Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 48 (2007) 5755–5759

A novel approach to phosphonic acids from hypophosphorous acid

Karla Bravo-Altamirano and Jean-Luc Montchamp*

Department of Chemistry, Box 298860, Texas Christian University, Fort Worth, TX 76129, USA

Received 10 May 2007; revised 15 June 2007; accepted 18 June 2007
Available online 23 June 2007

Abstract—A novel access to phosphonic acids via Pd-catalyzed tandem carbon–phosphorus bond formation–oxidation processes was developed. The procedures involve atom-economical and environmentally friendly functionalization reactions of hypophosphorous acid (H_3PO_2) and *H*-phosphinic acids [RP(O)(OH)(H)].

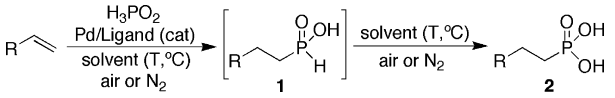
Over the last few years, the quest for synthetic efficiency has gained remarkable importance, partly due to the need to reduce waste.[1] Given the increasing biological and synthetic impact of organophosphorus compounds,[2] it has become crucial to develop atom-economical methods that address the functionalization of P–H bonds from basic feedstocks. Homogeneous catalysis is an ever increasingly useful and versatile alternative for the construction of C–P bonds.[3] Indeed, metal-catalyzed P–H bond activation has already shown some potential in the synthesis of various phosphines (free and protected),[4] phosphonates,[5] phosphine oxides,[6] phosphinates,[7] and more recently *H*-phosphinates.[8] Our laboratory has demonstrated that in spite of being powerful reducing agents, hypophosphorous compounds ($ROP(O)H_2$) can effectively participate in metal-catalyzed processes involving C–P bond formation, leading to *H*-phosphinic acids and their derivatives.[9] Of particular relevance are the Pd-catalyzed addition of hypophosphorous acid (H_3PO_2) across unsaturated carbon linkages,[8a,b] and the Pd-catalyzed dehydrative allylic substitution of H_3PO_2 with allylic alcohols,[10] which are both unique and highly atom-efficient transformations. *H*-phosphinic acids [RP(O)(OH)(H)] are characterized by the presence of a phosphinylidene [P(O)(H)] moiety that works as a bridge between the P(V) and P(III) forms via a tautomeric equilibrium,[11] and provides them with a unique versatility for further functionalization.[8c,12]

Guided by the prospect of exploiting the flexibility of *H*-phosphinates as synthons for the preparation of other organophosphorus compounds, we became interested in developing new reactions that involve formal P–H bond activation processes, particularly those which can fulfill 'green chemistry' requirements.[13] In this regard, we discovered that *H*-phosphinates were sensitive toward oxidation into phosphonic acids, particularly under an air atmosphere and in the presence of catalytic amounts of transition metals. Since phosphonic acids have been extensively studied as phosphate analogs in catalytic enzymatic pathways, and their biological, biochemical, and synthetic importance are diverse,[14] a convenient direct synthesis of these important compounds is highly desirable.

The literature syntheses of phosphonic acids generally involve the preparation of the phosphonate alkyl esters, which requires an additional deprotection step by treatment with trimethylsilyl bromide,[15] or acidic hydrolysis at high temperatures.[16] However, surprisingly few methods for their direct preparation via C–P bond formation have been described, such as the low-yielding free-radical mediated addition of phosphorous acid (H_3PO_3) to olefins,[17] where polymerization is difficult to avoid.[17,18] Another viable approach to phosphonic acids uses tris(trimethylsilyl) phosphite [$P(OTMS)_3$] in Arbuzov reactions with electrophiles (i.e. iodides, bromides, triflates, aziridine and oxazolidine ring-opening, etc),[19] as well as in Ni-catalyzed cross-couplings with aryl iodides and bromides.[20] This approach is not convenient because it requires strict anhydrous conditions and wasteful silylation. Furthermore, the synthesis of pure $P(OTMS)_3$ is cumbersome.[19a] On the other hand, phosphonic acids have also been previously prepared from

Keywords: Phosphonic acid; *H*-phosphinic acid; Hypophosphorous acid.
* Corresponding author. Tel.: +1 817 257 6201; fax: +1 817 257 5851; e-mail: j.montchamp@tcu.edu

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.06.090



Scheme 1.

