

Chemistry of the Versatile
(Hydroxymethyl)phosphinyl P(O)CH₂OH
Functional Group

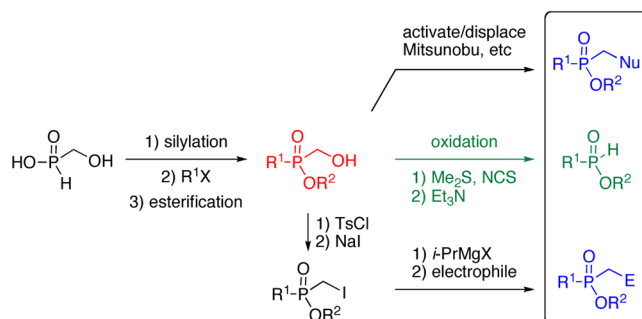
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ABSTRACT



(Hydroxymethyl)phosphorus compounds are well-known and valuable compounds in general; however the use of (hydroxymethyl)phosphinates $R^1P(O)(OR^2)CH_2OH$ in particular has been much more limited. The potential of this functionality has not yet been fully realized because the mild unmasking of the hydroxymethyl group was not available. The mild *oxidative* conversion of $R^1P(O)(OR^2)CH_2OH$ into $R^1P(O)(OR^2)H$ using the Corey–Kim oxidation is described. Other reactions preserving the methylene carbon are also reported.

Compounds containing the P–CH₂OH motif have been employed in various applications.¹ For example,

(1) For representative examples, see: (a) James, B. R.; Lorenzini, F. *Coord. Chem. Rev.* **2010**, 254, 420. (b) Swor, C. D.; Hanson, K. R.; Zakharov, L. N.; Tyler, D. R. *Dalton Trans.* **2011**, 40, 8604. (c) Hanton, M. J.; Tin, S.; Boardman, B. J.; Miller, P. J. *Mol. Catal. A: Chem.* **2011**, 346, 70. (d) Griffiths, D. V.; Groombridge, H. J.; Salt, M. C. *Phosphorus, Sulfur Silicon Relat. Elem.* **2008**, 183, 473. (e) Brown, G. M.; Elsegood, M. R. J.; Lake, A. J.; Sanchez-Ballester, N. M.; Smith, M. B.; Varley, T. S.; Blann, K. *Eur. J. Inorg. Chem.* **2007**, 1405. (f) Higham, L. J.; Whittlesey, M. K.; Wood, P. T. *Dalton Trans.* **2004**, 4202. (g) Raghuraman, K.; Pillarsetty, N.; Volkert, W. A.; Barnes, C.; Jurisson, S.; Katti, K. V. *J. Am. Chem. Soc.* **2002**, 124, 7276. (h) Henderson, W.; Alley, S. R. *J. Organomet. Chem.* **2002**, 658, 181. (i) Stark, G. A.; Riermeier, T. H.; Beller, M. *Synth. Commun.* **2000**, 30, 1703. (j) Berning, D. E.; Katti, K. V.; Barnes, C. L.; Volkert, W. A. *J. Am. Chem. Soc.* **1999**, 121, 1658. (k) Wiktelius, D.; Johansson, M. J.; Luthman, K.; Kann, N. *Org. Lett.* **2005**, 7, 4991. (l) Shioji, K.; Kurauchi, Y.; Okuma, K. *Bull. Chem. Soc. Jpn.* **2003**, 76, 833. (m) Nagata, K.; Matsukawa, S.; Imamoto, T. J. *Org. Chem.* **2000**, 65, 4185. (n) Folhr, A.; Aemissegger, A.; Hilvert, D. *J. Med. Chem.* **1999**, 42, 2633. (o) Phillion, D. P.; Andrew, S. S. *Tetrahedron Lett.* **1986**, 27, 1477. (p) Cristau, H.-J.; Hervé, A.; Virieux, D. *Tetrahedron* **2004**, 60, 877. (q) Cristau, H.-J.; Hervé, A.; Loiseau, F.; Virieux, D. *Synthesis* **2003**, 2216. (r) Kielbasiński, P.; Albrycht, M.; Luczak, J.; Mikołajczyk, M. *Tetrahedron: Asymmetry* **2002**, 13, 735. (s) Kielbasiński, P.; Omelanczuk, J.; Mikołajczyk, M. *Tetrahedron: Asymmetry* **1998**, 9, 3283. (t) Hall, R. G.; Riebli, P. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, 177, 1557.

