4-Aminophenyldiphenylphosphinite (APDPP), a new heterogeneous and acid scavenger phosphinite — Conversion of alcohols, trimethylsilyl, and tetrahydropyranyl ethers to alkyl halides with halogens or *N*-halosuccinimides

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Abstract: A new heterogeneous phosphinite, 4-aminophenyldiphenylphosphinite (APDPP), is prepared and used for the efficient conversion of alcohols, trimethylsilyl ethers, and tetrahydropyranyl ethers to their corresponding bromides, iodides, and chlorides in the presence of molecular halogens or *N*-halosuccinimides. The amino group in this phosphinite acts as an acid scavenger and removes the produced acid. A simple filtration easily removes the phosphinate by-product.

Key words: 4-aminophenyldiphenylphosphinite, alcohol, trimethylsilyl ether, tetrahydropyranyl ether, alkyl halide.

Résumé : On a préparé un nouveau phosphinite hétérogène, le phosphinite de 4-aminophényle et de diphényle, et on l'a utilisé pour la conversion efficace d'alcools et d'éthers triméthylsyles ou tétrahydropyranyles en bromures, chlorures et iodures correspondants en présence d'halogènes moléculaires ou de *N*-halogénosuccinimides. La groupe amino de ce phosphinite agit comme piège et permet d'enlever l'acide qui est produit. Une filtration simple permet d'enlever la phosphinate obtenu comme sous-produit.

Mots clés : phosphinite de 4-aminophényle et de diphényle, alcool, éther triméthylsilyle, éther tétrahydropyranyle, halogénure d'alkyle.

[Traduit par la Rédaction]

Introduction

The very useful application of tertiary phosphines as oxophiles has been widely studied in organic synthesis. Conversion of alcohols into alkyl halides using triphenylphosphine, one of the most popular phosphines under Mitsunobu conditions, or in the presence of molecular halogens has been widely studied (1–12). Isolation of the phosphine oxide by-product is considered a drawback of using homogeneous phosphine reagents. To simplify the workup procedure for the removal of phosphine oxides, the use of a limited number of heterogeneous phosphines is reported. The use of polymer-supported triphenylphosphine has the usual problem of lower efficiency of the polymeric reagents compared with monomeric ones (6*a*, 13–17). Tris{4-(1*H*,1*H*-perfluorooctyloxy)phenyl]phosphine has been reported as another heterogeneous phosphine (18). Using diphos-1,2-bis(diphenylphosphino)ethane as an interesting source of phosphines for this purpose still suffers from the problem that only 75% of diphos oxide can be removed under optimized conditions (19). Recently, we prepared a silica-based inorganic phosphine reagent (silphos) and applied it to the conversion of alcohols into their corresponding alkyl halides (17). Another drawback of using phosphines in conjunction with molecular halogens for the preparation of alkyl halides from alcohols is the production of HX in the reaction mixture, which may cause problems for acid-sensitive functional groups.

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Results and discussion

In this work, we introduce 4-aminophenyldiphenylphosphinite (APDPP) as a new heterogeneous monomeric phosphinite reagent. In the presence of molecular halogens, this reagent efficiently converts alcohols into alkyl halides. The presence of an amino group makes this reagent an efficient acid scavenger and removes the HX produced from the reaction mixture. A simple filtration separates the ammonium salt of the produced phosphinate and leaves the pure product.

We successfully applied this easily prepared heterogeneous phosphinite to the conversion of different classes of alcohols to alkyl halides in the presence of molecular bromine, iodine, and *N*-halosuccinimides (NXS, X = Cl, Br, I) in dichloromethane at room temperature (Scheme 1).

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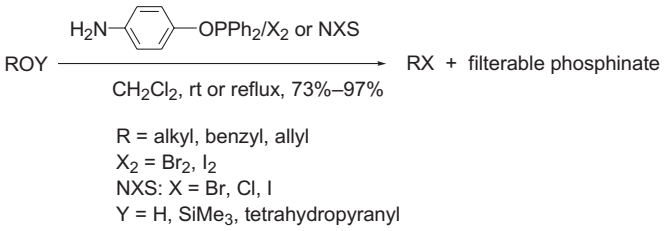
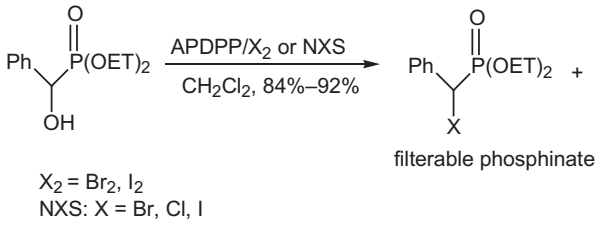
Scheme 1.



