Preparation and Chemistry of Phosphoranyl-Derived Iodanes

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The preparation and chemistry of novel phosphoranyl-derived λ^3-iodanes is reported. The phosphoranyl-derived phenyliodonium sulfonates were prepared in good yields by the reaction of stabilized phosphonium ylides [1-triphenylphosphoranylidene-2-propanone, methyl(triphenylphosphoranylidene)acetate, (triphenylphosphoranylidene)acetaldehyde, and (triphenylphosphoranylidene)acetonitrile] with the pyridinium complex of iodobenzene ditriflate or with [hydroxy(tosyloxy)-iodo]benzene under mild conditions. These compounds represent a potentially useful class of reagents that combine in one molecule synthetic advantages of a phosphonium ylide and an iodonium salt. Specifically, phosphorane-derived phenyliodonium tosylates can react with soft nucleophiles, such as iodide, bromide, benzenesulfinate, and thiophenolate anions, with a selective formation of the respective α-functionalized phosphonium ylides, which can be further converted to alkenes by the Wittig reaction with benzaldehyde. The phosphoranyl-derived benziodoxoles can be prepared by the reaction of 1-acetoxybenziodoxole with stabilized phosphonium ylides. An unusual ligand exchange on the iodine(III) center resulting in the substitution of a carbon ligand with an oxygen ligand was observed in the reaction of these compounds with strong acids.

Introduction

During the past 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.[1–3] In particular, alkenyliodonium salts have found synthetic application as powerful alkenylating reagents in the reactions with various nucleophiles.[1,2a–c] The high reactivity of iodonium salts in the reactions with nucleophiles is generally explained by the "hyperleaving group" properties of the phenyliodanyl group, which is a remarkably good nucleofuge with a leaving group ability about 10^6

times greater than the triflate.[2a] Mixed phosphonium–iodonium ylides, which are best described by the resonance contributors **1a** and **1b** (Figure 1), represent a potentially interesting, but underinvestigated, class of λ^3-iodanes combining in one molecule synthetic advantages of alkenyliodonium salts and phosphonium ylides.

The preparation of the tetrafluoroborate derivatives **1** by the reaction of phosphonium ylides with (diacetoxy-iodo)benzene in the presence of HBF$_4$ was first reported by Neilands and Vanag in 1964.[4] The same authors described the reaction of compounds **1** with HCl and HBr, leading to iodobenzene and the corresponding phosphonium salt resulting from nucleophilic substitution of PhI with the halide anion in the protonated molecule of **1**.[4] More recently, in 1984, Moriarty and co-workers reported the preparation of several new tetrafluoroborate derivatives **1** and the X-ray crystal structure for one of them.[5] Very recently, Huang and coauthors investigated the tandem reactions of tetrafluoroborates **1** and their arsonium analogues with several common nucleophiles and aldehydes.[6] In particular, this work[6] provided additional experimental support toward our earlier evaluation of mixed phosphonium–iodonium ylides as useful class of reagents that combine in one molecule synthetic advantages of a phosphonium ylide and an iodonium salt.[7]

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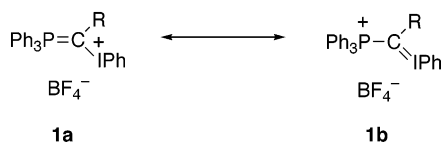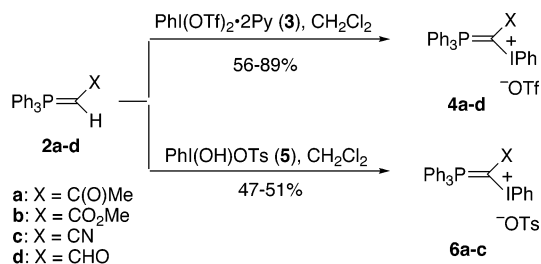
FIGURE 1. Mixed phosphonium−iodonium tetrafluoroborates.