phosphines $R^1R^2P(CH_2OH)$ are useful synthetic intermediates and ligands.^{1a–j} Similarly, their borane complexes $R^1R^2P(BH_3)CH_2OH$ have been elegantly employed in P-chiral synthesis.^{1k–m} (Hydroxymethyl)phosphonates are common precursors for nucleophilic substitution,^{1n,o} but the corresponding (hydroxymethyl)phosphinates $R^1P(O)(OR^2)CH_2OH$ **1** are less common, although they have been employed occasionally^{1p,q} and their enzymatic kinetic resolution has been described.^{1r,s} Interestingly, compounds **1** can also display significant biological activity.²

(2) (a) Vassiliou, S.; Kosikowska, P.; Grabowiecka, A.; Yiotakis, A.; Kafarski, P.; Berlicki, L. *J. Med. Chem.* **2010**, 53, 5597. (b) Coudray, L.; Kantrowitz, E. R.; Montchamp, J.-L. *Bioorg. Med. Chem. Lett.* **2009**, 19, 900. (c) Berlicki, L.; Obojska, A.; Forlani, G.; Kafarski, P. *J. Med. Chem.* **2005**, 48, 6340. (d) Furet, P.; Caravatti, G.; Denholm, A. A.; Faessler, A.; Fretz, H.; Garcia-Echeverria, C.; Gay, B.; Irving, E.; Press, N. J.; Rahuel, J.; Schoepfer, J.; Walker, C. V. *Bioorg. Med. Chem. Lett.* **2000**, 10, 2337. (e) Froestl, W.; Mickel, S. J.; Hall, R. G.; von Sprecher, G.; Diel, P. J.; Strub, D.; Baumann, P. A.; Brugger, F.; Gentsch, C.; Jaekel, J.; Olpe, H.-R.; Rihs, G.; Vassout, A.; Waldmeier, P. C.; Bittiger, H. *J. Med. Chem.* **1995**, 38, 3297. (f) Magnin, D. R.; Biller, S. A.; Dickson, J. K., Jr.; Logan, J. V.; Lawrence, R. M.; Chen, Y.; Sulsky, R. B.; Ciosek, C. P., Jr.; Harritty, T. W.; Jolibois, K. G.; Kunselman, L. K.; Rich, L. C.; Slusarchyk, D. A. *J. Med. Chem.* **1995**, 38, 2569.

Table 1. Oxidative Conversion of (Hydroxymethyl)-phosphinates into *H*-Phosphinates

$ \begin{array}{ccc} \text{R}^1\text{-P(=O)(OR}^2\text{)-CH}_2\text{OH} & \xrightarrow{\text{oxidation}} & \text{R}^1\text{-P(=O)(OR}^2\text{)-H} \\ \mathbf{1} & & \mathbf{2} \end{array} $				
entry	1	conditions ^a	product	isolated (³¹ P-NMR) yield %
1a	1a	A	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph-P-OBu} \\ \\ \text{H} \end{array} \quad \mathbf{2a} $	97 (100)
1b		B		68 (83)
2	1b	A	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph-P-OEt} \\ \\ \text{H} \end{array} \quad \mathbf{2b} $	95 (100)
3	1c	A	$ \begin{array}{c} \text{Pr} \\ \parallel \\ \text{Pr-P-OEt} \\ \\ \text{H} \end{array} \quad \mathbf{2c} $	75 (80)
4	1d	A	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph-P-OEt} \\ \\ \text{H} \end{array} \quad \mathbf{2d} $	92 (100)
5	1e	A	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Oct-P-OEt} \\ \\ \text{H} \end{array} \quad \mathbf{2e} $	66 (82)

