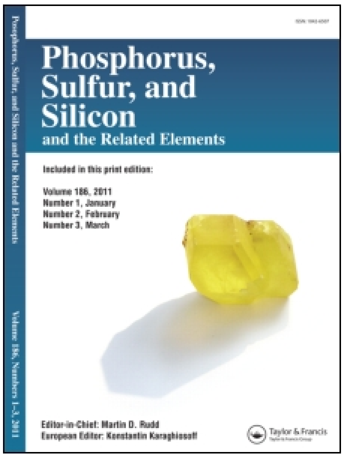

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Efficient Synthesis of 2-Methylene-3phosphorylalkanoates: Phosphorylation of Baylis-Hillman Bromides via an S<i>N</i>2-S<i>N</i>2' Strategy

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Efficient Synthesis of 2-Methylene-3-phosphorylalkanoates: Phosphorylation of Baylis–Hillman Bromides via an S_N2-S_N2' Strategy

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A novel synthesis of 2-methylene-3-phosphorylalkanoates under mild conditions is described. Thus, Balyis–Hillman bromides react with secondary phosphine oxides or H-phosphonites in the presence of DABCO via an S_N2-S_N2' protocol to produce the target compounds in good yields.

Keywords Baylis–Hillman bromides; DABCO; nucleophilic substitution; phosphorylation

INTRODUCTION

The Morita–Baylis–Hillman reaction produces highly functionalized molecules, which have been widely used for the synthesis of various biologically active molecules and natural products.[1–10] Recently, the Baylis–Hillman bromides **1**, (Z)-allyl bromides obtained from the Baylis–Hillman adducts, have attracted much attentions as synthetic intermediates.[4] Nucleophiles can substitute the bromide atom of **1** to give **2** (S_N2)[11–13] or attack the vinyl carbon of **1** to give **4** (S_N2')[14,15] depending on the starting materials and reaction conditions (Scheme 1). In many cases, the S_N2 and S_N2' reactions compete and lead to mixtures of **2** and **4**. Selective preparation of **4** can be achieved via the successive S_N2–S_N2' reaction of Baylis–Hillman bromides **1** via **3** as shown in Scheme 1. However, the first S_N2 type reaction leading to **3** by the first nucleophile, Nu′, must occur completely in order to

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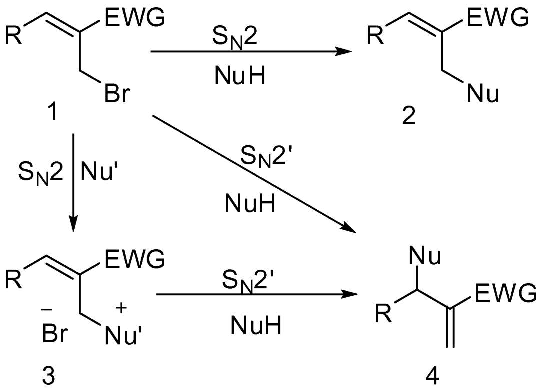


SCHEME 1

synthesize **4** in a pure state. Otherwise, the competing S_N2 reaction by the second nucleophile, NuH, leading to **2**, can occur along with the next S_N2' reaction. In such a situation, mixtures might be obtained. An additional requirement for the effective preparation of type **4** compounds is that the first nucleophile should be exchanged by a second nucleophile effectively. Transformation of **1** to **3** could be possible with DABCO[16] or DBU.[17,18] Some nucleophiles have been used in the next S_N2' step, which includes $LiBEt_3H$,[19] $NaBH_4$,[16] nitroalkenes,[17] hydroperoxides,[20] and zwitterion derived from DABCO and acrylonitrile.[18,21]

