lewis salts function as donors of dioxophosphorane in other reactions [2].



The chemical properties of tert-butyldioxaphosphorane confirm the structure of this compound:

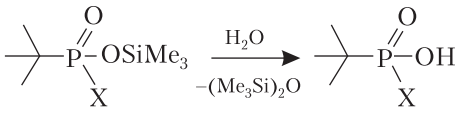
1) At room temperature, it converts into a trimer of tert-butyldioxophosphorane **(5)**, which was isolated, and its structure is confirmed by means of spectroscopy and elemental analysis.

2) It reacts with styrene oxide by the [2 + 3]-cycloaddition to give a five-membered phosphorus heterocycle, 2-tert-butyl-2-phenyl-1,3,2-dioxophospholane **(6)**. Compounds **(6)**

were obtained as a mixture of two diastereomers in 1 : 2 ratio and purified by the distillation at a reduced pressure.

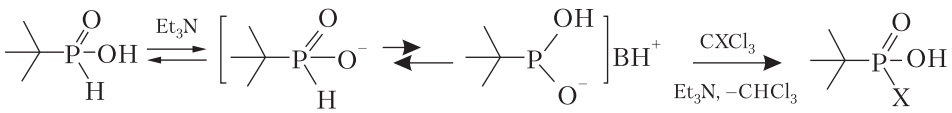
3) With an alcohol as a trapping reagent, the product forms esters of tert-butylphosphonic acid **(7)**.

Trimethylsilyl tert-butylhalogenophosphonates **(3)** can be easily desilylated upon the treatment with water in a dioxane-diethyl ether solution at room temperature to provide the hitherto unknown tert-butylhalogenophosphonic acids **(1)**. Under more vigorous conditions, in particular at the reflux during 4 hours, trimethylsilyl esters **(3a, b)** are converted into tert-butylphosphonic acids (**1**, R = H).



3a, b **4a, b**

Tert-butylchlorophosphonic acid **(1a)** was obtained also by the reaction of tert-butylphosphinic acid with chlorine. The reaction proceeded slowly in a carbon tetrachloride solution and is accelerated by UV irradiation. However, the yield and purity of **(1a)** were lower than in the case of the hydrolysis of trimethylsilyl tert-butylchlorophosphonate **(3)**. Tert-butylphosphinic acid **(4)** smoothly reacts with bromotrichloromethane to afford tert-butylbromophosphonic acid **(1b)** in a very good yield. This is the first example of the direct chlorination of phosphinic acid by carbon tetrahalogenide. Probably, in a diethyl ether solution, tert-butylphosphinic acid **(4)** is weakly ionized **(A)** to increase the concentration of the tricoordinate tautomer form **(B)**, which undergoes the halogenophilic attack of very active bromotrichloromethane



