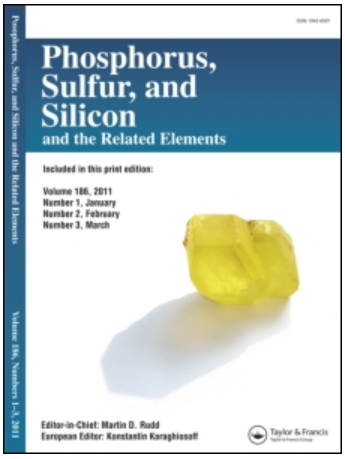

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TERT-BUTYLCHLORO- AND BROMOPHOSPHONIC ACIDS AS SOURCES OF DIOXOPHOSPHORANES

Oleg I. Kolodiazhnyi[a]; Evgen V. Grishkun[a]
[a] Institute of Bioorganic Chemistry, National Academy of Sciences of Ukraine, Kiev-94, Ukraine

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TERT-BUTYLCHLORO- AND BROMOPHOSPHONIC ACIDS AS SOURCES OF DIOXOPHOSPHORANES

OLEG I. KOLODIAZHNYI and EVGEN V. GRISHKUN
Institute of Bioorganic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya Str. 1, Kiev-94, 253094, Ukraine

Dedicated to Professor Reinhard Schmutzler's 60th birthday

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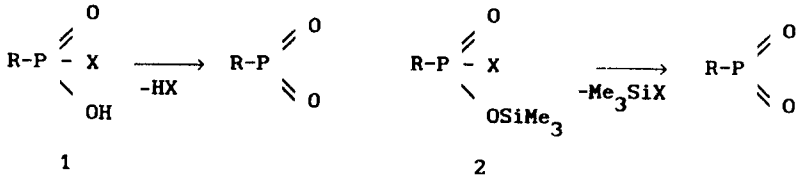
Methods for the synthesis of free halogenophosphonic acids are developed. The first stable chloro- and bromophosphonic acids (**4**) are synthesized. Flash-vacuum thermolysis (FVT) of trimethylsilyl *tert*-butylhalogenophosphonates was performed in an attempt to generate *tert*-butyldioxophosphorane (**5**). The FVT proceeds with elimination of halogenotrimethylsilane to give unstable *tert*-butyldioxophosphorane, readily transforming into trimer (**7**). *Tert*-butylhalogenophoshonic acids (**9**) form with triethylamine rather stable salts, which on heating eliminate triethylamine hydrohalohenide to afford trimer (**7**).

Key words: Trimethylsilyl *tert*-butylchlorophosphonate, trimethylsilyl *tert*-butylbromophosphonates, *tert*-butylchlorophosphonic acid, *tert*-butylbromophosphonic acid, triethylammonium salt of *tert*-butylchlorophosphonic acid, *tert*-butyldioxophosphorane, trimer of *tert*-butyldioxophosphorane, flesh-vacuum thermolysis.

INTRODUCTION

Highly reactive phosphorus compounds, such as dioxophosphoranes and metaphosphates, have attracted considerable interest in the last few years.[1–4] 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 (**2**) are prospective precursors of highly reactive dioxophosphoranes. The compounds of the type (**1**), X = Br, Cl, are little-known,[7a] though some derivatives of fluorophosphonic acids have been described.[7b]

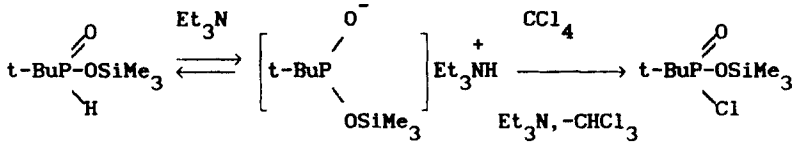


In the present paper we describe our study of the synthesis and properties of free chloro- and bromophosphonic acids and their trimethylsilyl esters.