SCHEME 1

In the present work, we report the preparation and chemistry of two new types of mixed phosphonium-iodonium ylides, namely, the phosphorane-derived phenyliodonium sulfonates and the phosphorane-derived benziodoxoles. X-ray crystal structures of these compounds were reported in our preliminary communications.[7,8]

Results and Discussion

Phosphoranyl-Derived Phenyliodonium Sulfonates. The synthesis of new sulfonate derivatives of phosphonium-iodonium ylides **4** and **6** is outlined in Scheme 1. The triflate iodonium derivatives **4** can be prepared in good yields by the reaction of phosphonium ylides **2** with the pyridinium complex of iodobenzene ditriflate (**3**)[9] under mild conditions. It should be emphasized that the use of the pyridinium complex **3** is essential in this procedure; the application of PhIO/Tf₂O in the absence of pyridine 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[10] in dichloromethane (Scheme 1). Products **4** and **6** in general were isolated in the form of stable, white, microcrystalline solids, with the exception of the nitrile derivatives **4c** and **6c**, which had lower thermal stability and were isolated as oils.

Sulfonates **4** and **6** were identified by NMR, IR, and elemental analysis. In particular, proton NMR spectra of these compounds showed signals of four phenyls as well as the respective signals of the substituent X and the tosylate anion for products **6**. ¹³C NMR displayed a low-intensity signal of the ylidic carbon at 60−30 ppm as a doublet with $J_{CP} \approx 100$ Hz and the signals corresponding to the aromatic rings and the X-groups.

A single-crystal X-ray structure of iodonium triflate **4a** was reported in our preliminary communication.[7] The structural data revealed a typical geometry of an iodo-
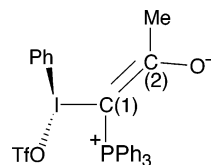

FIGURE 2. Compound **4a**.

nium salt and the triflate anion weakly associated with the iodine atom. The I−C bond distances of 2.068 Å (I−C1) and 2.108 Å (I−Ph) are within the range of a typical bond length in diaryliodonium salts (2.0−2.1 Å). 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 (P−O = 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 of **4a** (Figure 2) and typical of the carbonyl-stabilized phosphonium ylides. Structure of **4a** is in good agreement with the X-ray data on the related tetrafluoroborate derivative published in 1984 by Moriarty and co-workers.[5] Overall, the X-ray data indicate that the actual structure of mixed phosphonium−iodonium ylides is better described by the resonance contributor **1a**, which is similar to alkenyl-iodonium salts, rather than the contributor **1b**, analogous to iodonium ylides.

On the basis of these structural data, it could be anticipated that the chemical reactivity of the sulfonate derivatives **4** and **6** is similar to the reactivity of alkenyliodonium salts and phosphonium ylides. At the same time, due to the powerful electron-withdrawing ability of the phenyliodanyl group,[1b] the nucleophilicity of the ylidic carbon in these compounds is sharply decreased and, therefore, their reactivity as phosphonium ylides in the Wittig reaction with aldehydes should be low. As expected, we have found that no reaction is observed between compounds **6** and benzaldehyde, even at temperatures above 100 °C. In contrast, compounds **6** are highly reactive in the reactions with nucleophiles due to the excellent leaving group ability of the phenyliodanyl group. We have found that sulfonates **6** readily react with halide anions and with benzenesulfinate anion at room temperature, under the same conditions as previously reported by Ochiai for alkenyliodonium salts.[11,12]

Tosylate 6a reacts with potassium iodide or potassium bromide in methanol with a selective formation of the respective α-halogenated phosphonium ylides **7** (Scheme 2), which were isolated as analytically pure microcrystalline solids in high yield. Products **7** were identified on the basis of spectroscopic data and elemental analysis. Likewise, the reaction of tosylate **6b** with sodium benzenesulfinate under mild conditions affords sulfone **8** as the major product (Scheme 3).