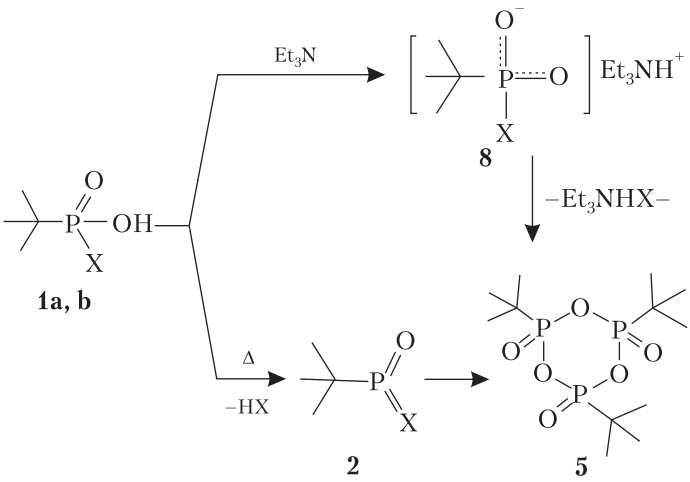
4 **A** **B** **1a, b**

B = Et_3N

Tert-butylhalogenophosphonic acids **(1)** are rather stable at room temperature and can be preserved for a long time below 0 °C. These compounds are distilled without decomposition at a reduced pressure. Tert-butylchloro- and bromo phosphonic acids **(1)** can be purified by the crystallization from hexane. Under more vigorous conditions, tert-butylhalogenophosphonic acids **(1)** eliminate hydrogen halogenide to convert into the trimer of tert-butyldioxophosphorane **(5)**. The structure of tert-butylhalogenophosphonic acids **(1)** was confirmed by spectroscopic data. In ^1H NMR spectra, acids **(1)** exhibit a doublet of signals at 1.3 ppm with coupling constant ~20 Hz and a broad singlet at 13 ppm due to the proton on the OH group. The chemical shifts δ_P are foundat ~ 50 ppm.

Tert-butylhalogenophosphonic acids **(1)** with triethylamine give a triethylammonium salts **(8)**, which are remarkably stable. Salts **(8)** exist for some time at room temperature. Upon the heating, they eliminate triethylamine hydrohalogenide converting into the trimer of tert-butyldi-

oxophosphorane. The unprecedented stability of compounds **(1, 8)** can be explained by the thermodynamic instability of tert-butyldioxaphosphorane **(2)**, which would be formed from these compounds.



Conclusions. Trimethylsilylic esters of chloro- and bromophosphonic acids are accessible through the reaction of trimethylsilylic esters of phosphonic acids. These compounds are interesting as precursors of stable free chloro- and bromophosphonic acids. Tert-butylbromophosphonic acid can be easily obtained by the reaction of tertbutylphosphinic acid with bromotrichloromethane. The thermolysis of trimethylsilyl esters of chloro- and bromophosphonic acids, as well as the dehydrohalogenation of free halogenophosphonic acids, is efficient to generate tert-butyldioxophosphorane.

Experimental Part. The NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 (^{1}H) and 126.16 MHz (^{31}P). All chemical shifts are expressed in δ (ppm). ^{1}H chemical shifts are expressed relative to Me_4Si as internal standard. ^{31}P NMR spectra are referenced to external 85 % H_3PO_4. All manipulations were carried out under inert atmosphere (N_2 or Ar), solvents were distilled under inert atmosphere from the following drying agents: diethyl ether, hexane, benzene, toluene (P_2O_5), and methanol (sodium). Tert-butylphosphonic acid 1 was obtained as described previously [8].

Tert-butylchlorophosphonic acid **(1a)**. A solution of 4.57 g (0.02 mol) of trimethylsilylic ester of tert butylchlorophosphonic acid **(3a)** in 10 ml of diethyl ether was cooled to −50 °C. To the stirred solution, a solution of 0.2 g (0.011 mol) of water in 2 ml dioxane was added dropwise. Then the mixture was allowed to stand for 1 hour at room temperature. The solution was evaporated, and the residue was crystallized from hexane. Tert-butylchlorophosphonic acid 1a is distilled without decomposition at a reduced pressure. Yield 2.44 (78 %), bp 130 °C (0.03 mm Hg). mp 47—49 °C.

Colorless solid. NMR spectra (δ, ppm; *J*, Hz, $CDCl_3$): δ_H: 1.23 d ($^3J_{HP}$ 22.0, t-Bu); 12.83, s (OH). δ_P 54.7.

Calcd. for the $C_4H_{10}ClO_2P$: Cl 22.65; P 19.79. Found Cl 22.44; P 19.61.

Tert-butylbromophosphonic acid **(1b).** a) To a stirred solution of 5.46 g (0.02 mol) of trimethylsilylic ester of tert-butylbromophosphonic acid **(3b)** in 10 ml of diethyl ether, a solution

of 0.198 g (0.011 mol) of water in 2 ml of dioxane at –50 °C was added dropwise. Then the mixture was stirred for 1 hour at room temperature. The solution was evaporated, and the residue was purified by the crystallization from hexane. Yield 3.0 g (75 %), mp 50 °C. Colorless crystalline solid.

b) A mixture of 2.44 g (0.02 mol) of tert-butylphosphinic acid (**4**) and 4.3 g (0.022 mol) of bromotri chloromethane in 10 ml of diethyl ether was allowed to stand for 1 day at room temperature. After the evaporation of volatile products at a reduced pressure, the residue was crystallized from hexane.