RESULTS AND DISCUSSION

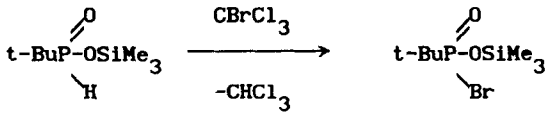
The most convenient method for the preparation of the chloro- and bromophosphonic acids is the hydrolysis of trimethylsilyl *tert*-butyl-halogenophosphonate. In

a previous publication we have briefly described tri-methylsilyl *tert*-butylchlorophosphonates which is the first stable representative of trimethylsilyl esters of chlorophosphonic acids.[8] Now we have also synthesized stable trimethylsilyl *tert*-butyl-bromophosphonate. Trimethylsilyl *tert*-butyl-halogenophosphonates may be easily obtained by treatment of trimethylsilyl *tert*-butylphosphinic acids with the carbon tetrachloride. The reaction proceeds slowly at reflux and only in the presence of the triethylamine, which displaces the tautomeric equilibrium of phosphinic acid to the side of the tricoordinated form.



3 4a

With more active bromotrichloromethane and carbon tetrabromide the reaction of the trimethylsilyl *tert*-butylphosphinate readily proceeds in the absence of triethylamine to give the trimethylsilyl *tert*-butyl-bromophosphonate in very good yield (**3**).



3 4 b

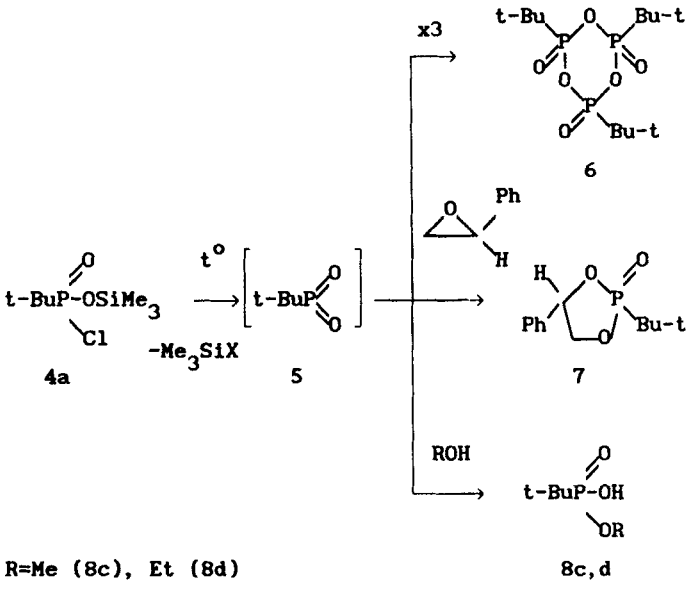
Halogenophosphonic acids (**4a**, **b**) are stable, colorless liquids at room temperature. These compounds are distilled without decomposition under reduced pressure and can be preserved for a long time below 0°C, when carefully protected from air. Upon heating above 120°C the halogenophosphonates (**4a**, **b**) eliminate chloro- or bromotrimethylsilane to form a mixture of compounds, containing dimer (δ_P +30 ppm)[8] and trimer (δ_P +24 ppm) of *tert*-butyldioxophosphorane. The trimer (**6**) was isolated by distillation in vacuum and purified by crystallization in moderate yield. The trimer of *tert*-butyldioxophosphorane (**6**) was isolated in the form of a stable colorless, crystalline compound reactive to moisture. The structure of the trimer (**6**) was shown by spectroscopic methods, elemental analysis and determination of molecular mass. The NMR ^{31}P spectrum of (**6**) 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.

Flash-vacuum thermolysis (FVT) is more effective for the generation of the dioxophosphorane (**5**) from halogenophosphonates (**4**). The FVT (600°, p = 0.01 mm Hg) of trimethylsilyl *tert*-butylchlorophosphonates proceeds with elimination of chlorotrimethylsilane to give an unstable product which was collected in a trap cooled with liquid nitrogen. The chemical reactions of this product correspond to the *tert*-butyldioxophosphorane:

1) At room temperature it converts into the trimer of *tert*-butyldioxophosphorane (**6**), which was isolated and its structure confirmed by means of spectroscopy and elemental analysis.