In connection to our ongoing research program in bioactive chemistry,[15] we directed our studies towards phosphorylation of Baylis–Hillman bromides **1** to produce 2-methylene-3-phosphorylalkanoates (type **4** compounds) as lead compounds. The target compounds contain active methylene and P-C bond, and will be versatile intermediates in bioorganic chemistry. Thus we aimed to prepare the intended compounds by the successive S_N2–S_N2' strategy from the Baylis–Hillman bromides **1**. To the best of our knowledge, there has been no reported use of any nucleophilic R′R″P(O)H in these transformations. Although Du et al.[22] have reported the preparation of one of 2-methylene-3-phosphorylalkanoates via *tert*-butyl carbonate of the Morita–Baylis–Hillman products, the use of cheap and easily obtained Baylis–Hillman bromides **1** as electrophiles provided a promising way to get 2-methylene-3-phosphorylalkanoates.

In this article, we would like to describe the results on the reaction of R′R″P(O)H, involving secondary phosphine oxides or H-phosphonites, with some DABCO salts of Baylis–Hillman bromides derived from arylaldehydes.

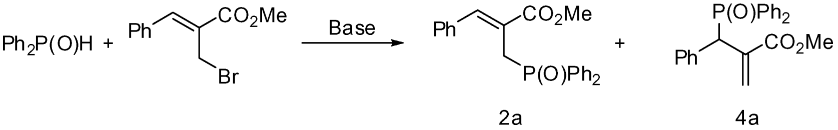
TABLE I Synthesis of 2-Methylene-3-phosphorylalkanoates (4a–i)

Entry	R′R″P(O)H	Baylis–Hillman bromides	Product	Yield (%)[a]
1	5a	1a	4a	82
2	5a	1a	4a	83[b]
3	5a	1b	4b	79
4	5a	1b	4b	81[b]
5	5a	1c	4c	80
6	5a	1c	4c	82[b]
7	5a	1d	4d	81
8	5a	1e	4e	75
9	5a	1f	4f	85
10	5b	1f	4g	84
11	5c	1f	4h	32
12	5c	1f	4h	61[b]
13	5c	1g	4i	34
14	5c	1g	4i	63[b]

[a]Isolated yields.
[b]Toluene as solvent.

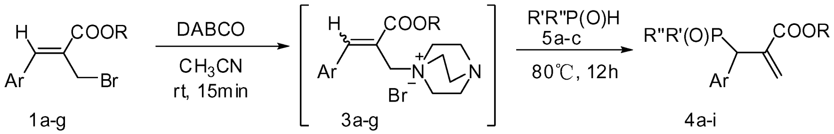
RESULTS AND DISCUSSION

Accordingly, we have first examined the reaction of (Z)-methyl 2-(bromomethyl)-3-phenylacrylate (**1a**)[23,24] with diphenylphosphine oxide (**5a**) in acetonitrile under various conditions. The best results were obtained when (Z)-methyl 2-(bromomethyl)-3-phenylacrylate (**1a**) (1 mmol) was treated with DABCO (2 mmol) in acetonitrile at room temperature for 15 min, followed by treatment with diphenylphosphine oxide (**5a**) (1 mmol) for 12 h at 80°C under nitrogen, thus providing the desired methyl 2-((diphenylphosphoryl) (phenyl)methyl)acrylate (**4a**) after the usual work-up, followed by column chromatography in 82% yield (Table I, Entry 1). However, when K_2CO_3 or Et_3N was added as base, mixture of **2a** and **4a** were obtained with the ratio of **2a**/**4a** 3/7 and 4/6 respectively (Scheme 2).