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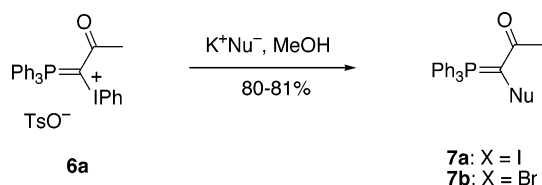
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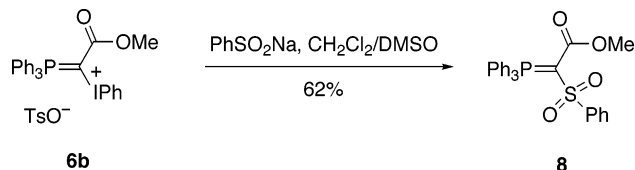(10) Koser, G. F. *Aldrichimica Acta* **2001**, *34*, 89.

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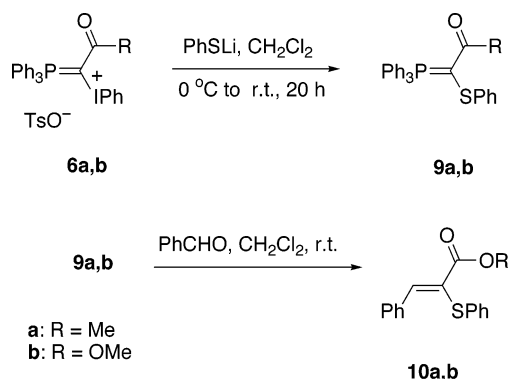
SCHEME 2

6a → 7a: X = I; 7b: X = Br

K+Nu−, MeOH, 80-81%

SCHEME 3

6b → 8

PhSO₂Na, CH₂Cl₂/DMSO, 62%

SCHEME 4

6a,b → 9a,b

PhSLi, CH₂Cl₂, 0 °C to r.t., 20 h

9a,b → 10a,b

PhCHO, CH₂Cl₂, r.t.

a: R = Me
b: R = OMe

SCHEME 5

11 + 2a,b → 12a,b

TMSOTf, Py, CH₂Cl₂, r.t.

a: R = CH₃
b: R = OCH₃

The mechanism of nucleophilic substitution in mixed ylides **6** is probably similar to the analogous reactions of alkenyliodonium salts and can be realized by several alternative pathways, such as an addition−elimination route, ligand coupling on iodine, or a direct S_N2-type process.[11,12] The α-substituted phosphonium ylides that can be conveniently prepared by the reactions of mixed ylides **6** with nucleophiles represent an important class of reagents useful in the synthesis of natural products.[13]

Mixed ylides **6** cannot react directly with carbonyl compounds, but their products of nucleophilic substitution can be easily converted to alkenes **9** by the Wittig reaction with benzaldehyde. A representative example of such a tandem reaction is shown in Scheme 4. Compounds **6a** and **6b** selectively react with lithium thiophenolate in dichloromethane to afford the respective ylide **9** along with iodobenzene as the byproduct. The subsequent reaction of ylides **9** with benzaldehyde yields alkenes **10** with a predominant formation of *Z* isomers.

