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A new P-heterocyclic type of phosphonium–iodonium ylides based on dibenzophosphole

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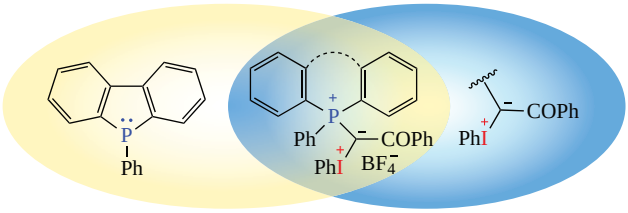
A novel mixed phosphonium–iodonium ylide was synthesized by alkylation of 5-phenyl-5*H*-dibenzophosphole with phenacyl bromide followed by deprotonation and oxidation of the resulting phosphonium ylide with (diacetoxyiodo)-benzene. The influence of the cyclic nature of the phosphonium moiety on the dynamic *E*/*Z* isomerism in the mixed ylide is discussed.

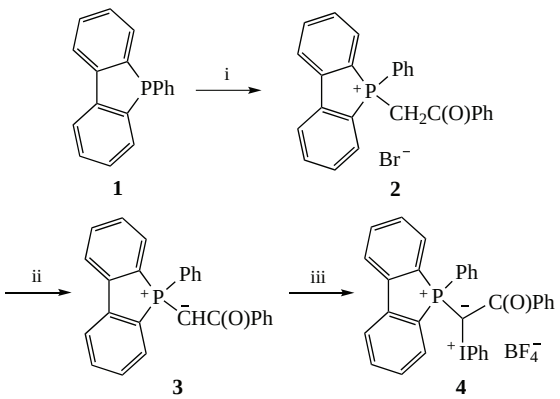


Keywords: mixed ylides, phosphonium ylides, phosphonium–iodonium ylides, dibenzophosphole, cyclic phosphines.

Dedicated to the memory of our head academician N. S. Zefirov

Mixed phosphonium–iodonium ylides represent a rather rare type of ylides[1] which was studied within the last two decades under the leadership of academician N. S. Zefirov and still has much potential for further developments. A systematic study of P-acyclic substituted phosphonium–iodonium ylides gave evidence of a wide synthetic potential, varying with substituents at phosphorus and the ylidic carbon atoms, the reaction medium and conditions as well as reactants, *e.g.*, nitriles or alkynes. A number of novel photochemical transformations of mixed ylides with nitriles[2] and alkynes[3] leading to unique phosphorus-containing heterocyclic systems were discovered. We recently accessed a new structural type of mixed ylides containing a conformationally fixed cyclic phosphonium moiety. Using the example of the six-membered 10-phenyl-10*H*-phenoxaphosphinine, we have shown that the general concept of the synthesis of mixed ylides is applicable to cyclic phosphonium systems.[4]

In this study, we turned to the five-membered 5-phenyl-5*H*-benzo[*b*]phosphindole, also often referred to as 5-phenyl-5*H*-dibenzophosphole (DBP) **1**, as a synthon to create mixed ylides.



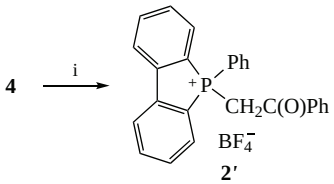
Scheme 1 *Reagents and conditions*: i, $BrCH_2COPh$, MeCN, 80 °C, 2 h; ii, MeONa, MeOH, 0 °C, 1 h; iii, $PhI(OAc)_2$, MeOH, 0 °C, 0.5 h, then HBF_4, 0 °C, 0.5 h.

Despite the fact that the chemistry of DBP and its derivatives is being actively studied, the number of classical phosphorus ylides based on them is desperately limited.[5] Even in these particular examples of ylides, including a five-membered phosphorus-containing cycle, a peculiarity of their chemical properties is observed. This arouses interest in terms of the possibility of creating mixed ylides based on them. In this work, a new mixed phosphonium–iodonium ylide was synthesized based on a phosphonium ylide[5(*a*)] containing a DBP fragment. Among the numerous approaches to *b*,*d*-fused phospholes,[6] we focused on the simplest and most convenient method for the synthesis of DBP **1** which consisted in the intramolecular cyclization of tetraphenylphosphonium bromide under the action of lithium diethylamide.[7]

Alkylation of DBP **1** with phenacyl bromide followed by deprotonation of the resulting salt **2** with sodium methoxide gave phospholium ylide **3**.[5(*a*)] The key stage in the synthesis was the oxidation of ylide **3** with (diacetoxyiodo)benzene, followed by the isolation of mixed ylide **4** in the form of tetrafluoroborate (Scheme 1).