Yield 3.0 g (75 %), mp 50 °C. Colorless crystalline solid. NMR spectra (δ, ppm; *J*, Hz, $CDCl_3$): δ_H: 1.28 d ('J_{HP} 22.0, t-Bu); 13.24, s (OH). δ_P 55.55.

Calcd. for $C_4H_{10}BrO_2P$: C, 23.90; H, 5.01; Br 39.75; P 15.41. Found: Br 39.48; P 15.51.

***Trimethylsilyc ester of tert-butylchlorophosphonic acid* (3a).** A solution of 3.9 g (0.02 mol) of trimethylsilylic ester (**4**) in 10 ml of diethyl ether was cooled with an ice bath to about 0 °C. To the stirred solution, a mixture of 6.1 g (0.04 mol) of carbon tetrachloride and 0.2 ml of triethylamine was added dropwise. The reaction mixture was stirred 2 hours at reflux temperature, then the solution was evaporated and the residue was distilled at a reduced pressure. Yield 3.9 g (85 %), bp 52—55 °C (0.035 mm Hg).

Colorless mobile liquid. NMR spectra (δ, ppm;*J*, Hz, $CDCl_3$): δ_H: 0.26 s (Me_3Si); 1.16 d ($^3J_{HP}$ 20.8, t-Bu). δ_C 0.9 s (Me_3Si); 24.9 d, *J* 16 (CH_3); 37.1 d *J* 68 (PC); δ_P 45.3.

Calcd. for $C_7H_{18}ClO_2PSi$: C 36.55 %; H 7.98 %; Found: C 36.76 %; H 7.93 %;

***Trimethylsilylic ester of tert-butylbromophosphonic acid* (3b)**. To a solution of 3.9 g (0.02 mol) of trimethylsilylic ester of tert-butylphosphinic acid (**4**) in 10 ml of diethyl ether, 4.3 g (0.022 mol) of bromotrichloromethane at 0 °C were added with stirring. Then the mixture was stirred for 4 hours at room temperature. The solution was evaporated, and the residue was distilled at a reduced pressure. Yield 4.4 g (80 %), bp 55 °C (0.06 mm Hg).

Colorless mobile liquid. NMR spectra (δ, ppm; *J*, Hz, $CDCl_3$): δ_P: 0.33 s (Me,Si); 1.20 d ($^3J_{HP}$ 21.8, t-Bu). δ_P 41.55.

Calcd. for the $C_7H_{18}BrO_2PSi$: Br 29.23; P 11.34. Found Br: 29.03; P 11.39.

***Trimethylsilylic ester of tert-butylphosphinic acid* (4).** To a stirred solution of 12.2 g (0.1 mol) of tertbutylphosphinic acid in 150 ml of hexane, 10.9 g (0.1 mol) of chlorotrimethylsilane and than 12.1 g (0.12 mol) of triethylamine at 0 °C were added dropwise. The mixture was stirred for 1 hour at room temperature and then was refluxed for 1 hour. The precipitate of triethylamine hydrochloride was filtered off and washed with 2 x 20 ml of hexane. The filtrate was evaporated and the residue was distilled under reduced pressure. Yield 16.6 g (85 %), bp 100—103 °C (20 mm Hg).

NMR spectra (δ, ppm; *J*, Hz, $CDCl_3$): δ_H 0.26 s (Me_3Si); 1.033, d ($^3J_{HP}$ 18, t-Bu); 6.65 d ($^1J_{HP}$ 520, P-H). δ_C 0.35, d *J* 8 (CH_3Si); 27.3 d, *J* 16 (CH_3); 31.9, d *J* 68 (PC). δ_P 37.61, d $^1J_{HP}$ 526.