Phosphoranyl-Derived Benziodoxoles. In the past decade, there has been considerable interest and research activity focused on the chemistry of five-membered iodine(III) heterocycles, derivatives of benziodoxole.[1,14] The most important and best-investigated heterocyclic iodane is 1-hydroxy-1,2-benziodoxol-3(1*H*)-one, the cyclic tautomer of 2-iodosylbenzoic acid. Other iodine-substituted benziodoxoles, such as the peroxide,[15a,b] azide,[15c]
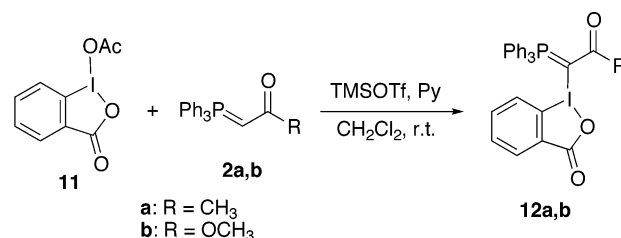
cyanide,[15d] amides,[15e] and tosylate,[15f,g] can be prepared by ligand exchange on iodine upon treatment of 1-hydroxy-1,2-benziodoxol-3(1*H*)-one with the appropriate nucleophile. These various benziodoxole derivatives have found practical application as the reagents for oxidative functionalization of organic substrates.[1,14b] Considering the importance of benziodoxole derivatives in organic chemistry, we decided to explore the preparation and chemistry of novel phosphoranyl-derived benziodoxoles.

Compounds **12** were prepared by the reaction of phosphoranes **2** with acetoxybenziodoxole **11** in the presence of trimethylsilyl triflate and pyridine (Scheme 5) and isolated in the form of stable, white, microcrystalline solids.

Benziodoxoles **12** were characterized by elemental analysis and spectroscopic data. In particular, proton NMR spectra of these compounds showed signals of the triphenylphosphonium group and the benziodoxole ring, as well as the respective signals of the substituent R. ¹³C NMR displayed a low-intensity signal of the ylidic carbon at 45−26 ppm as a doublet with $J_{CP} \approx 100$ Hz and the signals corresponding to the aromatic rings and the R groups.

Single-crystal X-ray structures of both products **12a** and **12b** were reported in our preliminary communication.[8] The structural data revealed a typical, essentially planar geometry of the benziodoxole ring system with the I−O bond lengths at about 2.5−2.6 Å. The I−C bond lengths in **12b** are 2.056 and 2.134 Å, which are values comparable to the analogous bonds in derivatives **4a**. The ylidic fragment in **12** has a planar, enolic geometry, with all parameters similar to **4a** (Figure 2); the plane of the enolate fragment in **12** is perpendicular to the benziodoxole ring system.

It is known from the literature that, in contrast to iodonium salts, benziodoxole derivatives are generally not reactive in nucleophilic substitution reactions.[1,14b,15] As

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SCHEME 6
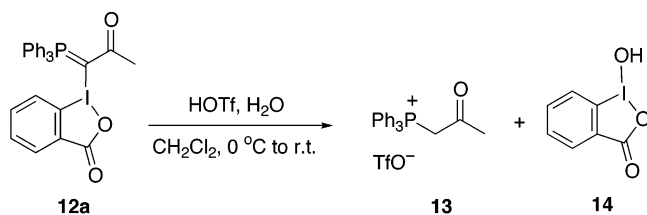
SCHEME 7
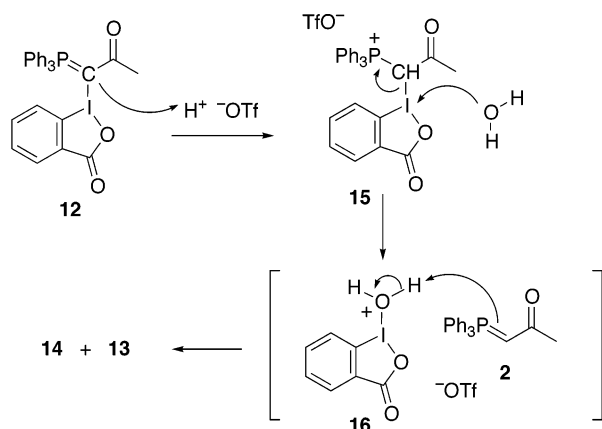
expected, we have found that the chemical properties of compounds **12** are quite different from the noncyclic phosphoranyl derivatives **6** and other known iodonium salts. In contrast to the noncyclic derivatives **6**, benziodoxoles **12** are not reactive toward soft nucleophiles, such as PhS⁻ and I⁻ anions, even at elevated temperature (up to 100 °C) and in the presence of copper or palladium catalysts. On the other hand, compounds **12** readily react with strong acids (e.g., HOTf), affording phosphonium salt **13** and benziodoxole **14** as major products (Scheme 6). Phosphonium triflate **13** was isolated from the reaction mixture as the major product and identified by elemental analysis, MS, and NMR spectroscopy. In particular, the ¹H and ¹³C NMR spectra of triflate **13** are close to the literature data reported for the similar phosphonium halides and tetrafluoroborate.[16]

