



# Stable Yldiides

# Synthesis, Structure, and Reactivity of a Stable Phosphonium– Sulfinyl Yldiide

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Dedicated to the 50th anniversary of Laboratoire Hétérochimie Fondamentale et Appliquée, LHFA

**Abstract:** The synthesis of a stable lithium phosphonium–sulfinyl yldiide was explored. The compound was fully characterized by NMR spectroscopy and X-ray crystallography. The electronic structure of **2** was analyzed by DFT calculations, which indicated strong ylidic character. Yldiide **2** was stable enough to catalyze the hydroacylation of benzaldehyde. More interestingly, the Wittig reaction with activated ketones proceeded smoothly at room temperature owing to the presence of the lithium cation.

## Introduction

Since more than a century, ylide chemistry has attracted considerable interest,<sup>[1]</sup> and without any doubt, the Wittig reaction is widely recognized as one of the most important reactions in organic chemistry.<sup>[2]</sup> Bisylide derivatives I are species containing two cumulated ylide functions, and they formally possess a central carbon atom with two negative charges, which are stabilized by two positively charged fragments.<sup>[3]</sup> Recently, considerable work on their electronic structure has shed new light on these compounds.<sup>[4]</sup> Indeed, rather than the classical zwitterionic representation, their description as divalent carbon(0) complexes featuring two L ligands seems to fit better with their reactivity.<sup>[5]</sup>

The replacement of a neutral L ligand by an anionic moiety (R) gives metalated congeners II,<sup>[6]</sup> which are called yldiides or metalated ylides (Figure 1). Despite limited examples (only three yldiides have been isolated),<sup>[7]</sup> some interesting applications were already described for organic synthesis as highly reactive Wittig-type reagents for sterically hindered ketones,<sup>[8]</sup> in transition-metal chemistry as ligands,<sup>[9]</sup> and in main-group chemistry for the synthesis of stable borenium cations.<sup>[10]</sup>

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Figure 1. Bisylides, yldiides, and isolated yldiides. Tipp = triisopropylphenyl.

Following our work on neutral mixed phosphonium–sulfonium bisylides,<sup>[11]</sup> in which we demonstrated their utility as asymmetric atomic carbon sources, we became interested in the synthesis and reactivity of the corresponding anionic phosphonium–sulfinyl yldiides.

### **Results and Discussion**

Precursor phosphonium sulfinyl ylide **1** was prepared in good yield (66 %) by reaction of the chlorophosphonium salt with methyl(triisopropylphenyl) sulfoxide in the presence of a non-nucleophilic strong base [i.e., lithium diisopropylamide (LDA, 2 equiv.)]. Deprotonation of **1** with butyllithium cleanly afforded desired lithium yldiide **2** (70 % yield) as a white solid (Scheme 1). As expected, in the <sup>31</sup>P NMR spectrum, the chemical shift of the signal for **2** ( $\delta$  = 18.0 ppm) appears at a higher field than that for **1** ( $\delta$  = 46.8 ppm). In the <sup>13</sup>C NMR spectrum, the metalated central carbon atom exhibits a characteristic doublet at  $\delta$  = 48.3 ppm ( $J_{PC}$  = 30.6 Hz), which is in the same range as that of the related sulfonyl-yldiide reported by Gessner et al.<sup>[7c]</sup>







Scheme 1. Synthesis of lithium yldiide 2.

Both compounds were isolated in crystalline form from a toluene/pentane solution at -20 °C for **1** and from a pentane solution with a minimum amount of THF for **2**, and both struc-



Figure 2. Molecular structure of **1**. Thermal ellipsoids represent 30 % probability. H atoms (except that on C1) and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.677(2), P1–C10 1.811(2), S1–O1 1.500(2), S1–C1 1.736(2), S1–C16 1.8162, P1–C1–S1 120.83(13).

tures were confirmed by X-ray diffraction analysis (Figures 2 and 3).<sup>[12]</sup>

X-ray analysis of **2** confirms metalation of the central carbon atom and reveals a dimeric structure incorporating a  $\text{Li}_2\text{O}_2$  core. The Li1–Li2 interatomic distance is greater (2.716 Å) than the sum of the covalent radii (2.68 Å).<sup>[13]</sup> The C–Li2 bond lengths (C1–Li2 2.158 and C2–Li2 2.139 Å) are slightly longer than those reported in previously described lithium yldiides (2.060– 2.085 Å) probably because of the coordination of oxygen atoms. Notably, the sulfinyl oxygen atoms coordinate less strongly to Li2 (O1–Li2 2.065 and O2–Li2 2.074 Å) than the two THF molecules to Li1 (O4–Li1 1.965 and O3–Li1 1.972 Å). More classical interactions are observed with Li1 (O2–Li1 1.894 and O1–Li1 1.896 Å).

