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A Convenient and Improved Preparation of Cyano Phosphates

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Abstract: Cyano phosphates derived from aldehydes or ketones are prepared in good yields using lithium cyanide in DMF and diethyl chlorophosphate as phosphorylating agent.

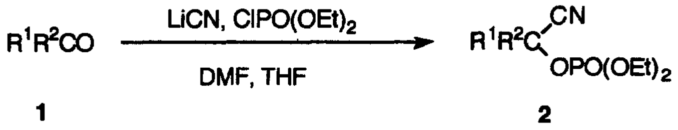
Introduction

Cyanohydrin diethyl phosphates are versatile intermediates in synthetic organic chemistry[1] specially: (a) in the preparation of saturated[2] and α,β-unsaturated [3] nitriles from carbonyl compounds by reductive elimination of the phosphate group, (b) for the regiospecific Friedel-Crafts type arylation of aromatic compounds[4], (c) in the synthesis of γ-hydroxy α,β-unsaturated nitriles [4b,5] and β-cyano α,β-unsaturated ketones[5] by [3,3]-sigmatropic rearrangement of α,β-unsaturated cyano phosphates, (d) as acyl anion equivalents[6] in the case of aldehydes derivatives, and (e) in the synthesis of indole derivatives[7]. We were interested in the synthesis of saturated nitriles from saturated ketones by reduction of the corresponding cyano phosphates with samarium iodide[2b]. The general method described for the preparation of diethylphosphoric esters of cyanohydrins is the treatment of carbonyl compounds either with a three-fold excess of lithium cyanide and *O,O'*-diethyl phosphorocyanidate [$(EtO)_2P(O)CN$, DEPC][1-7], or with DEPC in the presence of a catalytic amount of lithium diisopropylamide[8]. We have found a more simple and cheaper way to prepare cyano phosphates using as reagents lithium cyanide and diethyl chlorophosphate.

Results and Discussion

The reaction of carbonyl compounds **1** with a slight excess of a solution of lithium cyanide (1.5 eq) in *N,N*-dimethylformamide[9] and diethyl chlorophosphate (1.2 eq) in THF at room temperature gave cyanohydrin diethyl phosphates **2b-c**, **2g**, **2h** and **2j-m** in good yields (Scheme 1 and Table 1).

The process was monitorized by GLC and took place in less than one hour and with similar yields than in the DEPC method[1-7], and compounds **2** were obtained in most cases as crude products in >93% of purity (GLC and 300MHz ^{1}H-NMR). In the case of α,β-unsaturated carbonyl compounds such as *(E)*-crotonaldehyde (**1b**) and methyl vinyl ketone (**1g**) only the corresponding 1,2-addition products were formed. However,



Scheme 1

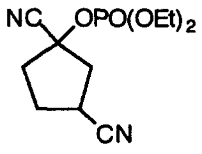
Table 1. Synthesis of Cyano Phosphates **2-4** and **6**.

Carbonyl compound			Reaction	Product		
no.	R^1	R^2	time[a]	no.	yield (%)[b]	bp(°C)[c]
1a	CH_2=CH	H	10 min	**3a**[d]	66	90
1b	*(E)*-MeCH=CH	H	10 min	**2b**	85	105[e]
1c	*t*-Bu	H	15 min	**2c**	85	100
1d	Ph	H	30 min	**2d**	88	135[f]
1e	$PhCH_2$	H	1 h	**2e**	93	160
1f	3-indolyl	H	2 h[g,h]	**6f**[i]	72	-[j,k]
1g	CH_2=CH	Me	10 min[g]	**2g**	81	90[l]
1h	Et	Et	10 min[g]	**2h**	67	110
1i	-(CH_2CH_2CH=CH)-		15 min	**4i**[m]	40	160[n]
1j	-$(CH_2)_5$-		40 min	**2j**	90	110[o]
1k	-[p]		45 min	**2k**	90	170
1l	Ph	Me	1 h	**2l**	84	140[q]
1m	-[r]		10 min	**2m**	51[s]	120