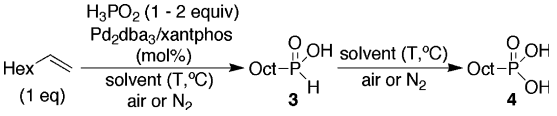
H-phosphinic acids, however the strong oxidizing agents and/or harsh conditions that are usually required are major drawbacks,[12a,21] along with the fact that, until recently, few effective synthetic methodologies for *H*-phosphinates were available.[22]

Initially, we studied a simultaneous P–H bond functionalization starting from H_3PO_2. This consisted of a one pot, one step hydrophosphinylation[8a]–oxidation process (Scheme 1), avoiding in this way the isolation of the intermediate *H*-phosphinic acid **1**.

A series of experiments was performed in order to investigate the influence of the catalyst, solvent, temperature, air, and water in the outcome of the reaction (Table 1). In a typical procedure, a DMF solution of freshly concentrated H_3PO_2 was heated with 1-octene in the presence of Pd_2dba_3 (1 mol%) and xantphos (2 mol%) under an air atmosphere. At 110 °C, we observed a smooth conversion of the in situ formed octyl-*H*-phosphinic acid **3** into the corresponding phosphonic acid **4** (entry 1), along with minor amounts of H_3PO_3 and H_3PO_4. The use of undried, reagent grade DMF (110 °C) proved to be optimum, and a decrease in the temperature and/or replacement of DMF by CH_3CN significantly slowed down the oxidation step (entries 2 and 3). When the reaction was performed with anhydrous DMF under a nitrogen atmosphere, *H*-phosphinic acid **3** was the main product (entry 4). However, the presence of oxygen completely reverses this behavior and leads mainly to the oxidized product **4** (entry 6). As expected, the C–P bond-forming step proceeds very inefficiently with H_3PO_2 in the absence of Pd catalyst (entry 7). Other experiments probed the influence of stoichiometry and catalyst loading (entries 8 and 9). It was found that 1.5–2 equiv of H_3PO_2 and 2 mol% of Pd provide excellent yields of the phosphonic acid **4** (entry 8), while lowering the amount of catalyst markedly decreases the yield of **4**, and *H*-phosphinic acid **3** becomes the exclusive product (entry 9). This, along with control experiments performed on isolated *H*-phosphinic acids,[23] supports an active role of the Pd catalyst in the oxidation step. Remarkably, the reaction still proceeds in excellent yield when conducted with the commercially available aqueous solution of H_3PO_2 (50 wt%) (entry 10). It should be noted that the use of concentrated vs aqueous H_3PO_2 did not show a significant impact on the formation of **4** (entry 4 vs 5), contrary to the presence of nitrogen vs air in the reaction atmosphere (entries 4 vs 6 and 5 vs 10). Additionally, the concentration of the reactants also plays a key role, and 0.5–1 M appears to be optimum.

Pursuant to the design of a more general tandem C–P bond formation–oxidation process using H_3PO_2 as precursor, other Pd-catalyzed reactions that lead to *H*-phosphinic acids were conducted under the optimized conditions for the hydrophosphinylation–oxidation of 1-octene (Method A). Various unsaturated substrates, allylic alcohols and aryl halides were examined in hydrophosphinylation,[8a] allylation,[10] and cross-coupling reactions,[24] respectively. However, we discovered that the presence of oxygen during the C–P bond-forming step was not always optimum in all cases. Therefore, a stepwise process (Method B) where the *H*-phosphinic acid is preformed under our published conditions (under N_2, with concentrated H_3PO_2) followed by in situ Pd-catalyzed oxidation (under air) provided overall better yields of products than the simultaneous version (Table 2). In