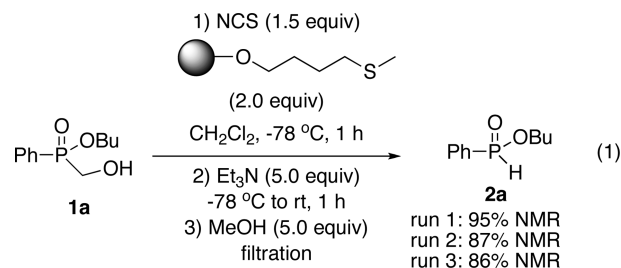
^a Conditions A: Corey–Kim oxidation; (i) *N*-chlorosuccinimide (1.5 equiv), Me₂S (1.5 equiv), CH₂Cl₂, –78 °C, 10 min; (ii) R¹P(O)(OR²)CH₂OH (1 equiv), –78 °C, 1 h; (iii) Et₃N (5 equiv), –78 °C to rt, 1 h. Conditions B: Swern oxidation; (i) DMSO (3 equiv), oxalyl chloride (1.5 equiv), CH₂Cl₂, –78 °C; (ii) R¹P(O)(OR²)CH₂OH (1 equiv), –78 °C, 1 h; (iii) Et₃N (5 equiv), –78 °C to rt.

However, one unexplored dimension is the conversion of (hydroxymethyl)phosphinates into the corresponding *H*-phosphinates R¹P(O)(OR²)H **2** so that the hydroxymethyl group becomes a P–H equivalent. Various methods have been developed for the synthesis of *H*-phosphinates,³ several of which rely on a protecting group strategy.⁴ To the best of our knowledge, however, cleavage of the protecting group is always conducted under either acidic or basic conditions.⁴

As part of our ongoing studies on the synthesis of phosphinic acids, we became interested in finding a new P–H equivalent, which could be unmasked under neutral conditions. We therefore investigated the *oxidative* cleavage of **1**. Based on the “Ciba-Geigy reagent”^{4a,b,e} the formation of an aldehyde should lead to P–C bond cleavage. At the outset, because the desired *H*-phosphinate ester is easily oxidized, many methods were expected to result in overoxidation and were not considered (for example conditions using air or other stoichiometric oxidants in the presence of a metal catalyst or reagent, or

TEMPO), even though the direct transformation of **1** into R¹P(O)(OR²)(OH) could be of interest in its own right. For example, chromate-based reagents gave low yields of *H*-phosphinate (20% with PCC, 28% with PDC, CH₂Cl₂, rt). Based on the above requirements, we quickly focused on sulfur-based oxidations such as Swern⁵ and Corey–Kim⁶ and then selected the latter as the method of choice.

Table 1 summarizes the results. Corey–Kim oxidation gave a cleaner reaction (entry 1a) than Swern oxidation (entry 1b) and consistently gave excellent results on various compounds. Although all the compounds in Table 1 were purified, in most cases the crude mixture is very clean and could be used directly in further reactions. Diethyl (hydroxymethyl)phosphonate also undergoes the reaction (76% ³¹P NMR, 62% isolated), but (hydroxymethyl)-diphenylphosphine oxide is unsatisfactory (22% ³¹P NMR). One advantage of the Corey–Kim oxidation is that the sulfide is regenerated at the end of the reaction. Because dimethyl sulfide is foul-smelling, the possibility of employing an odorless and reusable polymeric sulfide was investigated briefly (eq 1). Polystyrene supported 4-(methylthio)-1-butanol⁷ gave excellent results in three successive runs where the polymer was simply filtered, washed, dried, and reused.