[a] The reaction was carried out at room temperature. [b] Isolated crude yield based on compound **1**. All crude compounds **2-4** and **6** were >93% pure (GLC and 300MHz ^{1}H-NMR). [c] Kugelrohr (4 Torr). [d] *Z/E* ratio: 9/1 (GLC). [e] Lit.[4b]. [f] Lit.[6a]: 149°C (3 Torr). [g] At 0°C. [h] LiCN was slowly added during 30 min. [i] *Z/E* ratio: 65/35 (^{1}H-NMR). [j] Lit.[7]. [k] R_f 0.38 for the *Z*-isomer and 0.28 for the *E*-isomer, hexane/ethyl acetate: 1/1. [l] Lit.[4b]: 77-83°C (2 Torr). [m] *Cis/trans* ratio: 1/1 (^{1}H-NMR). [n] T_r 10.30 and 10.39 min (see Experimental). [o] Lit.[8]. [p] 1,4-Cyclohexanedione monoethylene ketal. [q] Lit.[2a]. [r] Norbornanone. [s] After column chromatography on silica gel (hexane/ethyl acetate).

2-cyclopentenone (**1l**) gave the 1,4-addition product **4l** as *cis/trans* mixture of diastereoisomers in *ca.* 1/1 molar ratio (Table 1), while the DEPC method gave the vinyl phosphate **5** under the similar reaction conditions[5]. When the reaction was carried out with acrolein (**1a**) the unsaturated cyano phosphate **3a** was exclusively obtained as a *Z/E* mixture of diastereoisomers in 9/1 molar ratio (Table 1), this product arises from the isomerization of compound **2a**. On the other hand, the reaction of acrolein (**1a**) with lithium cyanide and DEPC under the same reaction conditions gave a mixture 3/1 of compounds **2a** and **3a**.

The treatment of 3-indolecarbaldehyde (**1f**) as above at 0°C afforded a mixture of *(Z)*- and *(E)*-3-cyanomethyleneindolines **6f** in 72% yield, in 65 and 35% ratio respectively. The same result was obtained with the DEPC method, product *(E)*-**6f** being the major isomer[7]. Compounds **6f** were formed by [3,3]-sigmatropic rearrangement of the intermediate cyanophosphate **7**[7]. In the case of norbornanone (**1m**) only one diastereoisomer (**2m**), presumably with the cyano group in the *exo* position, was obtained.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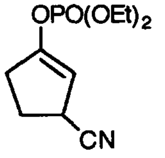
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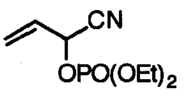
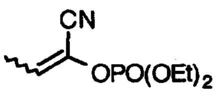

2a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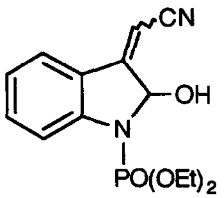
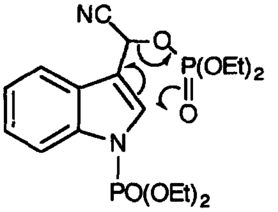

6f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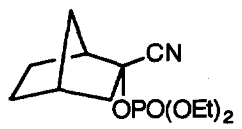
2m

The procedure of cyanophosphorylation described here is a good method for the synthesis of synthetic useful cyano phosphates and allows the use of diethyl chlorophosphate instead of diethyl cyanophosphate in stoichiometric amounts.

Experimental Part

General.- IR spectra were obtained as films in a Pye Unicam SP3-200 spectrophotometer as neat liquids. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC-300 spectrometer with $SiMe_4$ as internal standard or H_3PO_4 85% and using $CDCl_3$ as solvent. ^{13}C-NMR assignments were made on the basis of DEPT experiments. MS spectra were measured in a Hewlett-Packard 5988A by GLC injection (EI, 70eV). Elemental analyses were performed by the Microanalyses Service of the University of Alicante. Chromatographic analysis (GLC) were determined with a Hewlett-Packard HP-5890 instrument equipped with a 25 m WCOT capillary column (0.22 mm diam., 0.2 µm film thickness OV-101 stationary phase) using nitrogen (2 ml/min) as the carrier gas, $T_{injector}$=270°C, T_{column}=100°C, and 100-270 (10°C/min). Thin layer chromatography (TLC) was carried out on Schleicher &Schuell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel, using a mixture of hexane/ethyl acetate as eluant, and revealed, in general, with iodine. Column chromatography was performed using silica gel 60 of 70-270 mesh and hexane/ethyl acetate as eluant. All starting materials were commercially available (Aldrich, Fluka) of the best grade and were used without further purification. THF was dried with LiAlH$_4$ under argon atmosphere.