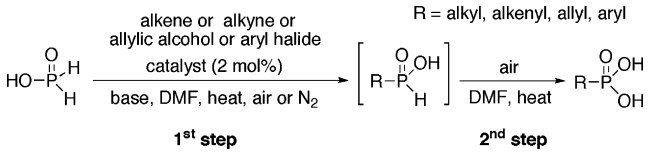
Table 1. Optimization of the tandem hydrophosphinylation–oxidation of 1-octene[a]

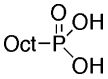
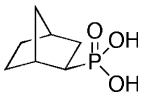
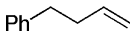
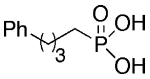
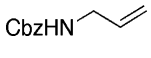
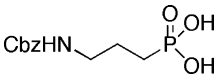
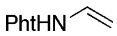
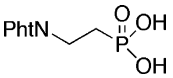
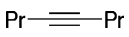
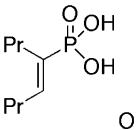
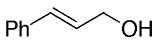
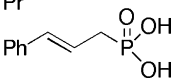
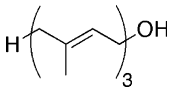
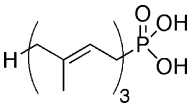
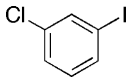
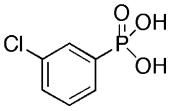
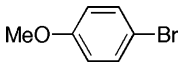
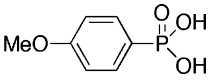
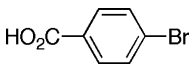
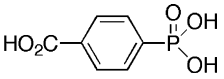


Entry	H_3PO_2[b] aq/concd (equiv)	Pd/L (mol%)	Air/N_2	Solvent	*T* (°C)	^{31}P NMR and/or [isolated][c] yields (%)	
						3	**4**
1	Concd (1)	2	Air	DMF	110	0	74 [72]
2	Concd (1)	2	Air	DMF	85	34	53
3	Concd (1)	2	Air	CH_3CN	82	46	34
4	Concd (1)	2	N_2	DMF (anhyd)[d]	110	82	10
5	Aq (1)	2	N_2	DMF	110	45	31
6	Concd (1)	2	Air	DMF (anhyd)[d,e]	110	13	77
7	Concd (1)	0	Air	DMF	110	6	0
8	Concd (1.5–2)	2	Air	DMF	110	0	100 [100]
9	Concd (2)	0.05	Air	DMF	110	100	0
10	Aq (2)	2	Air	DMF	110	0	100 [100]

[a] Unless otherwise noted, reactions were conducted in a one-step mode, using reagent grade, undried solvents [0.5 M]. Reaction times: 20–24 h.
[b] Concentrated H_3PO_2 was obtained by rotary evaporation of the commercial aqueous solution (50 wt%). See Supplementary data for details.
[c] Isolated yield after extractive workup.
[d] Freshly vacuum-distilled DMF (from CaH_2).
[e] Drierite trap was used to avoid moisture from air.

Table 2. Synthesis of phosphonic acids via tandem C–P bond formation–oxidation reactions



Entry	Subsrate	Method[a]	Catalyst	Base (equiv)	Product	1st step time (h)	2nd step time (h)	Isolated yield,[b] [NMR yield] (%)
1a		A	Pd_2dba_3/xantphos	—		20	—	100
1b		B				12	24	100
2a		A	Pd_2dba_3/xantphos	—		50	—	81
2b		B				12	64	97
3		A	Pd_2dba_3/xantphos	—		50	—	95
4		B	Pd_2dba_3/xantphos	—		12	50	86[c]
5		B	Pd_2dba_3/xantphos	—		12	20	[81]
6		B	Pd_2dba_3/xantphos	—		12	50	91
7		B	Pd_2dba_3/xantphos	—		12	22	89
8		B	Pd_2dba_3/xantphos	—		15	50	[92]
9		B	$Pd(OAc)_2$/dppp	Et_3N (3)		15	22	82[d]
10		B	$Pd(OAc)_2$/dppp	Et_3N (3)		15	22	55[d]
11		B	$Pd(OAc)_2$/dppp	Et_3N (3)		15	42	52[d]