SCHEME 2

This methodology was then extended to a representative class of the Baylis–Hillman bromides (**1b–g**)[23,24]; a variety of 2-methylene-3-phosphoryl-alkanoates (**4b–i**) have been synthesized in good to high



	Ar	R
1a:	Ar = Ph,	R= Me
1b:	4-ClPh,	Me
1c:	4-ClPh,	Et
1d:	2,4-Di-ClPh,	Et
1e:	Furan-2-yl,	Me
1f:	4-Nitrophenyl,	Et
1g:	Ph,	Me

5a: R' = R" = Ph
5b: R' = R" = $PhCH_2$
5c: R' = R" = EtO

SCHEME 3

yields (Scheme 3, Table I). Changing R from Me to Et had little effect on yields of the desired product (Table I, Entries 3, 5). However, when **5c** was used as nucleophile under similar conditions, only moderate yields of **4h** and **4i** were obtained (Entries 11, 13); presumably side reactions took place via the cleavage of P-O bonds. When toluene was used as solvent, higher yields of **4h** and**4i** were achieved (Entries 12, 14). Toluene was also a suitable solvent in the preparation of other 2-methylene-3-phosphoryl-alkanoates (Entries 2, 4, 6).

CONCLUSION

A new and convenient protocol for the synthesis of 2-methylene-3-phosphorylalkanoates involving successive S_N2–S_N2' reaction of the Baylis–Hillman bromides with secondary phosphine oxides or H-phosphonites was developed.

EXPERIMENTAL

General

All reactions were carried out under nitrogen atmosphere. Diphenylphosphine oxide (**1a**),[25] dibenzylphosphine oxide (**1b**),[26] and (Z)-allyl bromides (**2a–f**)[23,24] were prepared according to the reported procedures. Other reagents and solvents were commercially available and distilled, recrystallized, or dehydrated thoroughly. Melting points were determined on a Buchi melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were performed on a Mercury 300 spectrometer (Varian, ^1H: 300 MHz, ^{13}C: 75 MHz) with $CDCl_3$ as the solvent and TMS as the internal standard. ^{31}P NMR spectra were obtained on the Mercury 300 (Varian, 121 MHz) spectrometer using H_3PO_4 as an internal standard. Infrared spectra were recorded with a PE-983G instrument (Perkin-Elmer). Mass spectra were recorded on FTICR-MS (Ionspec 7.0T). Combustion analyses for C and H elemental composition were made with a Vario EL III analyzer (Elementar). Phosphorus contents were determined by oxygen flask method. All reactions were monitored by TLC.

General Procedure for the Preparation of 2-Methylene-3-phosphorylalkanoates

To a flask purged with N_2 containing acetonitrile or toluene (3 mL), Baylis–Hillman bromides (**1a–g**) (1mmol) and DABCO (2 mmol) were added. The reaction mixture was stirred at room temperature for 15min, then R′R″P(O)H (**5a–c**) (1 mmol) was added and stirred at 80°C for 8–16 h under nitrogen. The reaction was continued until complete consumption of the R′R″P(O)H, which is monitored by TLC or HPLC, then diluted with CH_2Cl_2 (15 mL), washed with water and brine, dried over anhydrous sodium sulphate, and concentrated under reduced pressure. Subsequent flash column chromatography over silica gel gave products **4a–i**.

Methyl 2-((Diphenylphosphoryl)(phenyl) methyl)acrylate (4a)

White solid: mp 146–147°C, IR (KBr): 3421, 3055, 2947, 1718, 1620, 1491, 1437, 1323, 1242, 1184, 1128 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.62 (s, 3H), 5.04 (d, J = 8.4 Hz, 1H), 6.43 (d, J = 1.8 Hz, 1H), 6.82 (d, J = 2.4 Hz, 1H), 7.16–7.23 (m, 3H), 7.25–7.28 (m, 2H), 7.32–7.37 (m, 3H), 7.44–7.50 (m, 5H), 7.50–7.91 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 45.61 (d, J = 67.3 Hz), 52.24, 127.14 (d, J = 2.0 Hz), 127.97, 128.13, 128.23, 128.46, 128.53, 128.61, 130.00, 130.08, 130.90, 131.02, 131.11, 131.23, 131.36(d, J = 2.6 Hz), 131.66 (d, J = 2.6 Hz), 132.84 (d, J = 5.4 Hz), 134.70 (d, J = 5.2 Hz), 136.45 (d, J = 2.0 Hz), 166.73 (d, J = 9.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ 31.55; Anal. calcd for $C_{23}H_{21}O_3P$: C, 73.39; H, 5.62; P, 8.23; found: C, 73.37; H, 5.65; P, 8.20.

