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Preparation, structure, and chemistry of phosphorane-derived phenyliodonium sulfonates

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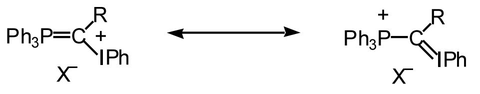
Abstract—New triphenylphosphorane-derived phenyliodonium triflates and tosylates were prepared by the reaction of the appropriate iodosobenzene sulfonate with stabilized phosphonium ylides. Structure of the triflate derivative was determined by a single-crystal X-ray analysis. These compounds represent a potentially useful class of reagents that combine in one molecule synthetic advantages of a phosphonium ylide and an iodonium salt. © 2002 Elsevier Science Ltd. All rights reserved.

During the last few years the chemistry of hypervalent iodine compounds (λ^3-iodanes) has experienced an unprecedented growth.[1] A broad variety of polyvalent iodine reagents have been prepared and new, highly useful synthetic procedures have been developed. Iodonium salts and ylides represent an especially important class of iodanes with rich and synthetically useful chemistry.[1,2] Mixed phosphonium–iodonium ylides, which are best described by the resonance contributors **1a** and **1b**, represent a potentially interesting, but underinvestigated, class of λ^3-iodanes combining in one molecule synthetic advantages of phosphonium ylides and iodonium salts. Several examples of the tetrafluoroborate derivatives **1** ($X = BF_4$) were previously prepared by the reaction of phosphonium ylides with (diacetoxyiodo)benzene in the presence of HBF_4,[3] but their chemistry was not elaborated.



1a **1b**

In this communication we report the preparation and structure of new sulfonate derivatives of phosphonium–iodonium ylides. We have found that the triflate iodonium derivatives **4** can be prepared as microcrystalline, off-white solids in good yields by the reaction of phosphonium ylides **2** with the pyridinium complex of iodobenzene ditriflate (**3**)[4] under mild conditions.[5] It should be emphasized that the use of the pyridinium complex **3** is essential in this procedure; the application of $PhIO/Tf_2O$ leads to the formation of a black tar due to the strongly acidic character of this reagent. The tosylate derivatives **6** can be conveniently prepared under similar conditions by treatment of phosphonium ylides **2** with Koser reagent[6] in dichloromethane (Scheme 1). Products **6** were isolated in the form of stable, white, microcrystalline solids; the yields and melting points of compounds **4** and **6** are listed in Table 1.

Sulfonates **4** and **6** were identified by NMR, IR, and elemental analysis.[5] In particular, proton NMR spectra of these compounds showed signals of four phenyls as well as the respective signals of the R-group and the tosylate anion for products **6**. ^{13}C NMR displays the signal of the ylidic carbon at 118–119 ppm as well as the signals corresponding to the aromatic rings and the R-groups.

The structure of iodonium triflate **4a** was unambiguously established by a single-crystal X-ray analysis.† The cationic portion of molecule **4a** is shown in Fig. 1.

Keywords: iodonium; phosphonium; hypervalent iodine; X-ray crystallography.

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† Crystallographic data (excluding structure factors) for structure **4a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 177487. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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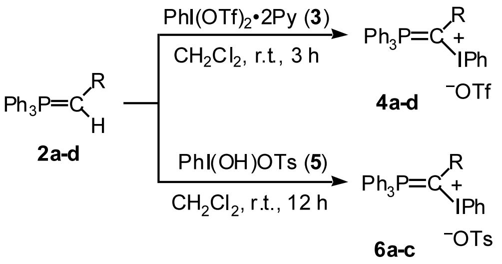


Scheme 1. Preparation of phosphonium–iodonium sulfonates.

Table 1. Yields and melting points of phosphonium–iodonium sulfonates

Product	R	Yield (%)	Mp (°C)
4a	C(O)CH$_3$	83	108–110
4b	CO$_2$CH$_3$	89	131–132
4c	CN	78	Oil
4d	CHO	56	129
6a	C(O)CH$_3$	50	110–111
6b	CO$_2$CH$_3$	47	118
6c	CN	51	102–107

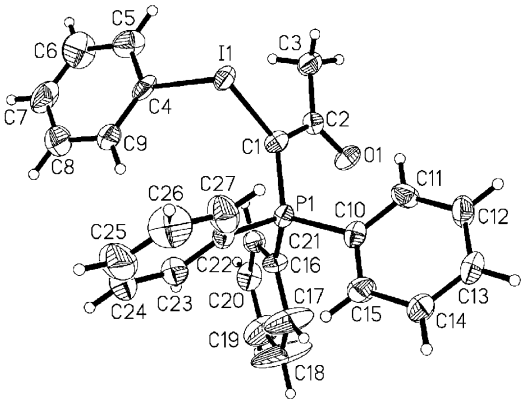
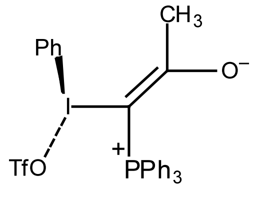


Figure 1. Perspective view of the cationic part of **4a**. Selected distances (Å) and angles (°): I–C(1) 2.068(7), I–C(4) 2.108(6), P–C(1) 1.749(7), P–C(10) 1.817(6), C(1)–C(2) 1.415(10) Å; I–C–P 121.8(4), C(1)–I–C(4) 101.4(3)°.