The P–C distance (1.649 Å) in [2.THF]<sub>2</sub> is shorter than that in 1 (1.677 Å), and the value is consistent with those previously reported for metalated ylides III-V (1.630-1.646 Å).<sup>[7]</sup> The S-C bond length also undergoes a shortening upon going from 1 (1.736 Å) to [2.THF]<sub>2</sub> (1.682–1.693 Å), and the P–C–S angle decreases significantly upon metalation from 120.82° in 1 to 117.51–115.53° in [2.THF]2. To gain more insight into electronic structures of 1 and 2, DFT calculations were performed at the M06-2X/6-31+G(d,p) level of theory (see the Supporting Information). The structure of 2 was considered with and without a countercation. In the presence of the cation, two minima were found depending on the coordination of the lithium ion, either on the central carbon atom (the most stable) or on the oxygen atom ( $\Delta E = 5.1$  kcal mol<sup>-1</sup> and  $\Delta G = 5.9$  kcal mol<sup>-1</sup>; see the Supporting Information). We consider  $2^{calcd.}$  without a cation for the rest of the discussion, as the ionic character of the C-Li bond has a minor influence on the rest of the electronic parameters. The optimized geometries, 1<sup>calcd.</sup> and anionic 2<sup>calcd.</sup>, agree quite well with the experimental crystal structures (Table 1).



Figure 3. Molecular structure of  $[2-THF]_2$ . Thermal ellipsoids represent 30 % probability. H atoms, solvent molecules, and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:O1-Li1 1.896(6), O1-Li2 2.065(6), O2-Li1 1.894(6), O2-Li2 2.074(6), Li1-O4 1.965(7), Li1-O3 1.972(10), Li1-Li2 2.716(8), C1-Li2 2.158(6), C2-Li2 2.139(7), P1-C1 1.649(3), P1-C11 1.823(3), P2-C2 1.649(3), P2-C40 1.826(4), S1-O1 1.546(2), S1-C1 1.682(3), S2-O2 1.554(2), S2-C2 1.693(3), P1-C1-S1 117.51(18), P2-C2-S2 115.53(19), S1-C1-Li2 85.6(2), Li2-C1-P1 142.3(3), S2-C2-Li2 86.0(2), Li2-C2-P2 142.8(3).



The only noticeable difference concerns the S–C bond length, which is overestimated by 0.04 Å in the calculation. The variation in the Wiberg bond indices on going from  $1^{calcd.}$  to  $2^{calcd.}$  (P–C, +0.36; C–S, +0.11) is in good agreement with an increase in the negative charge on the ylidic carbon atom. The value obtained for the atomic population on the central carbon atom (–1.358) is reminiscent of that reported by Gessner et al. (–1.33).<sup>[7c]</sup> The two highest occupied molecular orbitals (Figure 4) correspond to the two lone pairs at the central carbon atom in **2**, and the HOMO–1 and HOMO present  $\sigma$  and  $\pi$  symmetry, respectively.

Table 1. Selected geometrical parameters of the experimental crystal structures of 1 and  $[2-THF]_2$  and the related optimized structures.

	1	1 <sup>calcd</sup>	[ <b>2·</b> THF] <sub>2</sub>	2 <sup>calcd</sup>
P–C [Å]	1.677(2)	1.687	1.649(3)	1.642
			1.649(3)	
S–C [Å]	1.736(2)	1.750	1.682(3)	1.720
			1.693(3)	
P–C–S [°]	120.83(13)	117.7	117.51(18)	113.4
			115.53(19)	



Figure 4. HOMO-1 (left, -2.86 eV) and HOMO (right, -2.10 eV) of  $2^{calcd.}$  calculated at the M06-2X/6-31+G(d,p) level of theory (±0.05 isosurfaces).