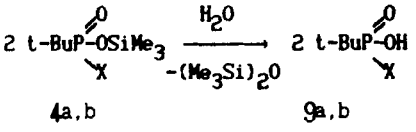
2) It reacts with styrene oxide by a [2+3]-cycloaddition to give according to Quin[5] a five-membered phosphorus heterocycle, 2-*tert*-butyl-2-phenyl-1,3,2-dioxophospholane (**7**). The compounds (**7**) was obtained as a mixture of two diastereomers in 1:2 ratio and purified by distillation under reduced pressure.

3) With an alcohol as a trapping reagent the product forms esters of *tert*-butylphosphonic acid (**8**).



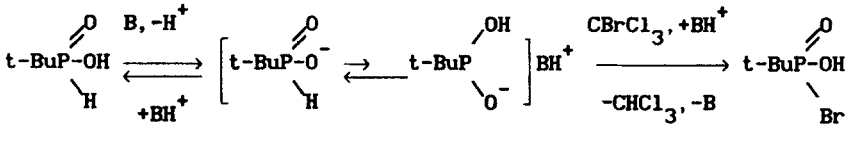
In the future we hope to perform studies of the product of thermolysis by low temperature spectroscopic methods. As is known, dioxophosphoranes are unstable and there is no report in the literature on the direct observation of such species.[3]

Trimethylsilyl *tert*-butylhalogenophosphonates (**1**) easily desilylate upon the treatment with water in dioxane-diethyl ether solution at room temperature to provide the hitherto unknown *tert*-butylhalogenophosphonic acids (**9**). Under more vigorous conditions, in particular at reflux during 4 hours, the trimethylsilyl esters (**4a**, **b**) are converted into *tert*-butylphosphonic acids (**8**, R = H).



Tert-butylchlorophosphonic acid (**9a**) was obtained also by reaction of *tert*-butylphosphinic acid with chlorine. The reaction proceeds slowly in carbon tetrachloride solution and is accelerated by UV irradiation. However the yield and purity of (**9a**) are lower than in the case of hydrolysis of trimethylsilyl *tert*-butylchlorophosphonate (**1**).

The *tert*-butylphosphinic acid (**3**) smoothly reacts with bromotrichloromethane to afford *tert*-butylbromophosphonic acid (**9b**) in very good yield. This is the first example of the direct chlorination of a phosphinic acid by carbon tetrahalogenide.

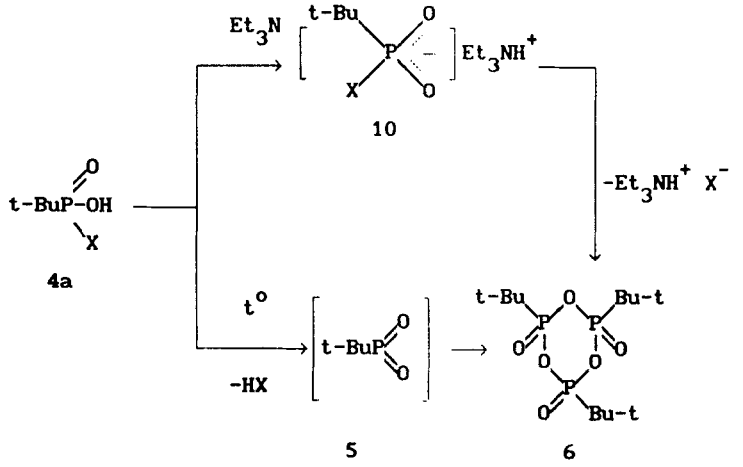


B= Et_2O:

Probably, in diethyl ether solution, the *tert*-butylphosphinic acid (**3**) is weakly ionized (**3**) ⇄ (**A**) to increase the concentration of the tricoordinate tautomer form (**B**), which undergoes halogenophilic attack of very active bromotrichloromethane.