Calcd. for $C_7H_{19}O_2PSi$: C, 43.27; H, 9.86; P 15.94. Found C, 43.27; H, 9.86; P: 16.10.

***2,4,6-Tri-tert-butyl-1,3,5,2,4,6-trioxotriphosphorinane* (5).** a) 4.57 g (0.02 mol) of trimethylsilylic ester of tert-butylchlorophosphonic acid (**3a**) were heated at 160 °C for 4 hours. Then the reaction mixture was distilled under reduced pressure, bp 160—180 °C (0.04 mm Hg) and the product was crystallized from toluene. Colorless needles. Yield 0.73 g (30 %), mp 150—152 °C. After the second crystallization, mp 160—162 °C was obtained.

b) 5.46 g (0.02 mol) of trimethylsilylic ester of tert-butylbromophosphonic acid **(3a)** were exposed to the flash-vacuum thermolysis at 650 °C and pressure 0.01 mm Hg to collect the thermolysate in a trap cooled by liquid nitrogen. After the heating of the thermolysate to room temperature, chlorotrimethylsilane was evaporated, and the residue was crystallized from toluene.

Yield 1.46 (50 %), mp 160—162 °C. MS; m/e: 360. NMR spectra (δ, ppm; *J*, Hz, $CDC1_3$): δ_H 1.34 d ($^1J_{HP}$ 13.8, t-Bu); 1.36 d ($^1J_{HP}$ 13.8, t-Bu). δ_P 24.12.

Calcd. for $C_{12}H_{27}O_6P_3$: C 39.99; H 7.56; P 25.80. M 360.27. Found: C 39.87; H 7.55; P 25.65. M 366.0 (cryoscopy in benzene).

2-(tert-butyl)-4-phenyl-1,3,2-dioxaphospholane 2-*oxide* **(6).** a) The mixture of 0.85 g (0.0037 mol) of (4a) and 0.45 g (0.0037 mol) of styrene oxide in 1ml of xylene was heated for 2 hours at 150 °C. After the evaporation of volatile products at a reduced pressure the residue was distilled in vacuum. Yield 0.58 g (65 %). Bp 120 °C (0.06 mmHg).

b) 3.0 g (0.025 mol) of styrene oxide in 1ml of xylene were added to the thermolysate of **(3a)** prepared as described in the previous experiment from 5.46 g (0.02 mol) of trimethylsilylic ester of tert-butyl bromophosphonic acid **(3b)**. The mixture was first heated to room temperature, then to 150 °C, and, after that, distilled in vacuum. Bp 120 °C (0.06 mm Hg). Colorless viscous liquid.

NMR spectra (δ, ppm; *J*, Hz, $CDCl_3$): δ_H 1.32 d ($^1J_{HH}$ 16, CH_3C); 1.34 d ($^3J_{HH}$ 16, CH,C′); 4.0 m (CH_2O + CH'_2O); 4.6 m (PhC<u>H</u> + PhCH′); 7.4 m (C_6H_5 + C_6H_5'). δ_P 57.6 and 56.5 (mixture of diastereomers).

Calcd. for the $C_{12}H_{16}O_3P$: C 60.25; H 6.74; P 12.95. Found C 60.45; H 6.84; P 12.61.

Ethyl tert-butylphosphonate **(7b)**. A solution of 2.3 g (0.05 mol) of ethanol in 5 ml of diethyl ether was added to the thermolysate prepared from 5.46 g (0.02 mol) of trimethylsilylic ester of tert-butyl bromophosphonic acid **(3b)** as described in the previous experiment. After the heating of the mixture to room temperature, the volatile products were evaporated, and the residue was distilled in vacuum.

Yield 1.7 g (50 %), bp 105—108 °C (0.1 mm Hg). Colorless liquid. NMR spectra (δ, ppm; *J*, Hz, $CDC1_3$): δ_H 1.09 d (J_{HH} 16, CH_3C); 1.24 t (J_{HH} 7.2, CH_3CH_2); 4.02 dq (J_{HH} 7.2, CH_2O); 8.0, s (H-Ar); 12.5 s (OH). δ_P 39.89.