It should be noted that in the crystalline state ylide **4** is quite stable, however in solutions it would readily decompose to form the corresponding phosphonium salt **2′** (analogue of salt **2** with different counter-anion, Scheme 2). Importantly, this decomposition rate is higher than we observed earlier for triarylphosphonium or phenoxaphosphonium models.[2(*b*),4]

The structure of the obtained compounds was confirmed by ^1H, ^{13}C, ^{31}P NMR spectra. For compounds **2**–**4**, IR spectra were also recorded. For mixed ylide **4**, high-resolution mass



Scheme 2 *Reagents and conditions*: i, MeCN, room temperature.

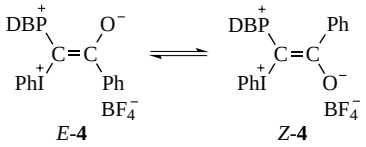


Figure 1 *E/Z* equilibrium of ylide **4**.

spectrometry data is provided. The presence of the BF_4^- counterion in the mixed ylide **4** was proved by IR and ^{19}F NMR spectroscopy. In the ^{31}P NMR spectrum of ylide **4** recorded at room temperature, the phosphorus singlet is observed as broad line, which is a signal coalescence of two geometric isomers *E*-**4** and *Z*-**4**. This is indicative of a certain degree of double-bond character of the ylide fragment (Figure 1). The carbonyl singlet in the ^{13}C spectrum is also broadened, however the signal for the ylide carbon atom appears at 21.53 ppm as a sharp doublet with a spin–spin coupling constant $^1J_{CP}$ = 101.7 Hz. For the C(O)Ph-substituted acyclic ylide containing Ph_3P^+ group a doublet of ylide carbon atom could be observed only at a reduced temperature.[8]

To conclude, an approach to a new type of mixed phosphonium–iodonium ylides containing a cyclic dibenzophospholium fragment was developed. The cyclic nature of phosphonium moiety increases the barrier and necessary activation energy for the isomerization of mixed ylide. Such modification of ylide molecule can extend the application potential towards new compound types with spiro- or multicyclic structures.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.09.009.

References

1 (*a*) V. V. Zhdankin, *Hypervalent Iodine Chemistry: Preparation, Structure, and Synthetic Applications of Polyvalent Iodine Compounds*, Wiley, Weinheim, 2013; (*b*) G. K. Murphy, L. Racicot and M. S. Carle, *Asian J. Org. Chem.*, 2018, **7**, 837.

2 (*a*) E. D. Matveeva, T. A. Podrugina, A. S. Pavlova, A. V. Mironov, R. Gleiter and N. S. Zefirov, *Eur. J. Org. Chem*., 2009, 2323; (*b*) T. D. Nekipelova, V. A. Kuzmin, E. D. Matveeva, R. Gleiter and N. S. Zefirov, *J. Phys. Org. Chem.*, 2013, **26**, 137.

3 (*a*) E. D. Matveeva, T. A. Podrugina, M. A. Taranova, A. M. Ivanova, R. Gleiter and N. S. Zefirov, *J. Org. Chem.*, 2012, **77**, 5770; (*b*) T. D. Nekipelova and T. A. Podrugina, *Kinet. Catal.*, 2020, **61**, 159 (*Kinet. Katal*., 2020, **61**, 151).

4 A. S. Nenashev, D. S. Vinogradov, A. V. Mironov and T. A. Podrugina, *Russ. Chem. Bull., Int. Ed*., 2020, **69**, 2333 (*Izv. Akad. Nauk, Ser. Khim*., 2020, 2333).

5 (*a*) I. F. Wilson and J. C. Tebby, *J. Chem. Soc., Perkin Trans. 1*, 1972, 2713; (*b*) E. Vedejs and T. J. Fleck, *J. Am. Chem. Soc*., 1989, **111**, 5861; (*c*) E. Vedejs and C. F. Marth, *J. Am. Chem. Soc*., 1990, **112**, 3905; (*d*) P. A. Byrne, J. Muldoon, Y. Ortin, H. Müller-Bunz and D. G. Gilheany, *Eur. J. Org. Chem.*, 2014, 86; (*e*) P. A. Byrne, Y. Ortin and D. G. Gilheany, *Chem. Commun.*, 2014, **51**, 1147; (*f*) P. A. Byrne and D. G. Gilheany, *Chem. – Eur. J.*, 2016, **22**, 9140.

6 V. Iaroshenko and S. Mkrtchyan, *Organophosphorus Chemistry: From Molecules to Applications*, ed. V. Iaroshenko, Wiley, Weinheim, 2019.

7 (*a*) J. Cornforth, R. H. Cornforth and R. T. Gray, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2289; (*b*) S. Affandi, R. L. Green, B. T. Hsieh, M. S. Holt, J. H. Nelson and E. C. Alyea, *Synth. React. Inorg. Met.-Org. Chem.*, 1987, **17**, 307.

8 E. D. Matveeva, T. A. Podrugina, Yu. K. Grishin, V. V. Tkachev, V. V. Zhdankin, S. M. Aldoshin and N. S. Zefirov, *Russ. J. Org. Chem.*, 2003, **39**, 536 (*Zh. Org. Khim*., 2003, **39**, 572).

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