Methyl 2-((4-Chlorophenyl)(diphenylphosphoryl) methyl)acrylate (4b)

White solid: mp 186–187°C, IR (KBr): 3429, 3055, 2951, 1724, 1614, 1489, 1437, 1309, 1244, 1180, 1130 cm^{-1}; ^1H NMR (300 MHz, CDCl3): δ 3.63 (s, 3H), 5.01 (d, J = 8.4 Hz, 1H), 6.43 (s, 1H), 6.79 (s, 1H), 7.15 (d, J = 8.4 Hz, 2H), 7.28–7.31 (m, 4H), 7.36–7.52 (m, 6H), 7.86 (t, J = 8.1 Hz, 2H);^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 45.04 (d, J = 69.2 Hz), 52.33, 128.16, 128.31, 128.42, 128.54, 128.69, 130.43, 130.51, 130.85, 130.96, 131.05, 131.17, 131.29, 131.36, 131.59, 131.82, 136.30 (d, J = 1.1 Hz), 165.90 (d, J = 8.2 Hz); ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ 31.21. Anal. calcd for $C_{23}H_{20}ClO_3P$: C, 67.24; H, 4.91; P, 7.54; found: C, 67.26; H, 4.94; P, 7.50.

Ethyl 2-((4-Chlorophenyl)(diphenylphosphoryl) methyl)acrylate (4c)

White solid: mp 114–115°C, IR (KBr): 3425, 3057, 2983, 1622, 1489, 1439, 1309, 1236, 1188, 1122 cm^{-1}; ^{1}H NMR (300 MHz, CDCl3): δ 1.18 (t, J = 6.9 Hz, 3H), 4.03–4.11 (m, 2H), 5.04 (d, J = 7.8 Hz, 1H), 6.44 (s, 1H), 6.77 (s, 1H), 7.13 (d, J = 7.8 Hz, 2H), 7.29–7.40 (m, 5H), 7.47–7.52 (m, 5H), 7.87 (t, J = 8.0 Hz, 2H);^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.97, 44.95 (d, J = 68.7 Hz), 61.40, 128.19, 128.34, 128.44, 128.56, 128.69, 130.31, 130.89, 131.00, 131.11, 131.23, 131.32, 131.38, 131.62, 131.84, 133.27, 133.41, 136.40, 166.12 (d, J = 9.2 Hz); ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ 31.60. Anal. calcd for $C_{24}H_{22}ClO_3P$: C, 67.85; H, 5.22; P, 7.29; found: C, 67.81; H, 5.24; Cl, 8.30; O, 11.35; P, 7.24.

Ethyl 2-((2,4-dichlorophenyl)(diphenylphosphoryl) methyl)acrylate (4d)

White solid: mp 128–129°C, IR (KBr): 3059, 2982, 1716, 1622, 1583, 1470, 1439, 1369, 1294, 1230, 1194, 1119, 1026 cm^{-1}; ^{1}H NMR (300 MHz, CDCl3): δ 1.17 (t, J = 7.2 Hz, 3H), 4.00–4.04 (m, 2H), 5.64 (d, J = 8.7 Hz, 1H), 6.50 (d, J = 2.4 Hz, 1H), 6.63 (d, J = 2.4 Hz, 1H), 7.19–7.33 (m, 4H), 7.39–7.53 (m, 6H), 7.83–7.90 (m, 2H), 7.98 (dd, J = 10.2 Hz, J = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.97, 40.65 (d, J = 66.4 Hz), 61.36, 127.30, 128.15, 128.31, 128.49, 128.65, 128.97, 130.98, 131.11, 131.37, 131.43, 131.49, 131.86 (d, J = 2.3 Hz), 131.99, 132.07 (d, J = 3.5 Hz), 132.62 (d, J = 4.0 Hz), 133.78 (d, J = 2.3 Hz), 135.31 (d, J = 8.0 Hz), 135.84 (d, J = 2.9 Hz), 165.68 (d, J = 8.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ 31.31. Anal. calcd for $C_{24}H_{21}Cl_2O_3P$: C, 62.76; H, 4.61; P, 6.74; found: C, 62.71; H, 4.63; P, 6.71.

