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METALATED METHYLENEDIPHOSPHONATE ESTERS. PREPARATION, CHARACTERIZATION AND SYNTHETIC APPLICATIONS

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SUMMARY

The metalation of esters of tetraalkyl methylenediphosphonates with sodium, potassium, sodium hydride and n-butyllithium to form the corresponding salts, $M^+[\bar{C}H(PO_3R_2)_2]$, is described. These compounds were characterized by ^{31}P and ^1H NMR; their synthetic usefulness was demonstrated by the preparation of a variety of alkylates, $R'CH(PO_3R_2)_2$, and by the preparation of mono and dihalo derivatives, $XCH(PO_3R_2)_2$ and $X_2C(PO_3R_2)_2$, by direct halogenation. A superior method of halogenation of tetraalkyl methylenediphosphonates is also described. The reaction of metalated tetraalkyl methylenediphosphonate with molecular oxygen in toluene solution is shown to be complex.

INTRODUCTION

Whereas the synthetic usefulness of metalated dialkyl malonates is well known, similar applications of metalated tetraalkyl methylenediphosphonates have been studied to a lesser extent. The recent discovery in our laboratories of a high-yield synthesis of tetraisopropyl methylenediphosphonate[1] has prompted this detailed study of the metalation of methylenediphosphonates and the synthetic usefulness of the metalated species. Metalated methylenediphosphonates have been found to undergo reactions with alkyl halides, halogens and molecular oxygen**.

METALATION

The potassium salt of tetraethyl MDP was first prepared by Kosolapoff[2] who reported one example of its alkylation. More recently the properties of certain metal salts of tetraethyl MDP have been studied by Baldeschwieler *et al.*[3] and by Cotton and Schunn[4].

In this study several methods of metalation were explored employing the tetramethyl, tetraethyl, and tetraisopropyl esters of MDP. High yields (>90%) of

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[**] Throughout the remainder of this paper MDP will refer to a tetraalkyl methylenediphosphonate, $CH_2(PO_3R_2)_2$. A particular ester will be referred to as tetraethyl MDP etc.

the metalated methylenediphosphonates were realized with sodium, potassium, or sodium hydride as the metalating agent. The reactions were carried out in a non-reactive organic solvent such as toluene. The reaction of tetraisopropyl MDP with n-butyllithium at 25° in tetrahydrofuran led to a 70% yield of the lithium derivative of MDP, the remainder of the starting material being converted to partial esters. As a general rule temperatures below 25° should be maintained during the preparation of tetraalkyl MDP salts to avoid undesirable side-products. Once formed, the tetraalkyl salts are reasonably stable.

The sodium salt of tetraisopropyl MDP may be isolated as a white crystalline solid exhibiting high solubility in typical organic solvents; a similar solubility has been observed for the tetraethyl MDP derivative[3]. The salt from tetramethyl MDP shows, in contrast, limited solubility in organic solvents. Since the sodium salt of tetraethyl MDP is known to be a hexamer in non-polar organic solvents[3], this low solubility suggests a polymeric structure for the tetramethyl homolog. Phosphorus NMR spectral data for the esters and their alkali metal salts are recorded in Table 1.

TABLE 1

^{31}P NUCLEAR MAGNETIC RESONANCE DATA^a

Species	δ (ppm)	$J(P\text{-}H_\alpha)$ (Hz)
$CH_2[PO(OC_2H_5)_2]_2$	-19.0^b	21^c
$NaCH[PO(OC_2H_5)_2]_2^d$	-41.5	
$CH_2[PO(OCH_3)_2]_2$	-23.0	20
$NaCH[PO(OCH_3)_2]_2^d$	-45.5	
$CH_2[PO(O\text{-iso-}C_3H_7)_2]_2$	-17.5	20
$NaCH[PO(O\text{-iso-}C_3H_7)_2]_2^d$	-40.5	
$Cl_2C[PO(OC_2H_5)_2]_2$	-8.5	
$Cl_2C[PO(OCH_3)_2]_2$	-10.0	
$Cl_2C[PO(O\text{-iso-}C_3H_7)_2]_2^e$	-6.5	
$Br_2C[PO(OC_2H_5)_2]_2$	-8.5	
$Br_2C[PO(O\text{-iso-}C_3H_7)_2]_2$	-6.5	
$I_2C[PO(O\text{-iso-}C_3H_7)_2]_2$	-10.5	
$ClCH[PO(O\text{-iso-}C_3H_7)_2]_2$	-11.5	17
$BrCH[PO(O\text{-iso-}C_3H_7)_2]_2$	-12.0	17
$ICH[PO(O\text{-iso-}C_3H_7)_2]_2$	-13.5	17