The oxidative cleavage methodology was then applied to the preparation of interesting *H*-phosphinates (Scheme 1). More than 35 years ago, Rosenthal described the Arbuzov reaction of bis(trimethylsilyl) [(trimethylsilyloxy) methyl]-phosphonite (TMSO)₂PCH₂OTMS **4**,⁸ a reagent prepared from the readily available (hydroxymethyl)-*H*-phosphinic acid **3**.⁹

In principle, silylated hypophosphorous acid (bis-(trimethylsilyloxy)phosphine, BTSP, (TMSO)₂PH) can be used directly, but there are problems with this reagent (pyrophoric, competitive disubstitution, stoichiometry)³ which is well illustrated by Coward’s work with PhNCH₂PO₂H₂.¹⁰ Combining Rosenthal’s reagent with the present reaction should provide access to *H*-phosphinates not easily accessible otherwise. Scheme 1 shows a few examples of this strategy. The syntheses of

(3) Review: Montchamp, J.-L. *J. Organomet. Chem.* **2005**, 690, 2388.

(4) For example: (a) Coudray, L.; Montchamp, J.-L. *Eur. J. Org. Chem.* **2009**, 4646. (b) Fougère, C.; Guénin, E.; Hardouin, J.; Lecouvey, M. *Eur. J. Org. Chem.* **2009**, 6048. (c) Belabassi, Y.; Antczak, M. I.; Tellez, J.; Montchamp, J.-L. *Tetrahedron* **2008**, 64, 9181. (d) Abrunhosa-Thomas, I.; Sellers, C. E.; Montchamp, J.-L. *J. Org. Chem.* **2007**, 72, 2851. (e) Baylis, E. K. *Tetrahedron Lett.* **1995**, 36, 9385. (f) Baylis, E. K. *Tetrahedron Lett.* **1995**, 36, 9389.

(5) (a) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, 43, 2480. (b) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165. (c) Harris, J. M.; Liu, Y.; Chai, S.; Andrews, M. D.; Vederas, J. C. *J. Org. Chem.* **1998**, 63, 2407.

(6) (a) Corey, E. J.; Kim, C. U. *J. Am. Chem. Soc.* **1972**, 94, 7586. (b) Corey, E. J.; Kim, C. U. *Tetrahedron Lett.* **1974**, 15, 287.

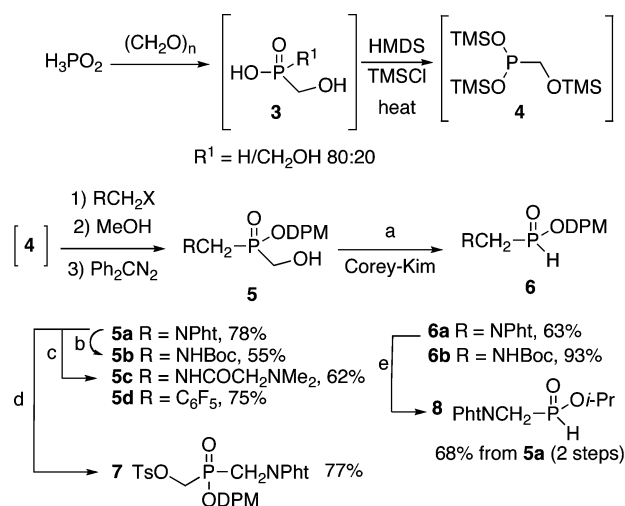
(7) Kerr, W. J.; Lindsay, D. M.; McLaughlin, M.; Pauson, P. L. *Chem. Commun.* **2000**, 1467. This is also available from Aldrich.

(8) Rosenthal, A. F.; Gringauz, A.; Vargas, L. A. *J. Chem. Soc., Chem. Commun.* **1976**, 384.

(9) For the preparation of **3**, see refs 1p and 2a.

(10) Chen, S.; Coward, J. K. *J. Org. Chem.* **1998**, 63, 502.

Scheme 1. A Strategy for the Synthesis of *H*-Phosphinates Based on the Hydroxymethyl Protecting Group^a