Scheme 2.



The optimized molar ratios of benzyl alcohol – APDPP – halogen were found to be 1:1.2:1.2 for bromination and 1:1.5:1.5 for iodination reactions. Primary, secondary, and tertiary alcohols were converted into their corresponding alkyl bromides and iodides in excellent yields using these optimized conditions (Table 1). The HX produced in this reaction reacts with the amino group of the reagent and its phosphinate is easily removed by filtration. To extend the applicability of this reagent, we replaced the molecular halogens with *N*-halosuccinimides (NXS, X = Cl, Br, I) as safer sources of halogens for the conversion of alcohols to their corresponding halides. Here again, the produced phosphinate is insoluble and can be removed by filtration.

α-Functionalized phosphonates are important organophosphorous compounds in biology, pharmacology, and organic chemistry. A few methods for the conversion of diethyl α-hydroxyphosphinates into their corresponding diethyl α-halophosphinates have been reported in the literature (20, 21*a*–21*c*). Among these methods, the use of PPh_3–Br_2 in the presence of pyridine as an acid scavenger has been also reported (21*a*).

We successfully applied APDPP to the conversion of diethyl α-hydroxyphosphinates into their corresponding diethyl α-halophosphinates in the presence of molecular halogens or *N*-halosuccinimides (Scheme 2, Table 1, entries 13 and 14). The presence of an acid scavenger amino group in the structure of APDPP for the conversion of diethyl α-hydroxyphosphinates into their corresponding diethyl α-halophosphinates eliminates the use of toxic pyridine, as reported in the literature (21*a*). The results of this study are tabulated in Table 1.

In continuation of this work, we used this new phosphinite reagent for the efficient conversion of trimethylsilyl and tetrahydropyranyl ethers to their corresponding alkyl halides in conjunction with molecular halogens or *N*-halosucinimides under heterogeneous conditions (Scheme 1). The conversion of trimethylsilyl and tetrahydropyranyl ethers to their corresponding alkyl halides with this reagent occurs at room temperature with high to excellent yields. The results are shown in Tables 2 and 3.

To show the stability of acid-sensitive compounds during the course of the reaction, we converted benzyl alcohol to its bromide and iodide in the presence of equimolar amounts of 2-phenyl-1,3-dioxolane as a highly acid-sensitive compound. The conversion of benzyl alcohol to its halides occurred quantitatively, but the 2-phenyl-1,3-dioxolane remained intact. Similarly, addition of styrene oxide to a mixture of benzyl alcohol, APDPP, and Br_2 in CH_2Cl_2 did not show the formation of any product from the ring opening of styrene oxide. These results show that the acid produced in the course of the reaction of alcohols with APDPP and halogens can be removed by the amino group of the reagent before affecting the acid-sensitive groups.

In summary, the present investigation has demonstrated the applicability of APDPP as a new heterogeneous phosphinite for the efficient conversion of alcohols, trimethylsilyl ethers, and tetrahydropyranyl ethers to their corresponding alkyl halides. α-Hydroxyphosphonates can also be converted heterogeneously into their α-halophosphonates without the need to use an additional base such as pyridine. In addition, the stability, heterogeneous nature, easy preparation, and acid-scavengering properties are considered other advantages of using APDPP for these transformations.

Experimental

Chemicals were either prepared in our laboratory or obtained from Fluka (Buchs, Switzerland) and Merck (Darmstadt, Germany) chemical companies. IR spectra were recorded on a PerkinElmer 781 spectrometer. NMR spectra were recorded on an Avance DPX 250 MHz spectrometer. GC analyses were recorded on a Shimadzu GC-14A. Mass spectra were run on Shimadzu GC-Mass-QP 1000 EX at 70 eV.