[a] See Supplementary data for details of the procedures. Method A: one step, 2 equiv 50% aq H_3PO_2, DMF, 110 °C, air. Method B: two steps, 2 equiv concd H_3PO_2; 1st step: P–C bond formation: DMF, 85 °C, N_2; 2nd step: oxidation: DMF, 110 °C, air.
[b] Unless otherwise noted, products were isolated in good purity (>95%) by a simple extractive workup.
[c] Purified by ion-exchange chromatography.
[d] Purified by recrystallization.

accordance with the literature, Pd_2dba_3/xantphos (2 mol% Pd) worked efficiently as a catalytic system for hydrophosphinylation and allylation reactions (entries 1–8), while $Pd(OAc)_2$/dppp (2 mol%) with Et_3N as base (3 equiv) proved successful in cross-coupling (entries 9–11). The products were generally isolated in moderate to good yields by an aqueous extractive work-up and, if required, recrystallization was performed (entries 9–11). However, N-containing phosphonic acids (entries 4–5) are soluble in water and ion-exchange chromatography was required for their isolation.

Even though the mechanism of this transformation is not completely clear at this time, it could proceed either, via a direct P–H bond activation where the palladium inserts into the P–H bond of the *H*-phosphinic acid[3b,c,f] or, most probably, through an indirect process where the metal complex first activates molecular oxygen pres-

ent in the solution forming a highly reactive species (as a radical), that in turn reacts with the *H*-phosphinic acid.[25] Further work will be required to delineate the mechanism of the reaction. In summary, an efficient step- and atom-economical method to access phosphonic acids was developed.

Acknowledgments

We gratefully acknowledge the National Institute of General Medical Sciences/NIH (1R01 GM067610), and the Chemistry Department at Texas Christian University for the financial support of this research.

Supplementary data

Supplementary data (Representative experimental procedures and spectroscopic data) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.06.090.