Preparation of Compounds **2-6**. *General Procedure*.- To a solution of carbonyl compound **1** (0.5 mmol) and diethyl chlorophosphate (0.09 ml, 0.6 mmol) in dry THF (4 ml) was added a 0.5 M solution of lithium cyanide[9] (1.5 ml, 0.75 mmol) in DMF and the mixture was stirred at room temperature (see Table 1). The reaction mixture was quenched with water and extracted with a mixture of hexane and ethyl acetate (1/1). The organic layer was washed three times with brine, dried over anhydrous sodium sulfate and evaporated (15 Torr) to yield crude pure cyano phosphates **2-4** and **6**, which were purified by distillation or column chromatography. Yields and bp values are given in Table 1, R_f values (hexane/ethyl acetate: 2/1), spectral, and analytical data for new compounds follow.

(Z/E)-2-(Diethylphosphonooxy)-2-butenenitrile (**3a**): R_f 0.48; ν_{max} 3060, 1630 (CH=C), 2225 (CN), 1280 (P=O), and 1020 cm^{-1} (P-O); δ_H 1.41 (t, J= 7.0Hz, 6H, 2xCH_3CH$_2$), 1.89 *(Z)*, 1.96 *(E)* (2dd, J= 7.5, 2.5Hz, 3H, CH_3CH), 4.26 (m, 4H, 2xCH$_2$), 6.11 (qd, J= 7.0, 1.0Hz, 0.9H, CH), 6.38 (qd, J=7.5, 2.5Hz, 0.1H, CH); δ_C 11.64 *(Z)*, 13.27 *(E)* (d, J= 1.0Hz, CH_3CH), 15.77 (d, J= 6.5Hz, 2xCH_3CH$_2$), 65.12 (d, J= 6.5Hz, 2xCH$_2$), 112.21 *(E)*, 113.84 *(Z)* (2d, J= 1.5, 2.5Hz, respectively, COP), 121.27 *(Z)*, 122.00 *(E)* (2d, J= 9.0 and 10.0, respectively, CN), 130.96 *(E)*, and 131.52 *(Z)* (2d, J= 5.5 and 6.9, respectively, CH); δ_P -5.5 (*E*-isomer) and -5.7 (*Z*-isomer); *m/z* 219 (M^+, 4%), 163 (64), 109 (40), 108 (20), 99 (43), 91 (18), 82 (35), 81 (100), 69 (10), 66 (21), 65 (20), 56 (61), 55 (41), 54 (23), 47 (10), 45 (11), and 43 (10). Anal. Calcd. for $C_8H_{14}NO_4P$: C, 43.84; H, 6.44; N, 6.39. Found: C, 44.03; H, 6.74; N, 6.66.

2-(Diethylphosphonooxy)-3-pentenenitrile (**2b**): R_f 0.49; ν_{max} 1270 (P=O) and 1100-940 cm^{-1} (P-O)[4b]; δ_H 1.35, 1.38 (2t, J= 7.0Hz, 6H, 2xCH_3CH$_2$), 1.82 (d, J= 6.5Hz, 3H, CH_3CH), 4.16 (m, 4H, 2xCH$_2$O), 5.46 (ddd, J= 8.0, 7.0, 1.0 Hz, 1H, CHO), 5.64 (ddq, J= 15.0, 7.0, 2.0Hz, 1H, CHCHO), and 6.17 (ddq, J= 15, 6.5, 2.0Hz, 1H, CHCH$_3$)[4b]; δ_C 15.71 (d, J= 7.0Hz, 2xCH$_3$), 17.28 (CH_3CH), 64.35, 64.42 (2d, J= 6.0Hz, 2xCH$_2$O), 64.72 (d, J= 5.0Hz, CHCN), 115.47 (d, J= 6.0Hz, CN), 122.23 (CHCHO), and 135.24 (CHCH$_3$); *m/z* 234 (M^++1, 0.2%), 233 (M^+, 1.2), 177 (29), 127 (20), 125 (11), 99 (100), 81 (29), 80 (15), 79 (11), and 53 (15).