Calcd. for the $C_6H_{15}O_3P$: C 43.37; H 9.10. Found C 43.50; H 9.12.

Methyl tert-butylphosphonate **(7a).** Similarly, a reaction of the thermolysate with methanol gave a liquid purified by the vacuum-distillation. Yield 50 %, bp 70 °C (0.02 mm Hg). Colorless liquid.

NMR spectra (δ, ppm; $CDCl_3$): δ_P 39.00.

Triethylammonium salt of tert-butylchlorophosphonic acid **(8)**. A solution of 1.1 g (0.011 mol) of triethylamine in 5 ml of diethyl ether was added dropwise to a stirred solution of 1.56 g (0.01 mol) of tert-butylchlorophosphonic acid **(3a)** in 10 ml of diethyl ether at 0 °C. Then the mixture was stirred 15 min at room temperature, and the solution was evaporated at a reduced pressure to give colorless oil.

Yield 2.5 g (98 %). NMR spectra (δ, ppm; *J*, Hz, $CDCl_3$): δ_H: 1.17 d ($^3J_{HP}$ 18.4, t-Bu); 1.31 t (J_{HH} 7.2, CH,); 3.09 d.q (J_{HH} 7.2, J_{HH} 4.5, CH_2N); 11.57, s (NH). δ_P 50.46.

Calcd. for $C_{10}H_{25}CINO_2P$: CI 13.6; N 5.45. Found: Cl 13.44; N 5.20.

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Received 27.01.2018

А.О. Колодяжна, Е.В. Гришкун, А.О. Гудима,
О.О. Колодяжна, С.Ю. Шейко О.І. Колодяжний

Інститут біоорганічної хімії та нафтохімії НАН України, Київ
E-mail: olegkol321@gmail.com

ТРЕТ-БУТИЛДІОКСОФОСФОРАН ЯК АНАЛОГ МЕТАФОСФАТІВ

У результаті флеш-вакуумного термолізу (ФВТ) триметилсиліл-трет-бутилгалогенфосфонатів утворюється трет-бутилдіоксофосфоран. ФВТ відбувається з відщепленням галогентриметилсилану і утворенням нестабільного трет-бутилдіоксифосфорану, який легко перетворюється в тример. Трет-бутилгалогенофосфонові кислоти з триетиламіном дають стійкі солі триетиламіну, які при нагріванні відщеплюють триетиламін галогенгідрат, перетворюючись у діоксофосфорани, які легко тримеризуються вже під час утворення.

Ключові слова: *трет-бутилдіоксофосфоран, тример трет-бутилдіоксофосфорану, флеш-вакуум термоліз.*

А.О. Колодяжна, Е.В. Гришкун, А.О. Гудыма,
О.О. Колодяжна, С.Ю. Шейко, О.И. Колодяжный

Институт биоорганической химии и нефтехимии НАН Украины, Киев
E-mail: olegkol321@gmail.com

ТРЕТ-БУТИЛДИОКСИФОСФОРАН КАК АНАЛОГ МЕТАФОСФАТОВ

В результате флеш-вакуумного термолиза (ФВТ) триметилсилил-трет-бутилгалогенфосфонатов образуется трет-бутилдиоксофосфоран. ФВТ проходит с отщеплением галогентриметилсилана и образованием нестабильного трет-бутилдиоксифосфорана, легко превращающегося в тример. Трет-бутилгалогенофосфоновые кислоты с триэтиламином дают устойчивые соли триэтиламина, которые при нагревании отщепляют триэтиламин галогенгидрат, превращаясь в диоксафосфораны, легко тримеризующиеся уже в момент образования.

Ключевые слова: *трет-бутилдиоксофосфоран, тример трет-бутилдиоксофосфорана, флеш-вакуум термолиз.*