[a] All values are relative to 85% H_3PO_4 (external reference). The spectra are consistent with the indicated structure and the PMR spectra. The δ values are accurate to ±0.5 ppm [b] Ref. 4a. [c] Ref. 3. [d] Measured in benzene. [e] Measured in chloroform.

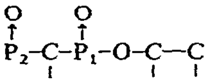
Proton NMR data for the tetramethyl, tetraethyl, and tetraisopropyl esters and their respective sodium salts appear in Table 2. All H_α 1 : 2 : 1 triplets were identified by their splitting and/or relative intensities. Comparable $J(H-P)$ values were observed in ^{31}P NMR spectra (Table 1). The $\tau(H_\alpha)$ values for the metalated materials show a consistent shift upfield of 1.2 to 1.8 ppm. Such a shift is indicative of a greater negative charge in the proximity of the H_α protons. A similar, though less dramatic, shift is indicated in the values attributed to the H_β nuclei.

The discussion pertaining to the ethyl and methyl esters has appeared elsewhere[3,5] and will not be treated here. It will suffice to say that the results indicate a strong coupling between the two ^{31}P nuclei in the metal derivatives.

TABLE 2

PROTON MAGNETIC RESONANCE DATA[a]

Species	Proton	Ester				Carbanion			
		Multiplicity	τ	J (Hz)		Multiplicity	τ	J (Hz)	
				H–H	H–P			H–H	H–P
Tetramethyl methylenediphosphonate	α	3	7.34		21.0	3[b]	9.07		6.5
	β	2	6.26		10.5	3	6.37		11.0[c]
Tetraethyl methylenediphosphonate[d]	α	3	7.71	0	20.3	3	9.52	0	7.4
	β	~5	5.95	6.9	8.3	~9	6.13	7.1	7.2[c]
	γ	3	8.67	6.9	0	3	8.78	7.1	0
Tetraisopropyl methylenediphosphonate	α	3	7.68	0	20.75	3[b]	(8.87)[b]	0	(6.75)[b]
	β	14	5.25	6.25[e]	8.0[e]	≧14	5.46	[f]	[f]
	γ	4	8.65[g] 8.67	6.5	0	4	8.60 8.72	6.0	0
			$\Delta\tau = 0.017$ ppm				$\Delta\tau = 0.12$ ppm		

[a] Numbering system refers to  $\overset{\overset{O}{\uparrow}}{P_2}-\underset{H_\alpha}{C}-\overset{\overset{O}{\uparrow}}{P_1}-O-\underset{H_\beta}{C}-\underset{H_\gamma}{C}$. All τ values are relative to TMS (10.00 ppm) as internal standard. J values are accurate to ±0.25 Hz. Carbanion spectra were measured in benzene. [b] Not easily resolved. The proximity of the H_γ absorption to the H_α absorption makes this assignment somewhat tenuous for the isopropyl derivative. [c] Assuming $J(H_\beta{-}P_2) = 0$ and $J(P_1{-}P_2)$ is large. [d] Ref. 3. [e] Decoupling used to make assignments. [f] Decoupling reveals a broad multiplet. [g] Previously it was reported[6] that the four methyl groups were equivalent. Those measurements were made at 60 Mc. The measurements at 60 Mc are in agreement with those reported here.

The quartet structure attributed to the methyl group H_γ's in the tetraisopropyl ester and the related salt has been shown to be due to coupling with H_β and a magnetic non-equivalence of the methyl groups. Measurements at 60 MHz showed that this extra splitting was due to a difference in chemical shifts and not due to spin–spin coupling. This magnetic non-equivalence may be due to either restricted rotation of the isopropyl groups[6] or pseudo-asymmetry at the phosphorus center, such as is observed for the methyleneoxy protons in bromoacetal[7].