2-(Diethylphosphonooxy)-3,3-dimethylbutanenitrile (**2c**): R_f 0.56; ν_{max} 1270 (P=O), 1020, and 980 cm^{-1} (P-O); δ_H 1.12 (s, 9H, 3xCH$_3$C), 1.38, 1.39 (2t, J= 7.0Hz, 2xCH_3CH$_2$), 4.20 (m, 4H, 2xCH$_2$), and 4.65 (d, J= 8.5Hz, CH); δ_C 15.73, 15.76 (2d, J= 6.5Hz, 2xCH$_3$CH$_2$), 24.59 (3xCH_3C), 35.43 (d, J= 6.0Hz, CCH), 64.43, 64.44 (2d, J= 6.0Hz, 2xCH$_2$), 73.19 (d, J= 7.0Hz, CH), and 115.82 (d, J= 2.0Hz, CN); δ_P -1.4; *m/z* 249 (M^+, 0.1%), 209 (13), 193 (46), 178 (15), 165 (28), 155 (32), 137 (100), 127 (62), 125 (22), 99 (78), 82 (24), 81 (43), 57 (23), 53 (12), and 41 (24).

2-(Diethylphosphonooxy)-2-phenylethanenitrile (**2d**): R_f 0.49; ν_{max} 1265 (P=O), 1030, and 970 cm^{-1} (P-O)[6a]; δ_H 1.22, 1.38 (2t, J=7.0Hz, 6H, 2xCH$_3$), 4.01, 4.17 (2m, 4H, 2xCH$_2$O), 6.08 (d, J= 9.0Hz, CHO), 7.45, and 7.57 (2m, 5H, Ph)[6a]; δ_C 15.76, 15.72 (2d, J= 7.0Hz, 2xCH$_3$), 64.41, 64.59 (2d, J= 6.0Hz, 2xCH$_2$), 66.25 (d, J= 4.5Hz, CHO), 115.93 (d, J= 6.0Hz, CN), 127.25, 129.00, 130.31 (3xCH-Ph), and 132.27 (d, J=

5.5Hz, C_i-Ph); *m/z* 270 (M^++1, 0.2%), 269 (M^+, 17), 213 (57), 125 (10), 117 (10), 116 (100), 115 (60), 105 (45), 99 (12), 89 (44), 81 (23), 77 (19), and 63 (14).

2-(Diethylphosphonooxy)-3-phenylpropanenitrile (**2e**): R_f 0.44; ν_{max} 1270 (P=O), 1030, and 970 cm^{-1} (P-O); δ_H 1.24-1.33 (m, 6H, 2xCH_3), 3.22 (d, *J*= 7.0Hz, 2H, CH_2C), 3.94-4.16 (2m, 4H, 2xCH_2O), 5.16 (dd, *J*= 15.0 y 7.0Hz, 1H, CHO), 7.32 (m, 5H, Ph); δ_C 15.70 (d, *J*= 6.5Hz, 2xCH_3), 40.15 (d, *J*= 6.0Hz, CH_2C), 64.40, 64.48 (2d, *J*= 6.0Hz, 2xCH_2O), 65.19 (d, *J*= 6.0Hz, CHO), 116.27 (d, *J*= 4.0Hz, CN), 127.70, 128.58, 129.46 (3xCH-Ph), and 132.80 (C_i-Ph); *m/z* 283 (M^+, 0.2%), 130 (15), 129 (100), and 91 (35).

2-(Diethylphosphonooxy)-2-methyl-3-butenenitrile (**2g**): R_f 0.44; ν_{max} 3080, 1660 (CH=C), 2240 (CN), 1265 (P=O), and 1080-950 cm^{-1} (P-O)[4b]; δ_H 1.36, 1.37 (2t, *J*= 7.0Hz, 6H, 2xCH_3CH_2), 1.90 (s, 3H, CH_3CO), 4.17 (m, 4H, 2xCH_2O), 5.47 (d, *J*= 10.5Hz, 1H, CH_2=C), 5.74 (d, *J*= 17.0Hz, 1H, CH_2=C), and 6.06 (dd, *J*= 17.0, 10.5Hz, 1H, CH)[4b]; δ_C 15.70, 17.79 (2d, *J*= 7.0Hz,2xCH_3CH_2), 27.73 (d, *J*= 5.0Hz, CH_3CO), 64.24, 64.32 (2d, *J*= 6.0Hz, 2xCH_2O), 74.15 (d, *J*= 7.0Hz, CO), 117.01 (d, *J*= 4.0Hz, CN), 118.62 (CH_2=C), and 134.57 (d, *J*= 4.5Hz, CH); *m/z* 233 (M^+, 0.8%), 177 (21), 127 (42), 125 (19), 109 (20), 99 (100), 97 (40), 82 (13), 81 (41), 80 (28), 79 (16), and 53 (20).