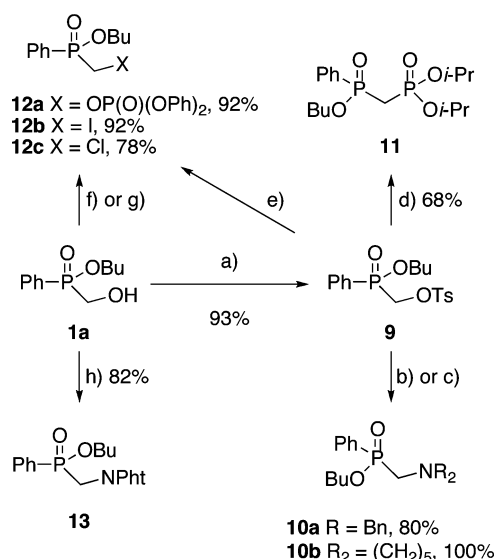
^a See Supporting Information for detailed experimental procedures. DPM = diphenylmethyl, Ph_2CH . (a) (i) *N*-Chlorosuccinimide (1.5 equiv), Me_2S (1.5 equiv), CH_2Cl_2 , $-78^\circ C$, 10 min; (ii) $R^1P(O)(OR^2)CH_2OH$ (1 equiv), $-78^\circ C$, 1 h; (iii) Et_3N (5 equiv), $-78^\circ C$ to rt, 1 h. (b) (i) H_2NNH_2 (3 equiv), THF, rt, 16 h; (ii) Boc_2O (5 equiv), $i-Pr_2NEt$ (5 equiv), THF, rt, 4 h. (c) (i) H_2NNH_2 (4 equiv), THF, rt, 16 h; (ii) Me_2NCH_2COOH (5 equiv), $HOBT$ (5 equiv), EDC (5 equiv), CH_2Cl_2 , rt, 2 h. (d) $TsCl$ (2 equiv), $i-Pr_2NEt$ (2.5 equiv), CH_2Cl_2 , rt, 24 h. (e) $i-PrOH$ (solvent), 4 Å MS, reflux, 3 h.

aminomethyl-*H*-phosphinates **6a** and **6b** and **8** were chosen because compounds of this type are very useful intermediates, often prepared through cumbersome sequences on limited scales.¹¹ Interestingly, compound **5a** is isolated as a solid, thus avoiding the need for chromatography. Direct oxidation of **5a** gave **6a**, but unfortunately pure **6a** could not be obtained because it is not very stable (purity ~85%). Therefore crude **6a** was treated with *i*-PrOH and transesterification to isopropyl ester **8** proceeded in good yield and purity (68% from **5a**). Intermediate **5a** was also converted into the Boc-protected **5b** which could then be oxidatively deprotected into **6b**. Conversion of **5a** into the *N,N*-dimethylglycine amide **5c** was uneventful. Deprotected **5c** is a known bacterial urease inhibitor.^{2a} Finally tosylation of **5a** gave compound **7**.

Having established the oxidative cleavage of (hydroxymethyl)phosphinates **1** as a viable synthetic methodology,

(11) For example, see: (a) Yamagishi, T.; Mori, J.-i.; Haruki, T.; Yokomatsu, T. *Tetrahedron: Asymmetry* **2011**, 22, 1358. (b) Yamagishi, T.; Ichikawa, H.; Haruki, T.; Yokomatsu, T. *Org. Lett.* **2008**, 10, 4347. (c) Li, S.; Whitehead, J. K.; Hammer, R. P. *J. Org. Chem.* **2007**, 72, 3116. (d) Yamagishi, T.; Haruki, T.; Yokomatsu, T. *Tetrahedron* **2006**, 62, 9210. (e) Zhukov, Y. N.; Vavilova, N. A.; Osipova, T. I.; Khurs, E. N.; Dzhevakhia, V. G.; Khomutov, R. M. *Mendeleev Commun.* **2004**, 93. (f) Cristau, H.-J.; Coulombeau, A.; Genevois-Borella, A.; Sanchez, F.; Pirat, J.-L. *J. Organomet. Chem.* **2002**, 643–644, 381. (g) Buchardt, J.; Ferreras, M.; Krog-Jensen, C.; Delaisse, J.-M.; Foged, N. T.; Meldal, M. *Chem.—Eur. J.* **1999**, 5, 2877. (h) Dorff, P. H.; Chiu, G.; Goldstein, S. W.; Morgan, B. P. *Tetrahedron Lett.* **1998**, 39, 3375. (i) Verbruggen, C.; De Craecker, S.; Rajan, P.; Jiao, X.-Y.; Borloo, M.; Smith, K.; Fairlamb, A. H.; Haemers, A. *Bioorg. Med. Chem. Lett.* **1996**, 6, 253. (j) Grobelny, D. *Synth. Commun.* **1989**, 19, 1177. (k) Dingwall, J. G.; Ehrenfreund, J.; Hall, R. G. *Tetrahedron* **1989**, 45, 3787. (l) Natchev, I. A. *Liebigs Ann. Chem.* **1988**, 861. (m) Baylis, E. K.; Campbell, C. D.; Dingwall, J. G. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2845.