The *tert*-butylhalogenophosphonic acids (**9**) are rather stable at room temperature and can be preserved for a long time below 0°C. These compounds are distilled without decomposition under reduced pressure. *Tert*-butylchloro- and bromophosphonic acids (**9**) can be purified by crystallization from hexane. Under more vigorous conditions the *tert*-butylhalogenophosphonic acids (**9**) eliminate hydrogen halogenide to convert into trimer of *tert*-butyldioxophosphorane (**6**). The structure of the *tert*-butylhalogenophosphonic acids (**9**) was confirmed by spectroscopic data. In ^1H NMR spectra the acids (**9**) exhibit a doublet of signals at 1.3 ppm with coupling constant $^1J_{HP} \sim 20$ Hz and a broad singlet at 13 ppm due to the proton on OH group. The chemical shifts δ_P are found at ~50 ppm.

The *tert*-butylhalogenophosphonic acids (**9**) with the triethylamine form triethylammonium salts (**10**), which are remarkably stable. Salts (**10**) exist for some time at room temperature. Upon heating they eliminate triethylamine hydrohalogenide to convert into the trimer of *tert*-butyldioxophosphorane. Unprecedented stability of the compounds (**9**, **10**) can be explained by the thermodynamic instability of *tert*-butyl-dioxaphosphorane (**5**), which would form from these compounds.



CONCLUSIONS

Trimethylsilylic esters of chloro- and bromophosphonic acids are accessible through a reaction of trimethylsilylic esters of phosphonic acids. These compounds are

interesting as precursors of stable free chloro- and bromophosphonic acids. The *tert*-butylbromophosphonic acid can be easily obtained by reaction of the *tert*-butylphosphinic acid with the bromotrichloromethane. The thermolysis of trimethylsilyl esters of chloro- and bromophosphonic acids, as well as dehydrohalogenation of free halogenophosphonic acids are effective for generating the *tert*-butyldioxophosphorane. Further studies of properties and reactivity of halogenophosphonic acids will be continued.

EXPERIMENTAL

Melting points were uncorrected. 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), methanol (sodium). *Tert*-butylphosphonic acid was obtained as described previously.[9]

Trimethylsilylic ester of tert-butylphosphinic acid (**3**). To a stirred solution of 12.2 g (0.1 mol) of *tert*-butylphosphinic acid in 150 ml of hexane was added dropwise 10.9 g (0.1 mol) of chlorotrimethylsilane and after 12.1 g (0.12 mol) of triethylamine at 0°C. 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 × 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_P 37.61, d $^1J_{HP}$ 526.
Calcd. for $C_{17}H_{19}O_2PSi$: P 15.94. Found P: 16.10.

Trimethylsilylic ester of tert-butylchlorophosphonic acid (**4a**). A solution of 3.9 g (0.02 mol) of trimethylsilylic ester (**3**) in 10 ml of diethyl ether was cooled with an ice bath to about 0°C. To the stirred solution was added dropwise a mixture of 6.1 g (0.04 mol) of carbon tetrachloride and 0.2 ml of triethylamine. The reaction mixture was stirred 2 hours at reflux temperature, then the solution was evaporated and the residue was distilled under 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_P 45.3.
Calcd. for $C_7H_{18}ClO_2PSi$: Cl 15.54. Found: Cl 15.45.

Trimethylsilylic ester of tert-butylbromophosphonic acid (**4b**). To a solution of 3.9 g (0.02 mol) of trimethylsilylic ester of *tert*-butylphosphinic acid (**3**) in 10 ml of diethyl ether was added with stirring 4.3 g (0.022 mol) of bromotrichloromethane at −0°C. Then the mixture was stirred for 4 hours at room temperature. The solution was evaporated and the residue was distilled under 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_H: 0.329 s (Me_3Si); 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.