ALKYLATION OF THE MDP CARBANION

An obvious demonstration of the synthetic utility of the metalated methylenediphosphonates involves alkylation with active organic halides. Kosolapoff[2] was the first to examine this specific application and several patents[8] have recently appeared describing the resulting alkylates. Hays and Logan[9] have described the reaction of sodium MDP with n-alkyl halides.

Exclusive monoalkylation in the MDP system seldom occurs. When an organic halide is allowed to react with an equivalent amount of sodium MDP, monoalkylation rarely accounts for more than 80% of the total reaction based upon a phosphorus NMR assay of the crude product. In all cases the product is contaminated with some starting MDP and normally contains 5–15% of the dialkylate, probably resulting from an exchange reaction between $RCH(PO_3R'_2)_2$ and $M[CH(PO_3R'_2)_2]$.

TABLE 3

SUBSTITUTED MDP ESTERS, $XYC(PO_3\text{-iso-}Pr_2)_2$[a], PREPARED BY ALKYLATION

X	Y	Alkylate (%)	Isolated yield (%)	^{31}P NMR of ester product (ppm)
H	H			−17.5
CH_3	H	60–70	20[b]	−22.0
CH_3	CH_3	80–90	60–70[c]	−25.0
$n\text{-}C_4H_9$	H	65–80	24[b]	−22.0
$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	95	25[b,c]	−25.5
$n\text{-}CH_3(CH_2)_{13}$	H	80	39[b]	
$C_6H_5CH_2$	H	< 70[d]	26[b]	−20.5
RO_2C[f]	H	25–30	5	−11.0
$C_2H_5OOCCH_2$	H	55–94	93[d]	−20.0
$R_2O_3PCH_2$	H	22–28	12	−24.0, −30.5[e]
$(R_2O_3P)_2CHCH_2$	H	84	40[b]	−22.0
Cl_2C		30–54	~3[b]	−6.0

[a] For NMR details see *Experimental Part.* % Alkylate derived from ^{31}P measurements. [b] Isolated either as free acid or as the sodium or aniline salt. Other purifications involved vacuum distillation [c] Two-step alkylation. [d] Maximum yield obtained. [e] Signal at $\delta = -30.5$ is due to the monophosphonate. The relative areas are consistent with this assignment. R refers to methyl groups. [f] Decomposes during acid hydrolysis.

Table 3 shows the results of the alkylations carried out in this study. Deliberate dialkylation was effected in two cases and high yields of $(CH_3)_2C(PO_3R_2)_2$ and $(n\text{-}C_4H_9)_2C(PO_3R_2)_2$[9] were obtained via two-step reactions. Higher temperatures appear to be necessary to cause direct dialkylation.

Several points regarding the compounds in Table 3 are worthy of mention. Carbon tetrachloride reacts with the tetraisopropyl MDP salt to form tetraisopropyl (2,2-dichlorovinylidene)diphosphonate, $Cl_2C{=}C[PO(O\text{-iso-}C_3H_7)_2]_2$, in low yield. Apparently this material results when the initially formed tetraisopropyl (2,2,2-trichloroethylidene)diphosphonate loses hydrogen chloride (eqn. 1). Baldeschwieler *et al.*[3] observed this reaction with the metalated tetraethyl MDP but did not isolate the product.

$$CCl_4 + Na^+[CH(PO_3R_2)_2]^- \rightarrow$$
$$NaCl + Cl_3CCH(PO_3R_2)_2 \xrightarrow{-HCl} Cl_2C{=}C(PO_3R_2)_2 \quad (1)$$

A low yield of pentaisopropyl (carboxymethylene)diphosphonate was obtained from the reaction of isopropyl chloroformate and sodium MDP. This material proved to be unstable to acid hydrolysis, yielding methylenediphosphonic acid and (presumably) carbon dioxide. These reactions are shown in eqn. (2).

$$ROOCCl + Na^+[CH(PO_3R_2)_2]^- \rightarrow$$
$$NaCl + ROOCCH(PO_3R_2)_2 \xrightarrow[\Delta]{HCl} CO_2 + 5\,RCl + H_2C(PO_3H_2)_2 \quad (2)$$

When the carboxyl group is separated from the bridging carbon of MDP by one CH_2 unit the compound becomes stable, *i.e.*, when ethyl chloroacetate is employed as the alkylating agent, the product, pentaalkyl (2-carboxyethylidene)diphosphonate, is formed in good yield and can be hydrolyzed without decomposition.