Preparation of 4-aminophenyldiphenylphosphinite (APDPP)

To a flask containing *t*-BuOH (15 mL) was added potassium (0.43 g, 11 mmol), which was stirred slowly until the potassium was completely consumed. 4-Aminophenol (1.09 g, 10 mmol) was added and the solution was stirred with a mechanical stirrer for 30 min at room temperature. To the resulting dark syrup, chlorodiphenylphosphine (1.9 mL, 10 mmol) was added dropwise for a period of 10 min at room temperature. The reaction was completed after 5 min. The obtained product was washed with 30 mL of water to remove the produced KCl. The filtered cake was washed with diethyl ether (2 × 20 mL) and dried under vacuum at room temperature. 4-Aminophenyldiphenylphosphinite was obtained as a milky white solid (0.27 g, 93%). IR (KBr): 3340 (w), 3250 (w), 2915 (m), 2361 (m), 1498 (s), 1434 (m), 1281(w), 1213 (m), 865 (m), 690 (s), 511 (m). ^{1}H NMR (DMSO, 250 MHz, ppm) δ: 4.5 (b, 2H, NH_2), 6.4–6.5 (AA′BB′, pattern, 4H), 7.1–7.74 (complex, 10H). EI-MS (70 eV) *m/e*: 293 (2.07%), 292 (4.08%), 201 (53.4%), 183 (100%), 152 (13.9%), 107 (16%), 77 (26%), 51 (14%). Anal. calcd. for $C_{18}H_{16}NOP$: C 73.71, H 5.50, N 4.78; found: C 73.35, H 5.36, N 4.65.

Table 1. Conversion of alcohols to their corresponding alkyl halides in the presence of APDPP and Br_2, I_2, NBS, NCS, and NIS.

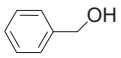
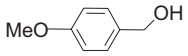
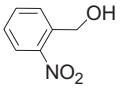
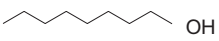
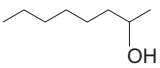
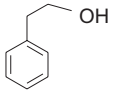
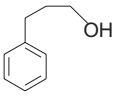
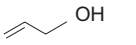
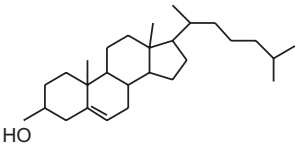
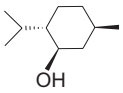
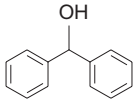
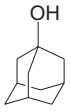
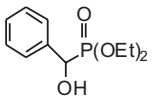
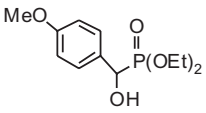
Entry	Substrate	Reagent (Time)	Conversion (%)	Isolated yield (%)
1		Br_2 (immediately)	100	95
		I_2 (immediately)	100	95
		NBS (1.5 h)	100	95
		NCS (1.5 h)	95	95
		NIS (1.5 h)	100	95
2		Br_2 (immediately)	100	95
		I_2 (immediately)	100	94
		NBS (1.5 h)	100	95
		NCS (1.5 h)	96	95
		NIS (1.5 h)	100	96
3		Br_2 (25 min)	100	97
		I_2 (2 h)	100	98
		NBS (2 h)	100	96
		NCS (10 h)	86	90
		NIS (2 h)	97	93
4		Br_2 (3 h)	100	92
		I_2 (20 min)	100	93
5		Br_2 (7 h)	94	86[a]
		I_2 (30 min)	100	91.8
		NBS (5 h)	98	89
		NCS (9 h)	87	90
		NIS (2.5 h)	97	90
6		Br_2 (2.5 h)	100	93
		I_2 (25 min)	100	91.6
		NBS (2.5 h)	92	87
		NCS (3 h)	94	87
		NIS (3.5 h)	94	85
7		Br_2 (3 h)	100	92
		I_2 (25 min)	100	92
8		Br_2 (5 min)	100	-
		I_2 (5 min)	100	-
9		Br_2 (90 min)	100	92
		I_2 (45 min)	100	95
10		Br_2 (3 h)	85	80
		I_2 (2 h)	100	92.5
11		Br_2 (2 h)	89.7	86
		I_2 (2.30 h)	95	87
		NBS (10 h)	92	82
		NCS (15 h)	95	88
		NIS (10 h)	95	88
12		Br_2 (10 h)	100	96[b]
		I_2 (24 h)	92	85[c]
		NBS (18 h)	80	75[d]
		NCS (24 h)	79	73[e]
		NIS (10 h)	77	73[f]

Table 1 (*concluded*).