The nucleophilic character of yldiide **2** was confirmed by a quantitative reaction with methyl iodide, which cleanly afforded corresponding C-methylated ylide **3** as a white solid in 95 % yield (Scheme 2). The <sup>31</sup>P NMR spectrum exhibits a singlet at  $\delta = 48.6$  ppm, and the C-methyl protons appear as a characteristic doublet signal at  $\delta = 2.02$  ppm ( $J_{PH} = 13.2$  Hz) in the <sup>1</sup>H NMR spectrum. The central carbon atom displays a high-



Scheme 2. Nucleophilic character of yldiide 2 and Wittig reaction with trifluoroacetophenone.



field doublet at  $\delta = 11$  ppm ( $J_{CP} = 12.2$  Hz) in the <sup>13</sup>C NMR spectrum. In the same vein, yldiide **2** can be easily reprotonated, and the addition of 1 equivalent of water immediately and quantitatively affords precursor phosphonium–sulfinyl ylide **1**.

Interestingly, 1 equivalent of trifluoroacetophenone readily reacts with 2, as indicated by the immediate appearance of a new signal at  $\delta = -39$  ppm in the <sup>31</sup>P NMR spectrum, which slowly evolves over 24 h at room temperature toward a new signal at  $\delta$  = 22 ppm. This high-field chemical shift is in good agreement with the formation of oxaphosphetane 4 with a pentacoordinate phosphorus atom, which is the key intermediate of the Wittig reaction. The new signal in the <sup>31</sup>P NMR spectrum was assigned to the corresponding phosphine oxide by comparison with an authentic sample, and after workup, cisvinyl sulfoxide 5 was isolated in 68 % yield (Scheme 2). Notably, decomposition of a related oxaphosphetane, obtained by reaction of a P,S-bisylide with trifluoroacetophenone, requires much stronger thermal activation (150 °C).<sup>[11b]</sup> The evolution of 4 at much lower temperature (room temperature) can be explained by the interaction of the lithium cation with the carbanion center, which triggers the Wittig reaction.[14]

In marked contrast, the reaction of **2** with 1 equivalent of benzaldehyde did not afford the Wittig product, but <sup>1</sup>H NMR spectroscopy revealed the formation of benzyl benzoate exhibiting a characteristic signal at  $\delta = 5.4$  ppm. The formation of benzyl benzoate can be rationalized by the hydroacylation of benzaldehyde; this transformation can be performed by using a catalytic amount of yldiide **2** (see the Supporting Information for kinetic studies). The reaction probably proceeds by a hydride transfer that is initiated upon the formation of **6**, which is trapped by a second equivalent of aldehyde to generate lithium alcoholate **7**. Then, the reaction between **6** and **7** gives rise to benzyl benzoate and regenerates catalyst **2** (Scheme 3). A similar catalytic transformation was already reported by using N-heterocyclic carbenes and P,S-bisylides as catalysts.<sup>[11b,15]</sup>



Scheme 3. Proposed mechanism for the catalytic transformation of benzaldehyde into benzyl benzoate.

### Conclusions

In conclusion, a stable lithium phosphonium–sulfinyl yldiide was synthesized and structurally characterized by X-ray crystallography. DFT calculations evidenced strong nucleophilic character, which was experimentally confirmed. Metalation of the central carbon induced some chemical behavior differences relative to its neutral P,S-bisylide analogue, and particularly, Wittigtype reactions could be performed at room temperature with-





out any additives. Detailed reactivity of **2** and its applications in synthesis are under active investigation.