This reaction represents an unusual example of a ligand exchange on the iodine(III) center resulting in the substitution of a carbon ligand with an oxygen ligand. A plausible mechanism of this reaction includes protonation of the ylidic carbon of **12** followed by substitution of the carbon ligand in intermediate **15** with water (Scheme 7). This remarkable substitution is most likely explained by a stabilizing effect of the phosphonium moiety on the carbon leaving group in the protonated intermediate **15**.

Conclusion

In conclusion, we have reported the preparation and chemistry of novel phosphoranyl-derived λ^3-iodanes. The sulfonate iodonium derivatives **4** and **6** can be prepared in good yields by the reaction of phosphonium ylides **2** with the pyridinium complex of iodobenzene ditriflate (**3**) or with [hydroxy(tosyloxy)iodo]benzene (**5**) under mild

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conditions. These compounds represent a potentially useful class of reagents that combine in one molecule synthetic advantages of a phosphonium ylide and an iodonium salt. Specifically, iodonium tosylates **6** can react with soft nucleophiles, such as iodide, bromide, benzenesulfinate, and thiophenolate anions, with a selective formation of the respective α-functionalized phosphonium ylides **7–9**, which can be further converted to alkenes **10** by the Wittig reaction with benzaldehyde.

The phosphoranyl-derived benziodoxoles **12** can be prepared by the reaction of acetoxybenziodoxole **11** with stabilized phosphonium ylides. An unusual ligand exchange on the iodine(III) center resulting in the substitution of a carbon ligand with an oxygen ligand was observed in the reaction of these compounds with strong acids.

Experimental Section

General. All reactions were performed under dry nitrogen atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Methylene chloride and acetonitrile were distilled from CaH₂ immediately prior to use. Diethyl ether was distilled from Na/benzophenone. Phenyl(dipyridinium)iodonium triflate **3** was prepared from (diacetoxyiodo)benzene, trimethylsilyl triflate, and pyridine by a known procedure.[9] 1-Acetoxybenziodoxole **1** was prepared by heating the commercial 2-iodosylbenzoic acid with acetic anhydride.[17] Infrared spectra were recorded as a KBr pellet; NMR spectra were recorded at 300 MHz (¹H NMR) and 75.5 MHz (¹³C NMR). Chemical shifts are reported in parts per million (ppm). ¹H and ¹³C chemical shifts are referenced relative to the residual nondeuterated solvent. Microanalyses were carried out by Atlantic Microlab, Inc., Norcross, GA.

Typical Procedure for the Preparation of Phosphoranyl-Derived Phenyliodonium Triflates. 1-Phenyliodonium[1-(triphenylphosphoranylidene)-2-propanone] Triflate, 4a. A solution of ylide **2a** (0.106 g, 0.335 mmol) in dichloromethane (3 mL) was added to a suspension of reagent **3**[9] (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 a 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 3065, 1534, 1440, 1252, 512 cm⁻¹; ¹H NMR (CDCl₃) δ 7.66–7.27 (m, 20H), 2.62 (s, 3H); ¹³C NMR (CDCl₃) δ 193.4, 133.7, 133.5, 131.3, 130.9, 129.5, 129.3, 123.2 (d, J_{CP} = 94 Hz), 121.0 (q, J_{CF} = 318 Hz), 118.1, 43.3 (d, J_{CP} = 104 Hz), 27.0; FAB HRMS *m/z* 521.0504 [M − OTf]⁺, calcd for C₂₇H₂₃IOP 521.050. Anal. Calcd for C₂₈H₂₃F₃IO₄PS: 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. For X-ray structure see ref 7.