Entry	Substrate	Reagent (Time)	Conversion (%)	Isolated yield (%)
13		Br_2 (6 h)	100	90
		I_2 (4 h)	100	92
		NBS (10 h)	97	88
		NCS (14 h)	95	84
		NIS (10 h)	95	87
14		Br_2 (3.5 h)	100	91
		I_2 (1.5 h)	100	95
		NBS (8.5 h)	98	89
		NCS (10 h)	95	85
		NIS (9 h)	95	87

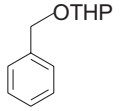
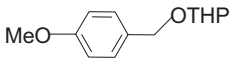
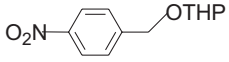
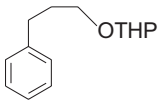
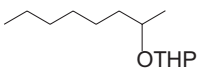
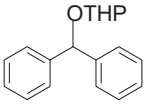
Note: The molar ratios of ROH–APDPP–Br_2, ROH–APDPP–I_2, and ROH–APDPP–NXS are 1:1.2:1.2, 1:1.5:1.5, and 1:2:2, respectively.

[a]The molar ratio of ROH–APDPP–Br_2 is 1:1.4:1.4.

[b,c]The molar ratio of ROH–APDPP–$Br_2(I_2)$ is 1:1.5:1.5.

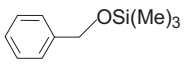
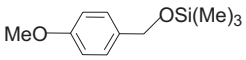
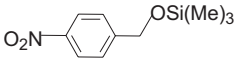
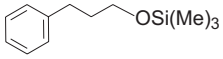
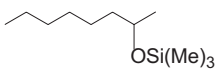
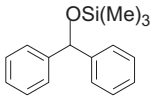
[d,e,f]The molar ratio of ROH–APDPP–NXS is 1:2.5:2.5.

Table 2. Conversion of THP ethers to alkyl halides in the presence of APDPP and Br_2, I_2, NBS, NCS, and NIS

Entry	Substrate	Reagent (Time)	Conversion (%)	Isolated yield (%)
1		Br_2 (40 min)	100	94
		I_2 (30 min)	100	95
		NBS (2 h)	100	95
		NCS (1.5 h)	100	95
		NIS (1.5 h)	100	95
2		Br_2 (30 min)	100	95
		I_2 (5 min)	100	95
		NBS (1.5 h)	100	95
		NCS (1.5 h)	100	95
		NIS (1.5 h)	100	96
3		Br_2 (75 min)	100	95
		I_2 (1 h)	100	97
		NBS (3.5 h)	95	91
		NCS (5 h)	91	85
		NIS (4 h)	93	88
4		Br_2 (5 h)	100	93
		I_2 (3 h)	100	95
		NBS (3 h)	100	95
		NCS (4 h)	89	80
		NIS (3 h)	100	95
5		Br_2 (7 h)	95	85
		I_2 (4 h)	96	87
		NBS (9 h)	88	80
		NCS (14 h)	76	70
		NIS (8.5 h)	96	87
6		Br_2 (14 h)	95	86
		I_2 (10 h)	93	84
		NBS (10 h)	90	84
		NCS (15 h)	81	75
		NIS (11 h)	92	86

Note: The molar ratios of ROTHP–APDPP–Br_2, ROTHP–APDPP–I_2, and ROTHP–APDPP–NXS are 1:1.3:1.3, 1:1.5:1.5, and 1:2:2, respectively.

Table 3. Conversion of trimethylsilyl ethers to alkyl halides in the presence of APDPP and Br_2, I_2, NBS, NCS and NIS.

Entry	Substrate	Reaction (Time)	Conversion (%)	Isolated yield (%)
1		Br_2 (immediately)	100	95
		I_2 (immediately)	100	95
		NBS (1 h)	100	95
		NCS (1 h)	100	95
		NIS (1 h)	100	95
2		Br_2 (immediately)	100	95
		I_2 (immediately)	100	96
		NBS (1 h)	100	95
		NCS (1 h)	100	96
		NIS (1 h)	100	95
3		Br_2 (50 min)	100	95
		I_2 (20 min)	100	97
		NBS (2 h)	95	91
		NCS (3 h)	90	87
		NIS (3.5 h)	95	91
4		Br_2 (5 min)	100	94
		I_2 (immediately)	100	96
		NBS (1.5 h)	100	95
		NCS (2 h)	100	95
		NIS (2.5 h)	95	86
5		Br_2 (25 min)	100	93
		I_2 (10 min)	100	95
		NBS (2 h)	100	94
		NCS (3 h)	100	94
		NIS (3 h)	100	93
6		Br_2 (1 h)	95	87
		I_2 (70 min)	100	96
		NBS (5 h)	91	81
		NCS (8 h)	86	82
		NIS (6 h)	94	88

Note: The molar ratios of $ROSiMe_3$–APDPP–Br_2, $ROSiMe_3$–APDPP–I_2, and $ROSiMe_3$–APDPP–NXS are 1:1.2:1.2, 1:1.5:1.5, and 1:2:2, respectively.