The structural data revealed a typical geometry of an iodonium salt with a C1–I–C4 bond angle of 101.4° and the triflate anion weakly associated with the iodine atom. The I–C bond distances of 2.068 and 2.108 Å are within the range of a typical bond length in diaryliodonium salts (2.0–2.1 Å).[1] The distance between the iodine atom and the nearest oxygen of the triflate anion, I···OTf, is 2.957 Å, while the shortest P···OTf distance is 4.370 Å, indicating the absence of secondary bonding between the phosphorus atom and the triflate anion. The phosphorus atom has a relatively short intramolecular interaction with the carbonyl oxygen (P1–O1 = 2.849 Å). The C1–C2 bond distance of 1.415 Å indicates a significant double bond character, which is consistent with the enolic structure **7** and typical of the carbonyl stabilized phosphonium ylides. In agreement with the enolic structure **7**, the atoms I1, P1, C3, O1, C1 and C2 are located in the same plane, while the phenyl of the iodonium group and the triflate group are outside of this plane. Structure **4a** is in good agreement with the X-ray data on the related tetrafluoroborate derivative published in 1984 by Moriarty and coworkers.[3]



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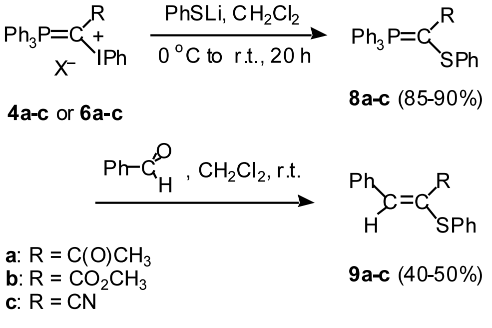
A preliminary investigation of chemical properties of compounds **4** and **6** has demonstrated that they react with soft nucleophiles, such as the thiophenolate anion, to afford products **8**, which can be further converted to alkenes **9** by the Wittig reaction with benzaldehyde (Scheme 2). In a representative example, the mixed ylide **6a** selectively reacts with lithium thiophenolate in dichloromethane to afford the respective ylide **8a** along with iodobenzene as the by-product. Products **8** were identified on the basis of NMR spectra and high-resolution FAB mass-spectrometry.[7] The reaction of ylides **8** with benzaldehyde afforded alkenes **9** as a mixture of *E* and *Z* isomers.

In conclusion, we report the preparation and X-ray structure of new phosphanylidene-derived iodonium salts. These compounds represent a potentially useful class of reagents that combine in one molecule synthetic advantages of a phosphonium ylide and an iodonium salt.



Scheme 2. Reactions of mixed phosphonium–iodonium ylides with thiophenolate anion.

Acknowledgements

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References

1. (a) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH Publishers: New York, 1992; (b) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic Press: London, 1997; (c) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123–1178.
2. Pirkuliev, N. S.; Brel, V. K.; Zefirov, N. S. *Russ. Chem. Rev.* **2000**, *69*, 105–120.
3. Moriarty, R. M.; Prakash, I.; Prakash, O.; Freeman, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 6082.
4. Weiss, R.; Seubert, J. *Angew. Chem., Int. Ed.* **1994**, *33*, 891.
5. **Representative experimental data**. *Preparation of* ***4a***: A solution of ylide **2a** (0.106 g, 0.335 mmol) in 3 ml dichloromethane was added to a suspension of triflate **3**[4] (0.221 g, 0.335 mmol) under a nitrogen atmosphere at room temperature. The solution was additionally stirred for 3 h, washed several times with water, dried, and concentrated in vacuum. Recrystallization of the residue from dichloromethane/diethyl ether afforded 0.556 g (83%) of product **4a** in the form of a white, microcrystalline solid; mp 108–110°C; IR (KBr): 3065, 1534, 1440, 1252, 512 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.27–7.66 (m, 20H, 4Ph), 2.62 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 193.4 (C=O), 134–122 (4Ph), 121 (q, $J_{CF}=318$ Hz, OTf), 118 (d, $J_{CP}=104$ Hz, C=P), 27 (CH_3). Anal. calcd for $C_{28}H_{23}F_3IO_4PS$: C, 50.16; H, 3.46; I, 18.93; S, 4.78. Found: C, 49.72; H, 3.48; I, 19.01; S, 4.65%. FAB HRMS *m/z* 521.0504 (M–OTf)$^+$, calcd for $C_{28}H_{23}F_3IO_4PS$ 521.05.
   Preparation of ***6a***: A mixture of reagent **5**[6] (0.196 mg, 0.5 mmol) and phosphonium ylide **2a** (0.151 g, 0.5 mmol) in dry dichloromethane was stirred overnight at room temperature under nitrogen. The resulting solution was concentrated in vacuum yielding a slightly yellow oil. The oil was recrystallized from dichloromethane and diethyl ester to afford 0.170 g (50%) of product **6a** as white crystals, mp 110–111°C; IR (KBr): 3050, 1550, 1223, 1176, 1114, 1031 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.4–8.0 (m, 20H), 7.34 (d, 2H, $J=8$ Hz), 7.12 (d, 2H, $J=8$ Hz) 2.63 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$): 190.0, 135–122 (4Ph and Ts), 119.0 (d, $J_{CP}=90$ Hz), 22.9, 16.8. Anal. calcd for $C_{34}H_{30}IO_4PS$: C, 58.97; H, 4.37; I, 18.32. Found C, 59.05; H, 4.34; I, 18.45%.
6. Koser, G. F. *Aldrichim. Acta* **2001**, *34*, 89.
7. Product **8a**: Oil, ^{1}H NMR ($CDCl_3$): δ 7.0–7.8 (m, 20H, 4Ph), 2.35 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 196.8 (C=O), 143–124 (4Ph), 55.5 (d, $J_{CP}=104.4$ Hz, C=P), 25.5 (CH_3). FAB HRMS *m/z* 427.13188 (M+H)$^+$, calcd for $C_{27}H_{24}OPS$ 427.12855.