HALOGENATION

Reaction of molecular halogen (chlorine, bromine and iodine) with sodium MDP does not yield simply the monohalo derivative. A phosphorus NMR assay of such a reaction mixture reveals the presence of three species: MDP, monohalo MDP, and dihalo MDP. The ratio of these three species does not change significantly regardless of the order of addition of the two reagents. The yield of monohalo MDP was never more than 50%. Some separation of the product mixtures by fractional distillation was accomplished but pure samples of the mono and dihalo MDP esters were difficult to obtain in this way.

Pure samples of some of the mono and dihalo MDP derivatives were obtained, however, through reaction of the MDP ester with aqueous alkaline hypohalite at ambient temperatures. Using this procedure the halo derivatives listed in Table 1 were obtained. The presence of iodo-MDP, chloro-MDP and diiodo-MDP were inferred from ^{31}P NMR spectra; no attempt to obtain analytically pure samples was made.

In order to obtain appreciable amounts of the halo-MDP, the increased reactivity of the proton on the XCH$<$ must be offset by minimizing its solubility in the aqueous phase. The most successful of several methods used to accomplish this employed a high concentration of electrolyte such as K_2CO_3 in the aqueous phase to decrease the total ester concentration. Ester solubility in the aqueous phase decreases with increasing halide content; therefore, the small amount of material in the aqueous phase is largely tetraisopropyl MDP itself. Upon adding the halogenating agent slowly, with stirring, most of the halo-MDP passes into the organic phase before conversion to dihalo-MDP. It was thus possible to prepare as much as 60% tetraisopropyl bromo-MDP (determined from a ^{31}P NMR assay), from which the pure material was obtained (see *Experimental Part*).

The dihalo-MDP derivatives are obtained quantitatively when one allows an ester of MDP to react with more than two equivalents of sodium hypohalite. Vacuum distillation afforded pure samples of the dichloro MDP and dibromo MDP esters.

OXIDATION

The crystalline sodium salt of tetraethyl MDP has been shown to be quite stable toward molecular oxygen[3]; nothing is known concerning the reaction of oxygen and the metalated materials in solution. With the aid of ^{31}P NMR we have briefly examined such a reaction and find it to be very complex.

Oxygen was passed through a solution of the sodium salt of tetramethyl MDP in toluene (18 h/25°). The solvent was then removed and a ^{31}P NMR spectrum of the residue obtained. At least seven species were found to be present, all absorbing between -40 ppm and the reference (85% H_3PO_4). The most abundant species comprised 19% of the mixture and the least abundant 8%. Because of its extreme complexity, the mixture was not further examined.

EXPERIMENTAL PART

All melting points reported herein are uncorrected. Elemental analyses were carried out in these laboratories. All manipulations involving oxygen- and moisturesensitive substances were carried out in an atmosphere of dry oxygen-free nitrogen.

The phosphorus NMR spectra were measured using spinning 9 mm glass tubes with a Varian HR-60 spectrometer operating at 24.3 MHz. Chemical shifts are accurate to ±0.5 ppm. Side band calibration was used. Varian HA-100 and HR-60 spectrometers were used to obtain the proton spectra.

The tetraisopropyl ester of methylenediphosphonic acid was prepared by the Michaelis–Arbuzov reaction of triisopropyl phosphite and methylene dibromide[1]. The methyl and ethyl esters were prepared by pyrolyzing the isopropyl ester at 180° followed by esterification of the resulting acid with the appropriate trialkyl orthoformate. The esters were purified by vacuum distillation (Table 4).

Preparation of metalated methylenediphosphonates

Tetraisopropyl MDP may be converted to the metal salt by direct metalation or by use of a strong base such as sodium hydride in an inert solvent such as toluene. The temperature should be kept below 25° during addition of the MDP to the dispersed metal or base. The salts of the methyl and ethyl esters may be similarly prepared.

TABLE 4

TETRAALKYL METHYLENEDIPHOSPHONATES, $CH_2(PO_3R_2)_2$, PREPARED

R	B.p. [°C (mm)]	n_D^{20}	Analyses, found/(calcd.) C	H	P	Mol.wt.[a]
Me	87–90(0.05)	1.4523	25.9 (25.9)	6.2 (6.1)	26.7 (26.7)	235 (232)
Et	90–94(0.1)	1.4412	37.4 (37.5)	7.8 (7.7)	21.8 (21.5)	280 (288)
iso-Pr	96–100(0.1)	1.4317	44.6 (45.3)	8.9 (8.8)	18.3 (18.0)	340 (344)

[a] In benzene.