Scheme 2. Activation/Nucleophilic Displacement of (Hydroxymethyl)phosphinate **1a**^a



^a (a) $TsCl$ (2 equiv), $i-Pr_2NEt$ (2.5 equiv), CH_2Cl_2 , rt, 24 h. (b) Bn_2NH (1.5 equiv), K_2CO_3 (3 equiv), CH_3CN , reflux, 48 h. (c) Piperidine (1.5 equiv), K_2CO_3 (2 equiv), CH_3CN , reflux, 16 h. (d) $(i-PrO)_2P(O)H$ (1.5 equiv), NaH (2 equiv), CH_2Cl_2 , rt, 20 h. (e) NaI (4 equiv), acetone, reflux, 24 h. (f) $ClP(O)(OPh)_2$ (1.5 equiv), $TiCl_4$ (2 mol %), Et_3N (1.5 equiv), CH_2Cl_2 , rt, 6 h. (g) (i) $SOCl_2$ (1.5 equiv), pyridine (1.2 equiv), $50^\circ C$, 20 h; (ii) $BuOH$. (h) Phthalimide (1.3 equiv), $PyPPh_2$ (1.3 equiv), $DIAD$ (1.3 equiv), CH_2Cl_2 , rt, 24 h.

we next turned our attention to reactions in which the methylene carbon is preserved. As mentioned earlier, this type of reaction although not unprecedented is surprisingly rare.^{1p,q} Butyl (hydroxymethyl)phenyl phosphinate **1a** was chosen as a representative model compound.¹² The first type of reaction investigated was the activation–nucleophilic substitution sequence, which has been useful in the chemistry of phosphonates.^{1n,o} Results are shown in Scheme 2. Tosylation to **9** was achieved in excellent yield under standard conditions. Displacement with a variety of nucleophiles proceeded in good to excellent yields. For example, the formation of **10a–b** with secondary amines takes place uneventfully.

Interestingly, reacting **9** with diisopropylphosphite under Michaelis–Becker conditions smoothly delivered (phosphinylmethyl)phosphonate **11**.¹³ This type of compound is of interest for the preparation of biologically active pyrophosphate analogs. The (phosphinylmethyl)-phosphate motif is an emerging but underutilized mimic for pyrophosphate and phosphoryl transfer.¹⁴ Precursor **12a** was easily synthesized from alcohol **1a**.¹⁵

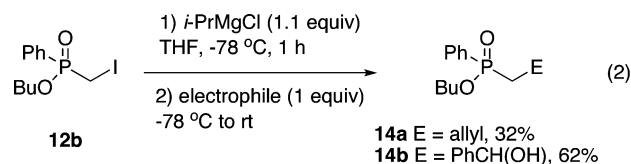
(12) $PhP(O)(OBu)CH_2OH$ **1a** was prepared in one pot and 83% yield from commercially available phenyl-*H*-phosphinic acid through Dean–Stark esterification (*n*-BuOH, 5 equiv, toluene, 24 h) followed by reaction with paraformaldehyde (1 equiv, reflux, 24 h). See Supporting Information.

(13) For a related reaction, see: Hall, R. G.; Kane, P. D.; Bittiger, H.; Froestl, W. *J. Labelled Compd. Radiopharm.* **1995**, 36, 129.