Tert-butylchlorophosphonic acid (**4a**). A solution of 4.57 g (0.02 mol) of trimethylsilylic ester of *tert*-butylchlorophosphonic acid (**4a**) in 10 ml of diethyl ether was cooled to −50°C. To the stirred solution was added dropwise a solution of 0.198 g (0.011 mol) of water in 2 ml dioxane. Then the mixture was allowed to stand for 1 hour at room temperature. The solution was evaporated and the residue crystallized from hexane. The *tert*-butylchlorophosphonic acid is distilled without decomposition under 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 (**4a**). a) To a stirred solution of 5.46 g (0.02 mol) of trimethylsilylic ester of *tert*-butylbromophosphonic acid (**4a**) in 10 ml of diethyl ether was added dropwise a solution of 0.198 g (0.011 mol) of water in 2 ml of dioxane at −50°C. Then the mixture was stirred for 1 hour at room temperature. The solution was evaporated and the residue was purified by 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 and 4.3 g (0.022 mol) of bromotrichloromethane in 10 ml of diethyl ether was allowed to stand for 1 day at room temperature. After evaporation of volatile products under 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 ($^3J_{HP}$ 22.0, *t*-Bu); 13.24, s (OH). δ_P 55.55.
Calcd. for $C_4H_{10}BrO_2P$: Br 39.75; P 15.41. Found: Br 39.48; P 15.51.

2,4,6-Tri-tert-butyl-1,3,5,2,4,6-trioxotriphosphorinane (**6**). a) 4.57 g (0.02 mol) of trimethylsilylic ester of *tert*-butylchlorophosphonic acid (**4a**) was 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. Yield 0.73 g (30%), mp 150–152°C. Colorless needles.

b) 5.46 g (0.02 mol) of trimethylsilylic ester of *tert*-butylbromophosphonic acid (**4a**) was exposed to flash-vacuum thermolysis at 600°C and pressure 0.01 mm Hg to collect thermolysate in the vessel cooled by liquid nitrogen. After heating of the thermolysate to room temperature the chlorotrimethylsilane was evaporated and the residue was crystallized from toluene.

Yield 1.46 (50%), mp 150–152°C.
NMR spectra (δ, ppm; J, Hz, $CDCl_3$):
δ_H 1.34 d ($^3J_{HP}$ 13.8, *t*-Bu); 1.36 d ($^3J_{HP}$ 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 (cryoscopy in benzene).

2-Tert-butyl-2-phenyl-1,3,2-dioxophospholane (**7**). a) The mixture of 0.85 g (0.0037 mol) of (**4a**) and 0.45 g (0.0037 mol) of styrene oxide in 1 ml of xylene was heated for 2 hours at 150°C. After evaporation of volatile products under reduced pressure the residue was distilled in vacuum. Yield 0.58 g (65%). Bp. 120°C (0.06 Hg).

b) 3.0 g (0.025 mol) of styrene oxide in 1 ml of xylene was added to the thermolysate of (**4a**) prepared as described in the previous experiment from 5.46 g (0.02 mol) of trimethylsilylic ester of *tert*-butylbromophosphonic acid (**4a**). 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 ($^3J_{HH}$ 16, CH_3C); 1.34 d ($^3J_{HH}$ 16, CH_3C'); 4.0 m (CH_2O + CH'_2O); 4.6 m (PhC<u>H</u> + PhC<u>H</u>'); 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 (**8d**). 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*-butylbromophosphonic acid (**4a**) as described in the previous experiment. After 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, $CDCl_3$):
δ_H 1.09 d (J_{HH} 16, CH_3C); 1.238 t (J_{HH} 7.2, $C\underline{H}_3CH_2$); 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 43.71; H 9.10. Found C 43.50; H 9.12.

Methyl tert-butylphosphonate (**8c**). Similarly a reaction of the thermolysate with methanol gave a liquid, purified by vacuum-distillation.

Yield 50%, bp 70°C (0.02 mm Hg). Colorless liquid.
NMR specra (δ, ppm; $CDCl_3$):
δ_P 39.00, that is in accordance with Reference 9.

Triethylammonium salt of tert-butylchlorophosphonic acid (**10**). 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 (**4a**) in 10 ml of diethyl ether at −0°C. Then the mixture was stirred 15 min at room temperature and the solution was evaporated under 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); 3.087 d.q (J_{HH} 7.2, J_{HH} 4.5, $CH_2\overset{+}{N}H$); 11.57, s ($CH_2\overset{+}{N}H$). δ_P 50.46.
Calcd. for $C_{10}H_{25}ClNO_2P$: Cl 13.6; N 5.45. Found: Cl 13.44; N 5.20.

ACKNOWLEDGEMENT

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