Alkylation

All alkylations were performed by combining an organic halide with an equivalent amount of sodium MDP in toluene solution and stirring at elevated temperature for about 1 h. The preparation of 1,1-pentylidenediphosphonic acid is considered typical and is given in detail below. Yields of alkylates prepared in this manner are collected in Table 3, and analytical data for the compounds are given in Table 5.

1,1-*Pentylidenediphosphonic acid.* Equimolar quantities of n-butyl bromide and the sodium salt of tetraisopropyl methylenediphosphonate were combined in toluene solution (total volume 500 cc) and heated to 115° for 1 h. The toluene was removed by flash evaporation and an equivalent amount of chloroform was added. This solution was washed three times with 200 cc of water, and the $CHCl_3$ was removed by flash evaporation leaving the crude product. Distillation through a 12 inch jacketed column gave the pure product, b.p. 107.5° (0.03 mm). (Found: C, 50.9; H, 9.7. $C_{17}H_{38}O_6P_2$ calcd.: C, 51.0; H, 9.6%.)

A sample of the ester was refluxed with an excess of constant-boiling HCl

TABLE 5

ANALYTICAL AND NMR RESULTS FOR ALKYLATED METHYLENEDIPHOSPHONIC ACIDS AND SALTS

$CXY(PO_3R_2)_2$		C (%)	H (%)	M.p. (°C) of	δ(^{31}P NMR)
X	Y	found (calcd.)	found (calcd.)	acid and/or aniline salt	of acid and/or Na salt
H	H[b]	6.5	3.6	203–6	−18.5
		(6.8)	(3.4)	(202–4)	(−17.0[a])
CH_3	H[b]	12.5	4.3	179–81	−23.0
		(12.6)	(4.2)	(194–6)	(−22.5[a])
CH_3	CH_3[c]	47.9	9.4	228.5–9.5	−27.5
		(48.4)	(9.2)	(254–6)	(−27.5[a])
n-C_4H_9	H[b]	25.4	6.0	151–2	−22.5
		(25.9)	(6.1)	—	—
n-C_4H_9	n-C_4H_9[b]	37.6	8.0	239–41	−26.0
		(37.5)	(7.7)	—	—
n-$CH_3(CH_2)_{13}$	H[b]	48.4	9.6	156–62	[d]
		(48.4)	(9.2)	—	—
$C_6H_5CH_2$	H[b]	36.3	4.6	210–12	−21.0
		(36.1)	(4.5)	—	—
RO_2CCH_2	H[e]	41.6	7.7	—	−20.0
		(41.7)	(7.5)	—	(−19.5[f])
$R_2O_3PCH_2$	H[g]	27.4	6.2	—	−24.0, −19.0
		(27.1)	(6.0)	—	(−21.0[h])
$(R_2O_3P)_2CHCH_2$	H[b]	10.2	3.4	227–9	−20.5
		(9.9)	(3.3)	(178–80)	(−20.5[i])
Cl_2C[j]		8.4	1.3	—	−7.5
		(8.0)	(0.7)	(241.5–2.5)	(−9.5[j])
RO_2C	H[k]	48.4	8.7	—	—
		(47.4)	(8.4)	—	—

[a] Refers to the Na_3H salt. [b] Analytical values pertain to the acid. [c] Analyzed as the tetraisopropyl ester. [d] Too insoluble for measurement. [e] Analyzed as the pentaethyl ester (b.p. 108–12° at 0.04 mm). [f] Refers to the Na_4H salt. [g] Analyzed as the hexamethyl ester. [h] Refers to the Na_4H_2 salt. [i] Refers to the Na_6H_2 salt. [j] Analyzed as the Na_2H_2 salt; Cl calcd. 23.6, found 23.3%. [k] Analyzed as the pentaisopropyl ester.

for 3 h. The excess HCl was removed and the remaining acid was crystallized successively from acetic acid/benzene, benzene/acetone, and ethyl acetate (m.p. 151–2). (Found: C, 25.4; H, 6.0. $C_5H_{14}O_6P_2$ calcd.: C, 25.9; H, 6.1%.)