References and notes

1. For reviews, see: (a) Trost, B. M. *Science* **1991**, *254*, 1471–1477; (b) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695–705.
2. For general references, see: (a) Quin, L. D. *A Guide to Organophosphorus Chemistry*; Wiley: New York, 2000; (b) *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: New York, 1996; Vol. 4, (c) Corbridge, D. E. *Phosphorus 2000. Chemistry, Biochemistry and Technology*; Elsevier: Amsterdam, 2000; (d) Engel, R.; Cohen, J. I. *Synthesis of Carbon–Phosphorus Bonds*, 2nd ed.; CRC Press: Boca Raton, 2003; (e) *Handbook of Organophosphorus Chemistry*; Engel, R., Ed.; Marcel Dekker: New York, 1992.
3. For recent reviews on metal-catalyzed C–P bond formation, see: (a) Schwan, A. *Chem. Soc. Rev.* **2004**, *33*, 218–224; (b) Tanaka, M. *Top. Curr. Chem.* **2004**, *232*, 25–54; (c) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079–3159; (d) Baillie, C.; Xiao, J. *Curr. Org. Chem.* **2003**, *7*, 477–514; (e) Beletskaya, I. P.; Kazankova, M. A. *Russ. J. Org. Chem.* **2002**, *38*, 1391–1430; (f) Wicht, D. K.; Glueck, D. S. In *Catalytic Heterofunctionalization*; Togni, A., Grützmacher, H., Eds.; Wiley–VCH: Weinheim, 2001; pp 143–170, and references therein.
4. For a review on hydrophosphination that includes catalytic methods for P–H bond activation (a) Delacroix, O.; Gaumont, A. C. *Curr. Org. Chem.* **2005**, *9*, 1851–1882; For examples of metal-catalyzed hydrophosphination: (b) Komeyama, K.; Kobayashi, D.; Yamamoto, Y.; Takehira, K.; Takaki, K. *Tetrahedron* **2006**, *62*, 2511–2519; (c) Join, B.; Mimeau, D.; Delacroix, O.; Gaumont, A.-C. *Chem. Commun.* **2006**, 3249–3251; (d) Shulyupin, M. O.; Trostyanskaya, I. G.; Kazanova, M. A.; Beletskaya, I. P. *Russ. J. Org. Chem.* **2006**, *42*, 17–22; (e) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 2368–2370; (f) Kawaoka, A. M.; Douglass, M. R.; Marks, T. J. *Organometallics* **2003**, *22*, 4630–4632; (g) Jérôme, F.; Monnier, F.; Lawicka, H.; Dérien, S.; Dixneuf, P. H. *Chem. Commun.* **2003**, 696–697; (h) Wicht, D. K.; Kourkine, I. V.; Kovacik, I.; Glueck, D. S.; Concolino, T. E.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5381–5394; (i) Costa, E.; Pringle, P. G.; Worboys, K. *Chem. Commun.* **1998**, 49–50.
5. For examples of metal-catalyzed hydrophosphorylation, see: (a) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571–1572; (b) Han, L.-B.; Mirzaei, F.; Zhao, C.-Q.; Tanaka, M. *J. Am. Chem. Soc.* **2000**, *122*, 5407–5408; (c) Zhao, C.-Q.; Han, L.-B.; Goto, M.; Tanaka, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1929–1932; (d) Zhao, C.-Q.; Han, L.-B.; Tanaka, M. *Organometallics* **2000**, *19*, 4196–4198; (e) Reichwein, J. F.; Patel, M. C.; Pagenkopf, B. L. *Org. Lett.* **2001**, *3*, 4303–4306; (f) Reichwein, J. F.; Pagenkopf, B. L. *J. Org. Chem.* **2003**, *68*, 1459–1463; (g) Levine, A. M.; Stockland, R. A., Jr.; Clark, R.; Guzei, I. *Organometallics* **2002**, *21*, 3278–3284; (h) Stockland, R. A., Jr.; Levine, A. M.; Giovine, M. T.; Guzei, I. A.; Cannistra, J. C. *Organometallics* **2004**, *23*, 647–656; (i) Shulyupin, M. O.; Francio, G.; Beletskaya, I. P.; Leitner, W. *Adv. Synth. Catal.* **2005**, *347*, 667–672.