Methyl 2-((Diphenylphosphoryl)(furan-2-yl)methyl)acrylate (4e)

White solid: mp 82–83°C, IR (KBr): 3059, 2926, 2854, 1718, 1622, 1587, 1500, 1437, 1392, 1271, 1203, 1120 cm^{-1}; ^{1}H NMR (300 MHz, CDCl3): δ 3.54 (s, 3H), 5.38 (d, J = 10.5 Hz, 1H), 6.20–6.22 (m, 1H), 6.39–6.41 (m, 1H), 6.53 (dd, J = 10.2 Hz, J = 3.5 Hz, 2H), 7.23 (s, 1H), 7.35–7.48 (m, 6H), 7.65–7.81 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 34.81 (d, J = 67.0 Hz), 47.09, 104.67, 105.55, 123.13, 123.28, 126.25, 126.37, 126.50, 126.59, 126.64, 126.68, 126.70, 126.74, 128.14

(d, J = 4.1 Hz), 136.95 (d, J = 1.7 Hz), 143.24 (d, J = 4.0 Hz), 161.23 (d, J = 5.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ 29.59. Anal. calcd for $C_{21}H_{19}O_4P$: C, 68.85; H, 5.23; P, 8.45; found: C, 68.90; H, 5.26; P, 8.41.

Ethyl 2-((Diphenylphosphoryl)(4-nitrophenyl)methyl)acrylate (4f)

White solid: mp 155–156°C, IR (KBr): 3417, 3059, 2980, 1713, 1626, 1516, 1437, 1319, 1244, 1180, 1124 cm^{-1}; ^{1}H NMR (300 MHz, CDCl3): δ 1.19 (t, J = 6.9 Hz, 3H), 4.06–4.14 (m, 2H), 5.17 (d, J = 8.1 Hz, 1H), 6.51 (d, J = 1.5 Hz, 1H), 6.85 (d, J = 2.1 Hz, 1H), 7.27–7.33 (m, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.48–7.55 (m, 7H), 7.86–7.91 (m, 2H), 8.02 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.92, 45.49 (d, J = 67.3 Hz), 61.21, 127.08 (d, J = 2.0 Hz), 127.94, 128.10, 128.20, 128.40, 128.55, 129.97, 130.05, 130.87, 130.99, 131.09, 131.21, 131.31 (d, J=2.6 Hz), 131.60 (d, J=2.6 Hz), 132.86 (d, J = 5.2 Hz), 134.85 (d, J = 5.4 Hz), 136.67, 166.21 (d, J = 9.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ 31.60. Anal. calcd for $C_{24}H_{22}NO_5P$: C, 66.20; H, 5.09; P, 7.11; found: C, 66.23; H, 5.11; P, 7.10.

Ethyl 2-((Dibenzylphosphoryl)(4-nitrophenyl)methyl)acrylate (4g)