2-Ethyl-2-(diethylphosphonooxy)butanenitrile (**2h**): R_f 0.44; ν_{max} 1270 (P=O) and 1020 cm^{-1} (P-O); δ_H 1.12 (t, *J*= 7.5Hz, 6H, 2xCH_3CH_2C), 1.37 (t, *J*= 7.0Hz, 2xCH_3CH_2O), 2.08 (m, 4H, 2xCH_2C), and 4.18 (m, 4H, 2xCH_2O); δ_C 8.04 (2xCH_3CH_2C), 15.82 (d, *J*= 6.5Hz, 2xCH_3CH_2O), 31.29 (d, *J*= 4.0Hz, 2xCH_2C), 64.22 (d, *J*= 6.0Hz, 2xCH_2O), 79.80 (d, *J*= 8.0Hz, CO), and 117.76 (d, *J*= 5.5Hz, CN); δ_P -5.4; *m/z* 234 (M^+-15, 0.7%), 164 (15), 155 (41), 127 (63), 109 (13), 99 (100), 81 (26), and 57 (13). Anal. Calcd. for $C_{10}H_{20}NO_4P$: C, 48.19; H, 8.09; N, 5.60. Found: C, 48.60; H, 7.80; N, 5.75.

cis/trans-*1-(Diethylphosphonooxy)-1,3-cyclopentanedicarbonitrile* (**4i**): ν_{max} 2240 (CN), 1270 (P=O), and 1000 cm^{-1} (P-O); δ_H 1.38 (t, *J*= 7.0Hz, 6H, 2xCH_3), 2.63 (m, 6H, 3xCH_2C), 3.28 (m, 1H, CH), and 4.21 (m, 4H, 2xCH_2O); δ_C 15.77 (d, *J*= 6.5Hz, 2xCH_3), 25.27, 25.39 (CH), 27.74, 28.20 (CH_2CH_2CH), 38.83, 39.15 (2d, *J*= 5.0 and 4.5Hz, respectively, $OCCH_2CH_2$), 43.48, 43.55 (2d, *J*= 5.5 and 5.0Hz, respectively, $OCCH_2CH$), 64.60, 64.76 (2d, *J*= 5.5 and 6.0, respectively, CH_2O), 104.25, 104.32 (CO), 116.85 (d, *J*= 1.5Hz, OCCN), 117.14 (OCCN), 120.42 and 120.43 (CHCN); δ_P -4.7 and -4.9; *m/z* 271 (M^+-1, 0.6%), 127 (39), 125 (12), 99 (100), 92 (15), 91 (82), 82 (15), 81 (45), 65 (19), 64 (15), and 63 (12). Anal. Calcd. for $C_{11}H_{17}N_2O_4P$: C, 48.53; H, 6.29; N, 10.29. Found: C, 48.09; H, 6.57; N, 10.41.

1-(Diethylphosphonooxy)cyclohexanecarbonitrile (**2j**)[8]: R_f 0.47; ν_{max} 1270 (P=O), 1030, and 1000 cm^{-1} (P-O); δ_H 1.37, 1.38 (2t, *J*= 7.0Hz, 6H, 2xCH_3), 1.64, 1.84, 1.97, 2.30 (4m, 10H, 5xCH_2C), and 4.18 (m, 4H, 2xCH_2O); δ_C 15.79 (d, *J*= 7.0Hz, 2xCH_3), 22.30, 23.89 (3xCH_2), 36.81 (d, *J*= 5.0Hz, 2x CH_2CO), 64.18 (d, *J*= 6.0Hz, 2xCH_2O), 75.59 (d, *J*= 8.0 Hz, CO), and 118.34 (d, *J*= 3.5Hz, CN); *m/z* 246 (M^+-15, 0.2%), 155 (43), 127 (58), 94 (100), 81 (31), and 41 (17).