6. For examples of metal-catalyzed synthesis of phosphine oxides via hydrophosphinylation, see: (a) Han, L.-B.; Choi, N.; Tanaka, M. *Organometallics* **1996**, *15*, 3259–3261; (b) Han, L.-B.; Hua, R.; Tanaka, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 94–96; (c) Han, L.-B.; Zhao, C.-Q.; Tanaka, M. *J. Org. Chem.* **2001**, *66*, 5929–5932; (d) Allen, A., Jr.; Ma, L.; Lin, W. *Tetrahedron Lett.* **2002**, *43*, 3707–3710; (e) Van Rooy, S.; Cao, C.; Patrick, B. O.; Lam, A.; Love, J. A. *Inorg. Chim. Acta* **2006**, *359*, 2918–2923; (f) Niu, M.; Fu, H.; Jian, Y.; Zhao, Y. *Chem. Commun.* **2007**, 272–274.
7. For examples of metal-catalyzed synthesis of phosphinates via hydrophosphinylation, see: (a) Han, L.-B.; Zhao, C.-Q.; Onozawa, S.-y.; Goto, M.; Tanaka, M. *J. Am. Chem. Soc.* **2002**, *124*, 3842–3843; (b) Han, L.-B.; Zhang, C.; Yazawa, H.; Shimada, S. *J. Am. Chem. Soc.* **2004**, *126*, 5080–5081; (c) Han, L.-B.; Ono, Y.; Yazawa, H. *Org. Lett.* **2005**, *7*, 2909–2911.
8. For examples of metal-catalyzed synthesis of *H*-phosphinates via hydrophosphinylation, see: (a) Deprèle, S.; Montchamp, J.-L. *J. Am. Chem. Soc.* **2002**, *124*, 9386–9387; (b) Deprèle, S.; Montchamp, J.-L. *Org. Lett.* **2004**, *6*, 3805–3808; (c) Ribière, P.; Bravo-Altamirano, K.; Antczak, M.; Hawkins, J.; Montchamp, J.-L. *J. Org. Chem.* **2005**, *70*, 4064–4072.
9. For a review, see: Montchamp, J.-L. *J. Organomet. Chem.* **2005**, *690*, 2388–2406.
10. Bravo-Altamirano, K.; Montchamp, J.-L. *Org. Lett.* **2006**, *8*, 4169–4171.
11. Stawinski, J.; Kraszewski, A. *Acc. Chem. Res.* **2002**, *35*, 952–960.
12. For examples of functional group interconversion related to *H*-phosphinic acids, see: (a) Frank, A. W. *Chem. Rev.* **1961**, *60*, 389–424; (b) Nifant'ev, E. E. *Russ. Chem. Rev.* **1978**, *47*, 835; (c) Yudelevich, V. I.; Sokolov, L. B.; Ionin, B. I. *Russ. Chem. Rev.* **1980**, *49*, 46; (d) Frank, A. W. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley: New York, 1972; Vol. 4, Chapter 10; (e) Soulier, E.; Clement, J.-C.; Yaouanc, J.-J.; Des Abbayes, H. *Tetrahedron Lett.* **1998**, *39*, 4291–4294; (f) Anderson, N. G.; Ciaramella, B. M.; Feldman, A. F.; Lust, D. A.; Moniot, J. L.; Moran, L.; Polomski, R. E.; Wang, S. S. Y. *Org. Process Res. Dev.* **1997**, *1*, 211–216.
13. Van Aken, K.; Strekowski, L.; Patiny, L. *Beilstein J. Org. Chem.* **2006**, *2*, 3, and references cited therein.
14. Selected references (a) Savignac, P.; Iorga, B. *Modern Phosphonate Chemistry*; CRC Press: Boca Raton, 2003; (b) Engel, R. *Chem. Rev.* **1977**, *77*, 349–367; (c) Palacios, F.; Alonso, C.; de los Santos, J. M. *Chem. Rev.* **2005**, *105*, 899–931; (d) Ma, J.-A. *Chem. Soc. Rev.* **2006**, *35*, 630–636; (e) Kafarski, P.; Lejczak, B. *Phosphorus, Sulfur Silicon*