White solid: mp 110–111°C, IR (KBr): 3063, 2982, 2929, 1711, 1622, 1599, 1522, 1495, 1454, 1402, 1348, 1311, 1242, 1186, 1128 cm^{-1}; ^{1}H NMR (300 MHz, CDCl3): δ 1.26 (t, J = 7.2 Hz, 3H), 2.85–2.90 (m, 2H), 3.17–3.24(m, 2H), 4.12–4.17 (m, 2H), 4.34 (d, J = 6.9 Hz, 1H), 6.49 (s, 1H), 6.80 (s, 1H), 7.00–7.03 (m, 2H), 7.14–7.17 (m, 5H), 7.17–7.29 (m, 3H), 7.61 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 14.02, 34.95 (d, J = 20.6 Hz), 35.77 (d, J = 18.6 Hz), 44.30 (d, J = 59.4 Hz), 61.65, 123.65, 126.90 (d, J = 2.3 Hz), 127.147 (d, J = 2.6 Hz), 128.49 (d, J = 1.4 Hz), 128.79 (d, J = 1.7 Hz), 129.68, 129.74, 130.44, 130.50, 130.61, 130.68, 130.74, 130.83, 131.42 (d, J = 6.6 Hz), 136.01(d, J = 2.6 Hz), 143.62 (d, J = 4.6 Hz), 147.17, 165.72 (d, J = 8.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ 43.77. Anal. calcd for $C_{26}H_{26}NO_5P$: C, 67.38; H, 5.65; P, 6.68; found: C, 67.37; H, 5.67; P, 6.67.

Ethyl 2-((Diethoxyphosphoryl)(4-nitrophenyl)methyl)acrylate (4h)

Pale yellow oil, IR (KBr): 3059, 2983, 2906, 1714, 1651, 1622, 1493, 1439, 1392, 1319, 1240, 1205, 1132,1053, 1026, 966, 700 cm^{-1}; ^{1}H NMR (300 MHz, CDCl3): δ 1.07 (t, J = 7.2 Hz, 3H), 1.17–1.30 (m, 6H), 3.68–3.74 (m, 1H), 3.86–3.91 (m, 1H), 4.04–4.19 (m, 4H), 4.60 (d, J = 24.3 Hz, 1H), 6.54–6.56 (m, 2H), 7.16–7.28 (m, 2H), 7.44–7.49 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.94, 16.03 (d, J = 5.7 Hz), 16.22 (d, J = 6.0 Hz), 44.2 (d, J = 140.8 Hz), 61.16, 62.32 (d, J = 7.1 Hz), 62.80 (d, J = 6.9 Hz), 127.28 (d, J = 2.6 Hz), 128.33 (d, J = 1.73 Hz), 128.43, 128.52, 129.50, 129.59, 134.81 (d, J = 6.1 Hz), 136.21 (d, J = 1.7 Hz), 165.99 (d, J = 14.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ 24.62. Anal. calcd for $C_{16}H_{22}NO_7P$: C, 51.75; H, 5.97; P, 8.34; found: C, 51.73; H, 5.99; P, 8.30.

Ethyl 2-((Diethoxyphosphoryl)(phenyl)methyl)acrylate (4i)

Colorless oil, IR (KBr): 3063, 2983, 2933, 1716, 1651, 1622, 1493, 1454,1392, 1296, 1242, 1132, 1055, 1026, 964 cm^{-1}; ^{1}H NMR (300 MHz, CDCl3): δ 1.07 (t, J = 7.1 Hz, 3H), 1.22–1.31 (m, 6H), 3.68–3.74 (m, 1H), 3.86–3.91 (m, 1H), 4.04–4.20 (m, 4H), 4.59 (d, J = 24.0 Hz, 1H), 6.53–6.55 (m, 2H), 7.25–7.34 (m, 3H), 7.44–7.47 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.97, 16.06 (d, J = 5.8 Hz), 16.25 (d, J = 5.7 Hz), 43.94 (d, J = 140.8 Hz), 61.18, 62.36 (d, J = 7.4 Hz), 62.83 (d, J = 6.9 Hz), 127.30 (d, J = 2.9 Hz), 128.36 (d, J = 1.65 Hz), 128.45, 128.53, 129.54, 129.64, 134.89 (d, J = 6.3 Hz), 136.29 (d, J = 2.3 Hz), 166.04 (d, J = 14.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ 24.60. Anal. calcd for $C_{16}H_{23}O_5P$: C, 58.89; H, 7.10; P, 9.49; found: C, 58.90; H, 7.13; P, 9.46.

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