1-(Diethylphosphonooxy)-4-oxocyclohexanecarbonitrile Ethylene Ketal (**2k**): R_f 0.31; ν_{max} 1270 (P=O) and 1000 cm^{-1} (P-O); δ_H 1.38 (t, *J*= 7.0Hz, 2xCH_3), 1.83 (m, 4H, 2xCH_2CO), 2.33 (m, 4H, 2xCH_2CCN), 3.96 (s, 4H, OCH_2CH_2O), and 4.18 (m, 4H, CH_2CH_3); δ_C 15.87 (d, *J*= 7.0Hz, 2xCH_3), 30.37 (2xCH_2CO), 34.38 (d, *J*= 5.0Hz, 2xCH_2CCN), 64.38, 64.42 (OCH_2CH_2O), 64.41 (d, *J*= 5.5Hz, 2xCH_2OP), 73.48 (d, *J*= 8.0Hz, COP), 106.16 ($COCH_2$), and 118.18 (d, *J*= 2.5Hz, CN); δ_P -4.9; *m/z* 291 (M^+-28, 1.1%), 163 (38), 99 (65), 86 (100), and 81 (11).

2-(Diethylphosphonooxy)-2-phenylpropanenitrile **(2l)**[2a]: R_f 0.41; ν_{max} 2220 (CN), 1270 (P=O), 1030, and 980 cm^{-1} (P-O); δ_H 1.28, 1.32 (2t, J= 7.0Hz, 6H, 2xCH_3CH_2), 2.14 (s, 3H, CH_3CO), 4.09 (m, 4H, 2xCH_2), 7.46, and 7.64 (2m, 5H, Ph); δ_C 15.70, 15.72 (2d, J= 7.0Hz, 2xCH_3CH_2), 30.13 (d, J= 5.0Hz, CH_3CO), 64.22, 64.31 (2d, J= 6.5Hz, 2xCH_2), 75.44 (d, J= 8.0Hz, CO), 118.15 (CN), 124.91, 128.65, 129.48 (3xCH-Ph), and 137.73 (d, J= 5.5Hz, C_i-Ph); *m/z* 284 (*M*$^+$+1, 1%), 283 (*M*$^+$, 13), 155 (15), 147 (70), 131 (12), 130 (56), 129 (100), 128 (15), 127 (32), 125 (14), 105 (19), 103 (52), 102 (25), 99 (58), 91 (10), 82 (10), 81 (35), 78 (14), 77 (48), and 51 (15).

2-(Diethylphophonooxy)bicyclo[2.2.1]heptane-2-carbonitrile **(2m)**: R_f 0.58; ν_{max} 2225 (CN), 1280 (P=O), and 1025 cm^{-1} (P-O); δ_H 1.38 (m, 6H, 2xCH_3), 1.57, 1.87, 2.36 (3m, 7H, CH_2CH_2 and $CHCH_2CO$), 2.39 (d, J= 3.0Hz, 2H, CH_2CO), 2.89 (m, CHCO), and 4.20 (m, 4H, 2xCH_2O); δ_C 15.79 (d, J= 7.0Hz, 2x CH_3), 20.75, 27.93, 37.20 (CH_2CH_2 and $CHCH_2CH$), 39.09 ($CHCH_2CO$), 44.36 (d, J= 4.5Hz, CH_2CO), 48.15 (d, J= 5.0Hz, CHCO), 64.20, 64.27 (2d, J= 5,5Hz, 2xCH_2O), 77.99 (d, J= 9.0Hz, COP), and 119.95 (CN); δ_P -4.0; *m/z* 273 (*M*$^+$, 0.3%), 206 (14), 155 (100), 150 (21), 127 (37), 99 (54), 91 (19), 81 (32), 67 (16), 65 (12), and 41 (13). Anal. Calcd. for $C_{12}H_{20}NO_4P$: C, 52.74; H, 7.38; N, 5.13. Found: C, 52.32; H, 7.29; N, 5.12.

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