Typical procedure for the conversion of benzyl alcohol to benzyl bromide using APDPP–Br_2.

To a flask containing APDPP (0.35 g, 1.2 mmol) was added Br_2 (0.06 mL, 1.2 mmol) at room temperature in CH_2Cl_2 (7 mL) and stirred. Then benzyl alcohol (0.1 mL, 1 mmol) was added. The progress of the reaction was monitored by TLC and GC analysis. Benzyl alcohol was completely converted to benzyl bromide immediately. The reaction mixture was filtered to remove the produced insoluble phosphinate and enough powdered sodium thiosulfate was added to the solution, with vigorous stirring, to react with excess bromine. After filtration, the solvent was evaporated under vacuum in a rotary evaporator. For further purification, the product was washed over a silica gel pad (2 cm thick) using *n*-hexane – ethyl acetate as eluent. Benzyl bromide was obtained as a colourless liquid (0.16 g, 95% yield), bp 195 to 196 °C (lit. value (22) bp 196–198 °C).

Typical procedure for the conversion of benzyl alcohol to benzyl bromide with APDPP–*N*-bromosuccinimide.

To a two-necked flask containing APDPP (0.58 g, 2 mmol) and benzyl alcohol (0.1 mL, 1 mmol) in reflux dichloromethane (10 mL) was added dropwise a solution of *N*-bromosuccinimide (0.35 g, 2 mmol) in CH_2Cl_2 (10 mL) for a 1.5 h period. After the addition, GC analysis of the reaction mixture indicated when the reaction was complete. The reaction mixture was then filtered to remove the insoluble phosphinate and enough powdered sodium thiosulfate was added, with vigorous stirring, to remove any bromine produced. After filtration, the solvent was evaporated under vacuum in a rotary evaporator. The purification of the product was achieved using chromatography over a silica gel pad using *n*-hexane – ethyl acetate as eluent. Benzyl bromide was obtained as colourless liquid (0.16 g, 90% yield).

Typical procedure for the conversion of 1-octanol to 1-iodooctane using APDPP–I_2

To a flask containing a stirring mixture of APDPP (0.44 g, 1.5 mmol) in dichloromethane (20 mL) was added I_2 (0.38 g, 1.5 mmol) at room temperature. After 5 min, 1-octanol (0.15 mL, 1 mmol) was added. GC analysis showed completion of the reaction after 20 min. After removal of the produced phosphinate by filtration, enough powdered sodium thiosulfate was added, with vigorous stirring, to react with the unreacted iodine. After filtration, the solvent was evaporated under vacuum in a rotary evaporator. For further purification, the product was washed over a silica gel pad (2 cm thick) using *n*-hexane as eluent to give 1-iodooctane

(0.18 g, 93% yield, bp 226 to 227 °C (lit. value (22) bp 225 to 226 °C).

Typical procedure for the conversion of benzyltrimethylsilyl ether to benzyl bromide using APDPP–Br_2

To a flask containing a stirring mixture of APDPP (0.35 g, 1.2 mmol) was added Br_2 (0.06 mL, 1.2 mmol) at room temperature in dichloromethane (15 mL), after which benzyltrimethylsilyl ether (0.18 g, 1 mmol) was also added. TLC monitoring of the reaction showed completion of the reaction after 1 min. After filtration of the reaction mixture, enough powdered sodium thiosulfate was added, with vigorous stirring, to react with the unreacted bromine. The reaction mixture was filtered and the solvent was evaporated under vacuum in a rotary evaporator. The product was chromatographed on a short silica gel pad (2 cm thick) using *n*-hexane as eluent. Benzyl bromide was produced (0.12 g, 95% yield).

Typical procedure for the conversion of benzyltetrahydropyranyl ether to benzyl iodide by APDPP–I_2

To a stirring mixture of APDPP (0.44 g, 1.5 mmol) and I_2 (0.38 g, 1.5 mmol) in CH_2Cl_2 (10 mL) was added benzyltetrahydropyranyl ether (0.18 g, 1 mmol) at room temperature. After 30 min, TLC and GC analysis indicated that the reaction was complete. The reaction mixture was filtered and the unreacted iodine was removed by the addition, with vigorous stirring, of enough powdered sodium thiosulfate. The mixture was then filtered and the resulting solution was evaporated. To purify the product, it was passed through a short column of silica gel using *n*-hexane – ethyl acetate as eluent. Benzyl iodide was obtained (0.2 g, 95% yield). It was identified by comparison with a known sample.