Related Elem. **1991**, *63*, 193–215; (f) Dembitsky, V. M.; Al Quntar, A. A. A.; Haj-Yehiaa, A.; Srebnik, M. *Mini-Rev. Org. Chem.* **2005**, *2*, 91–109; (g) Romanenko, V. D.; Kukhar, V. P. *Chem. Rev.* **2006**, *106*, 3868–3935; (h) Moonen, K.; Laureyn, I.; Stevens, C. V. *Chem. Rev.* **2004**, *104*, 6177–6215; (i) Blackburn, M. G. *Chem. Ind. (London)* **1981**, 134–144; (j) Krise, J. P.; Stella, V. J. *Adv. Drug Delivery Rev.* **1996**, *19*, 287–310; (k) Flett, D. S. *J. Organomet. Chem.* **2005**, *690*, 2426–2438; (l) Fields, S. C. *Tetrahedron* **1999**, *55*, 12237–12273.

15. McKenna, C. E.; Higa, M. T.; Cheung, N. H.; McKenna, M. C. *J. Tetrahedron Lett.* **1977**, 155–158.
16. Kosolapoff, G. M. *J. Am. Chem. Soc.* **1945**, *67*, 1180–1182.
17. Griffin, C. E.; Wells, H. J. *J. Org. Chem.* **1959**, *24*, 2049–2051.
18. Griffin, C. E. *J. Org. Chem.* **1960**, *25*, 665–666.
19. For examples, see: (a) Sekine, M.; Okimoto, K.; Yamada, K.; Hata, T. *J. Org. Chem.* **1981**, *46*, 2097–2107; (b) Lazukina, L. A.; Kukhar, V. P. *Zh. Obshch. Khim.* **1988**, *58*, 939–940; (c) Nifant'ev, E. E.; Popkova, T. N.; Kukhareva, T. S.; Bekker, A. R. *Zh. Obshch. Khim.* **1988**, *58*, 1550–1557; (d) Vaghefi, M. M.; Bernacki, R. J.; Dalley, N. K.; Wilson, B. E.; Robins, R. K. *J. Med. Chem.* **1987**, *30*, 1383–1391; (e) Bhattacharya, A. K.; Stolz, F.; Kurzeck, J.; Rüger, W.; Schmidt, R. R. *Can. J. Chem.* **2002**, *80*, 973–982; (f) Wedel, M.; Walter, A.; Montforts, F.-P. *Eur. J. Org. Chem.* **2001**, 1681–1687.
20. Demik, N. N.; Kabachnik, M. M.; Novikova, Z. S.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1992**, *10*, 2432–2435.
21. H_2O_2: (a) Andreev, N. A.; Grishina, O. N.; Enikeev, K. M. *Zh. Obshch. Khim.* **1982**, *52*, 1530–1537; H_2O_2/SO_2: (b) Barton, D. H. R.; Vonder Embse, R. A. *Tetrahedron* **1998**, *54*, 12475–12496; I_2/DMSO: (c) Albouy, D.; Brun, A.; Munoz, A.; Etemad-Moghadam, G. *J. Org. Chem.* **1998**, *63*, 7223–7230; $HgCl_2$ or Br_2/H_2O: (d) Baylis, E. Keith; Campbell, C. D.; Dingwall, J. G. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2845–2853; (e) Fastrez, J.; Jespers, L.; Lison, D.; Renard, M.; Sonveaux, E. *Tetrahedron Lett.* **1989**, *30*, 6684–6861; HNO_3: (f) Guichard, F. *Chem. Ber.* **1899**, *32*, 1572–1581; I_2/HI(AcOH) or HI: (g) Hatt, H. H. *J. Chem. Soc.* **1933**, 776–786; (h) Albouy, D.; Etemad-Moghadam, G.; Koenig, M. *Eur. J. Org. Chem.* **1999**, 861–868; (i) Zhukov, Y. N.; Khomutov, A. R.; Osipova, T. I.; Khomutov, R. M. *Russ. Chem. Bull.* **1999**, *48*, 1348–1351; $CCl_4/Et_3N/H_2O$: (j) Belakhov, V. V.; Yudelevich, V. I.; Ionin, B. I. *Zh. Obshch. Khim.* **1986**, *56*, 1749–1755; AcOH (k) Vysotskii, V. I.; Levan'kov, S. V. *Zh. Obshch. Khim.* **1991**, *61*, 1315–1321; $NaIO_4$: (l) Karanewsky, D. S.; Badia, M. C. *Tetrahedron Lett.* **1986**, *27*, 1751–1754; Thermolysis (250 °C): (m) Andreev, N. A.; Grishina, O. N. *Zh. Obshch. Khim.* **1981**, *51*, 1743–1747; Kinetic and mechanistic studies of the oxidation of phenyl-*H*-phosphinic acid: (n) Moondra, A.; Mathur, A.; Banerji, K. K. *J. Chem. Soc., Dalton Trans.* **1990**, 2697–2700; (o) Sharma, K.; Mehrotra, R. N. *Ind. J. Chem., Sect. A* **2002**, *41A*, 270–278; (p) Sharma, K.; Prakash, A.; Mehrotra, R. N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 4009–4015.
22. Montchamp, J.-L. *Speciality Chem. Mag.* **2006**, *26*, 44–46.
23. Pure *H*-phosphinic acids (i.e. alkyl- and allylic-) underwent complete oxidation into phosphonic acids when heated in DMF (under air) with catalytic amounts of palladium.
24. Montchamp, J.-L.; Dumond, Y. R. *J. Am. Chem. Soc.* **2001**, *123*, 510–511.
25. Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879–2932.