Halogenation

Direct bromination of metalated MDP. Sodium tetraisopropyl MDP (0.5 mole), in diglyme, was added to bromine (0.55 mole) in diglyme; during addition the temperature was maintained at 15°. The ^{31}P NMR measurements on the crude product showed mole percentages of phosphorus distributed as follows: 45% MDP, 40% Br-MDP and 15% Br_2-MDP. Using hexane as the solvent for the reaction, the ratios were 40:50:10, respectively.

Tetraisopropyl dichloro-MDP. Tetraisopropyl MDP (172 g, 0.5 mole) was added with vigorous stirring to 1850 g of a solution containing 5.25% sodium hypochlorite and 4.1% sodium chloride. After stirring for 30 min at ice-bath temperature, the bath was removed and stirring continued for an additional 30 min. The white solid which had formed was separated by filtration. The aqueous filtrate was extracted with chloroform (560 ml). The white solid was dissolved in the chloroform extracts and the solution extracted with water until a negative halide test was observed. The chloroform was removed by flash evaporation and the residue distilled through a short-path column. The distillate slowly solidified to a white solid. An analytical sample (m.p. 50°) was taken at 119° (500 μ). (Found: C, 37.8; H, 6.9; Cl, 16.9; P, 15.1; mol. wt. in benzene, 425. $C_{13}H_{28}Cl_2O_6P_2$ calcd.: C, 37.8; H, 6.8; Cl, 17.2; P, 15.0%; mol. wt., 413.)

TABLE 6

ANALYTICAL RESULTS FOR $X_2C(PO_3R_2)_2$

Compound	Analyses, found (calcd.)					B.p. [°C (mm)]	n_D^{20}
	C	H	X	P	Mol. wt.		
$Cl_2C[PO(OC_2H_5)_2]_2$[a]	30.3 (30.3)	5.9 (5.6)	20.3 (19.9)	17.7 (17.3)	370 (357)	119–120(0.05)	1.4619
$Br_2C[PO(O\text{-iso-}C_3H_7)_2]_2$[b]	31.1 (31.1)	5.9 (5.6)	30.7 (31.8)	12.6 (12.3)	500 (502)	~90(< 0.04)[b]	1.4910
$Br_2C[PO(OC_2H_5)_2]_2$	24.0 (24.2)	4.9 (4.5)	36.3 (35.8)	14.1 (13.9)	455 (446)	117–120(0.08)	1.4750

[a] Tetraethyl dichloromethylenediphosphonate has been prepared from triethyl phosphite and bromotrichloromethane[10]. [b] Distillation accomplished with a molecular still.

Table 6 contains the analytical data for other dihalo derivatives prepared and purified by means similar to those described above. The tetraethyl dihalomethylenediphosphonates were prepared in a two-phase reaction using chloroform.

Tetraisopropyl bromo-MDP. Tetraisopropyl MDP (34.4 g, 0.1 mole) was added to 320 g of a 55% potassium carbonate solution; bromine (0.1 mole) in 25 ml heptane was added dropwise (over a period of 2 h) with the temperature maintained at 40°. Water (150 ml) was added to the crude mix and the two layers were separated. The water layer was extracted with 150 ml of chloroform and discarded. The chloroform layer was combined with the organic layer and extracted with water. The extraction was repeated and the organic phase dried over magnesium sulfate. The organic solvents were removed by flash evaporation. A ^{31}P NMR assay on the crude mix showed 32% MDP, 57% Br-MDP, and 11% Br_2-MDP. The crude mix was dried at 35 μ and crystallized from a hexane/ether mixture (3 : 1) at $-75°$. The crystals were washed with hexane ($-70°$), collected, and recrystallized once from hexane/ether (3 : 1) at $-70°$ and washed as before. A ^{31}P NMR assay of the recrystallized sample indicated pure Br-MDP ($\delta = -12$ ppm). (Found: C, 36.6; H, 7.0; Br, 18.7; P, 14.8; mol. wt. in benzene, 430. $C_{13}H_{29}BrO_6P_2$ calcd.: C, 36.9; H, 6.9; Br, 18.9; P, 14.7%; mol. wt., 423.)

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