Typical procedure for the conversion of diethyl α-hydroxybenzylphosphinate to diethyl α-bromobenzylphosphinate using APDPP–Br_2

To a flask containing a stirring mixture of APDPP (2 mmol, 0.58 g) was added Br_2 (2 mmol, 0.1 mL) in CH_2Cl_2 (7 mL) at room temperature. Then, diethyl α-hydroxyphosphinate (0.24 g, 1 mmol,) was added. After 6 h, the reaction mixture was filtered to remove the insoluble phosphinate and enough powdered sodium thiosulfate was added to the solution, with vigorous stirring, to react with the unreacted bromine. After filtration, the product was washed over a silica gel pad (2 cm thick) using *n*-hexane – ethyl acetate (4:1) as eluent to give α-bromophosphinate (0.275 g. 90% yield). ^{1}H NMR ($CDCl_3$, 250 MHz, ppm) δ: 1.08 (t, 3H, $^3J_{HH}$ = 7.1 Hz, 2-OCH_2CH_3), 1.26 (t, H, $^3J_{HH}$ = 7.1 Hz, 2-OCH_2CH_3), 3.79–4.00 (m, 2H, 2-OCH_2CH_3), 4.03–4.17 (m, 2H, 2-OCH_2CH_3), 4.79 (d, 1H, $^2J_{PH}$ = 12.5 Hz, -CH), 7.25–7.28 (m, 3H, -C_6H_5), 7.47–7.49 (m, 2H, -C_6H_5). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz) δ: 16.57 (d, $^3J_{CP}$ = 5.8 Hz, 2-OCH_2CH_3), 16.78 (d, $^3J_{CP}$ = 5.8 Hz, 2-OCH_2CH_3), 41.85 (d, $^1J_{CP}$ = 159.2 Hz, -CH), 64.46 (d, $^2J_{CP}$ = 4.2 Hz, 2-OCH_2CH_3), 64.57 (d, $^2J_{CP}$ = 4.2 Hz, 2-OCH_2CH_3), 129.05–129.95, 134.94, 134.99 (-C_6H_5). MS (70 eV) *m/e*: 307 [M^+], 227 [M – Br], 90 [227 – P(O)$(OEt)_2$]. Anal. calcd. for $C_{11}H_{16}BrO_3P$ (%): C 43.00, H 5.21; found: C 43.10, H, 5.30.

Typical procedure for the preparation of diethyl α-iodobenzylphosphinate from diethyl α-hydroxybenzylphosphinate using APDPP–NIS

A two-necked flask, equipped with a dropping funnel and a reflux condenser, was charged with APDPP (0.67 g, 2.3 mmol) and α-hydroxybenzylphosphinate (0.24 g, 1 mmol) in CH_2Cl_2 (10 mL) in reflux condition. Then a solution of *N*-iodosuccinimide (2.3 mmol) in CH_2Cl_2 (10 mL) was added dropwise for a 1.5 h period. TLC monitoring showed the completion of the reaction after 10 h. After filtration of the reaction mixture, the residue was chromatographed on a silica gel column, using *n*-hexane – ethyl acetate (4:1) as eluent, to give α-iodobenzylphosphinate (0.31 g, 87% yield). ^{1}H NMR ($CDCl_3$, TMS, 250 MHz, ppm) δ: 3.80–4.08 (m, 2H, 2-OCH_2CH_3), 4.18–4.27 (m, 2H, 2-OCH_2CH_3), 4.98 (d, 1H, $^2J_{PH}$ = 13.4 Hz, -CH), 7.28–7.31 (m, 3H, -C_6H_5), 7.56–7.59 (m, 2H, -C_6H_5). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz, ppm) δ: 15.41 (d, $^1J_{CP}$ = 139.9 Hz, -CH), 16.57 (d, $^3J_{CP}$ = 5.9 Hz, 2-OCH_2CH_3), 16.7 (d, $^3J_{CP}$ = 5.9 Hz, 2-OCH_2CH_3), 64.42 (d, $^2J_{CP}$ = 8.6 Hz, 2-OCH_2CH_3), 64.55 (d, $^2J_{CP}$ = 8.6 Hz, 2-OCH_2CH_3), 128.95–130.04 (-C_6H_5). MS (70 eV) *m/e*: 354 [M], 226 [M – Br], 89 [226 – P(O)$(OEt)_2$]. Anal. calcd. for $C_{11}H_{16}IO_3P$ (%): C 37.29, H, 4.52; found: C 37.5, H, 4.48.

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