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- a) A. W. Johnson (Ed.), Ylides and Imines of Phosphorus, Wiley, New York, 1993; b) S. J. Clark (Ed.), Nitrogen, Oxygen, and Sulfur Ylide Chemistry, Oxford University Press, Oxford, 2002; c) A. D. Abell, M. K. Edmonds in Organophosphorus Reagents (Ed.: P. J. Murphy), Oxford University Press, Oxford, 2004, pp. 99; d) V. K. Aggarwal, C. L. Winn, Acc. Chem. Res. 2004, 37, 611; e) X. Huang, B. Peng, M. Luparia, L. F. R. Gomes, N. Maulide, Angew. Chem. Int. Ed. 2012, 51, 8886; Angew. Chem. 2012, 124, 9016; f) J. He, J. Ling, P. Chiu, Chem. Rev. 2014, 114, 8037.
- [2] a) A. Michaelis, H. V. Gimborn, Ber. Dtsch. Chem. Ges. 1894, 27, 272; b) G. Wittig, M. Rieber, Justus Liebigs Ann. Chem. 1949, 562, 177; c) G. Wittig, G. Geissler, Justus Liebigs Ann. Chem. 1953, 580, 44; d) F. Ramirez, S. Dershowitz, J. Org. Chem. 1957, 22, 41; e) G. Aksnes, Acta Chem. Scand. 1961, 15, 438; f) G. Wittig, Science 1980, 210, 600; g) O. I. Kolodiazhnyi in Phosphorus Ylides: Chemistry and Application in Organic Synthesis, Wiley-VCH, Weinheim, 1999.
- [3] Selected examples of bisylides: a) F. Ramirez, B. N. Desai, B. Hansen, N. McKelvie, J. Am. Chem. Soc. 1961, 83, 3539; b) O. I. Kolodiazhnyi, Tetrahedron 1996, 52, 1855; c) S. Marrot, T. Kato, H. Gornitzka, A. Baceiredo, Angew. Chem. Int. Ed. 2006, 45, 2598; Angew. Chem. 2006, 118, 2660; d) C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand, Angew. Chem. Int. Ed. 2008, 47, 3206; Angew. Chem. 2008, 120, 3250; e) O. Kaufhold, F. E. Hahn, Angew. Chem. Int. Ed. 2008, 47, 4057; Angew. Chem. 2008, 120, 4122; f) M. Alcarazo, K. Radkowski, G. Mehler, R. Goddard, A. Fürstner, Chem. Commun. 2013, 49, 3140; g) T. Morosaki, T. Suzuki, W.-W. Wang, S. Nagase, T. Fujii, Angew. Chem. Int. Ed. 2014, 53, 9569; Angew. Chem. 2014, 126, 9723; h) T. Morosaki, W.-W. Wang, S. Nagaze, T. Fujii, Chem. Eur. J. 2015, 21, 15405; i) T. Morosaki, R. lijima, T. Suzuki, W.-W. Wang, S. Nagase, T. Fujii, Chem. Eur. J. 2017, 23, 8694; j) T. Troadec, T. Wasano, R. Lenk, A. Baceiredo, N. Saffon-Merceron, D. Hashizume, Y. Saito, N. Nakata, V. Branchadell, T. Kato, Angew. Chem. Int. Ed. 2017, 56, 6891; Angew. Chem. 2017, 129, 6995.
- [4] H. J. Bestmann, A. J. Kos, K. Witzgall, P. v. R. Schleyer, Chem. Ber. 1986, 119, 1331.