(14) (a) Guranowski, A.; Starzynska, E.; Pietrowska-Borek, M.; Rejman, D.; Blackburn, G. M. *FEBS J.* **2009**, 276, 1546. (b) Nguyen, L. M.; Niesor, E.; Bentzen, C. L. *J. Med. Chem.* **1987**, 30, 1426.

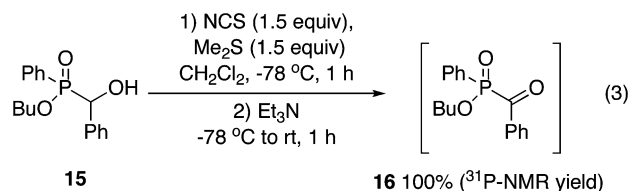
(Halomethyl)phosphinates **12b** and **12c** were synthesized either from **9** under Finkelstein conditions or directly from **1a** using thionyl chloride. The latter reaction required treatment with *n*-BuOH in order to reconvert the chlorophosphinate intermediate formed under the conditions. Finally, Mitsunobu reaction produced phthalimide **13**. Diphenyl-2-pyridylphosphine was used in order to facilitate the removal of the phosphine oxide byproduct from the desired compound. Surprisingly few examples of the Mitsunobu reaction of (hydroxymethyl)phosphinates have been reported.¹⁶

We recently reported the functionalization of organophosphorus carbenoids with organoboranes.¹⁷ Unfortunately, treatment of (chloromethyl)phosphinate **12c** under our published conditions with *s*-BuLi and Bu₃B was not successful, nor were the reactions of **9** and **12b**. On the other hand, the conversion of diethyl (iodomethyl)-phosphonate to the corresponding Grignard reagent via metal–halogen exchange is known.¹⁸ Therefore, the corresponding reaction was attempted on **12b**. The result is shown in eq 2. Further work will be required to fully develop/optimize this type of reaction.



Finally, the Corey–Kim oxidation of PhP(O)(OBu)CH(OH)Ph **15** was conducted. The corresponding acyl phosphinate **16** was obtained cleanly and in quantitative yield (eq 3). This functionality is rare and not stable to chromatographic purification: deacylation to the *H*-phosphinate

took place to produce PhP(O)(OBu)H **2a** in 69% isolated yield. Like their acylphosphonate counterparts, acylphosphinates have been synthesized from the Arbuzov reaction between a phosphonite and an acid chloride.¹⁹ Exploiting the mild synthesis of acylphosphinates might be another promising area of research to explore reactivity without intermediate purification.



In conclusion, this work provides a new dimension in the chemistry of (hydroxymethyl)phosphinates for organophosphorus synthesis, either through functionalization preserving the methylene carbon or, even more importantly, through oxidative cleavage to unmask the *H*-phosphinate moiety. (Hydroxymethyl)phosphinates are versatile intermediates, which should prove useful both in the synthesis of complex organophosphorus compounds and, possibly, as pharmacophores in biologically active molecules. The sila-Arbuzov with **3**/esterification/oxidation sequence represents a novel and versatile approach to the synthesis of *H*-phosphinate esters. Further applications, and especially the development of this reaction for the asymmetric synthesis of P-chiral compounds, will be reported in due course.

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Supporting Information Available. Detailed experimental procedure, spectral data, and copies of NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.

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 (16) (a) Coudray, L.; Pennebaker, A. F.; Montchamp, J.-L. *Bioorg. Med. Chem.* **2009**, *17*, 7680. (b) Nawrot, B.; Michalak, O.; De Clercq, E.; Stec, W. J. *Antiviral Chem. Chemother.* **2004**, *15*, 319. (c) Gajda, T. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *85*, 59. (d) Maier, L.; Spörri, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *70*, 49.
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 (18) Coutrot, P.; Youssefi-Tabrizi, M.; Grison, C. *J. Organomet. Chem.* **1986**, *316*, 13.
 (19) (a) Samanta, S.; Perera, S.; Zhao, C.-G. *J. Org. Chem.* **2010**, *75*, 1101. (b) Walker, D. M.; McDonald, J. F.; Franz, J. E.; Logusch, E. W. *J. Chem. Soc., Perkin Trans. 1* **1990**, 659.