- [5] a) R. Tonner, F. Öxler, B. Neumüller, W. Petz, G. Frenking, Angew. Chem. Int. Ed. 2006, 45, 8038; Angew. Chem. 2006, 118, 8206; b) R. Tonner, G. Frenking, Chem. Eur. J. 2008, 14, 3260; c) R. Tonner, G. Frenking, Chem. Eur. J. 2008, 14, 3273; d) R. Tonner, G. Frenking, Pure Appl. Chem. 2009, 81, 597; e) G. Frenking, Angew. Chem. Int. Ed. 2014, 53, 6040; Angew. Chem. 2014, 126, 6152 and references cited therein.
- [6] a) L. T. Scharf, D. M. Andrada, G. Frenking, V. H. Gessner, *Chem. Eur. J.* 2017, 23, 4422; b) L. T. Scharf, V. H. Gessner, *Inorg. Chem.*, https://doi.org/ 10.1021/acs.inorgchem.7b00099.
- [7] a) T. Baumgartner, B. Schinkels, D. Gudat, M. Nieger, E. Niecke, J. Am. Chem. Soc. **1997**, *119*, 12410; b) S. Goumri-Magnet, H. Gornitzka, A. Baceiredo, G. Bertrand, Angew. Chem. Int. Ed. **1999**, *38*, 678; Angew. Chem. **1999**, *111*, 710; c) T. Scherpf, R. Wirth, S. Molitor, K.-S. Feichtner, V. H. Gessner, Angew. Chem. Int. Ed. **2015**, *54*, 8542; Angew. Chem. **2015**, *127*, 8662.
- [8] a) E. J. Corey, J. Kang, J. Am. Chem. Soc. 1982, 104, 4725; b) E. J. Corey, J. Kang, K. Kyler, *Tetrahedron Lett.* 1985, 26, 555; c) H. J. Bestmann, M. Schmidt, Angew. Chem. Int. Ed. Engl. 1987, 26, 79; Angew. Chem. 1987, 99, 64.
- [9] R. Zurawinski, C. Lepetit, Y. Canac, M. Mikolajczyk, R. Chauvin, Inorg. Chem. 2009, 48, 2147.
- [10] a) M. Hermann, G. Frenking, *Chem. Eur. J.* 2017, *23*, 3347; b) T. Scherpf,
  K. S. Feichtner, V. H. Gessner, *Angew. Chem. Int. Ed.* 2017, *56*, 3275; *Angew. Chem.* 2017, *129*, 3323.
- [11] a) S. Pascual, M. Asay, O. Illa, T. Kato, G. Bertrand, N. Saffon-Merceron, V. Branchadell, A. Baceiredo, Angew. Chem. Int. Ed. 2007, 46, 9078; Angew. Chem. 2007, 119, 9236; b) N. Dellus, T. Kato, X. Bagan, N. Saffon-Merceron, V. Branchadell, A. Baceiredo, Angew. Chem. Int. Ed. 2010, 49, 6798; Angew. Chem. 2010, 122, 6950; c) N. Dellus, T. Kato, N. Saffon-Merceron, V. Branchadell, A. Baceiredo, Inorg. Chem. 2011, 50, 7949.
- [12] CCDC 1551893 (for 1) and 1551894 (for 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
- [13] a) R. A. Wanat, D. B. Collum, G. Van Duyne, J. Clardy, R. T. DePue, J. Am. Chem. Soc. 1986, 108, 3415; b) R. H. Howard, C. Alonso-Moreno, L. M. Broomfield, D. L. Hughes, J. A. Wright, M. Bochman, Dalton Trans. 2009, 8667; c) G. T. Sazama, T. A. Betley, Organometallics 2011, 30, 4315; d) N. Maudoux, J. Fang, T. Roisnel, V. Dorcet, L. Maron, J.-F. Carpentier, Y. Sarazin, Chem. Eur. J. 2014, 20, 7706; e) J. Francos, P. C. Gros, A. R. Kennedy, C. T. O'Hara, Organometallics 2015, 34, 2550; f) M. W. Drover, J. N. Murphy, J. C. Flogeras, C. M. Schneider, L. N. Dawe, F. M. Kerton, Polyhedron 2015, 102, 60; g) A. Alhashmialameer, N. Ikpo, J. Collins, L. N. Dawe, K. Hattenhauer, F. M. Kerton, Dalton Trans. 2015, 44, 20216.
- [14] We previously showed in a related oxaphosphetane that a negative charge on the carbon atom in the  $\alpha$  position prior to the phosphorus atom resulted in an increased reluctance to undergo Wittig-type reactions because of delocalization towards the phosphorane center (see ref.<sup>[11b]</sup>). Similar to the case of P,S-bisylides, the simple addition of a Lewis acid (e.g., CuOTf) or a Brønsted acid allowed immediate decomposition of oxaphosphetane **4**. Theoretical calculations for oxaphosphetane decomposition were performed, and additional data can be found in the Supporting information.
- [15] A. Chan, K. A. Scheidt, J. Am. Chem. Soc. 2006, 128, 4558-4559.

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A stable lithium phosphonium-sulfinyl yldiide is isolated and fully characterized. Between methandiides and bisylides, the metalated center allows Wittig-type reactions under soft conditions. Theoretical calculations indicate strong ylidic character, which is experimentally confirmed through addition reactions with alkyl halides and its use as a catalyst for the hydroacylation of benzaldehyde.

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