Phenyliodonium[methyl(triphenylphosphoranylidene)-acetate] Triflate, 4b. In a similar procedure, the reaction of ylide **2b** (300 mg, 0.85 mmol) with the generated in situ reagent **3** (0.85 mmol) afforded 0.519 g (89%) of product **4b**: mp 131–132 °C; IR 3062, 1598, 1435, 1250, 1115, 500 cm⁻¹; ¹H NMR (CDCl₃) δ 7.62–7.26 (m, 20H), 3.56 (s, 3H); ¹³C NMR (CDCl₃) δ 168.1, 134.1, 133.9, 132.0, 131.1, 129.6, 129.5, 123.5 (d, J_{CP} = 98 Hz), 121 (q, J_{CF} = 318 Hz), 118.3, 53.0, 26.7 (d, J_{CP} = 98 Hz). Anal. Calcd for C₂₈H₂₃F₃IO₅PS·H₂O: C, 47.74; H, 3.58; I, 18.02; S, 4.55. Found: C, 47.55; H, 3.36; I, 18.12; S, 4.51.

Phenyliodonium[(triphenylphosphoranylidene)acetonitrile] Triflate, 4c. The reaction of ylide **2c** (300 mg, 0.995

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mmol) with reagent **3** (0.995 mmol) under similar conditions afforded 0.507 g (78%) of product **4c** as a colorless oil: IR 3065, 2153, 1440, 1251, 1024, 565 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.36–7.77 (m). ^{13}C NMR (CDCl$_3$) δ 137.4, 133.8, 132.3, 132.1, 131.9, 129.6, 129.5, 124.0 (d, J_{CP} = 100 Hz), 121 (q, J_{CF} = 318 Hz), 118.3, 117.7, 31.5 (d, J_{CP} = 100 Hz). Due to the compound's low stability, C, H, N analysis was not possible.

Phenyliodonium[(triphenylphosphoranylidene)acetaldehyde] Triflate, 4d. The reaction of ylide **2d** (200 mg, 0.660 mmol) with reagent **3** (0.660 mmol) under similar conditions afforded 0.243 g (56%) of product **4d**: mp 129–130 °C; IR 3062, 2812, 1735, 1440, 1260, 1029, 500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 9.55 (d, J_{PH} = 26 Hz, 1H), 7.24–7.96 (m, 20H); ^{13}C NMR (CD$_3$CN) δ 179.5, 136.1, 135.6, 134.7, 134.2, 133.8, 132.5, 122.7 (d, J_{CP} = 93 Hz), 121 (q, J_{CF} = 318 Hz), 116.4, 56.0 (d, J_{CP} = 94 Hz). FAB HRMS m/z 507.0363 [M – OTf]$^+$, calcd for C$_{26}$H$_{21}$IOP 507.040. Anal. Calcd for C$_{27}$H$_{21}$F$_3$IO$_4$PS: C, 49.40; H, 3.22; I, 19.33; S, 4.89. Found: C, 49.54; H, 3.42; I, 19.45; S, 4.95.

Typical Procedure for the Preparation of Phosphoranyl-Derived Phenyliodonium Tosylates. 1-Phenyliodonium[1-(triphenylphosphoranylidene)-2-propanone] Tosylate, 6a. A mixture of reagent **5** (0.196 mg, 0.5 mmol) and phosphonium ylide **2a** (0.151 g, 0.5 mmol) in dry dichloromethane (20 mL) was stirred overnight at room temperature under nitrogen. The resulting solution was concentrated in a 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 111–112 °C; IR 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 (CDCl$_3$) δ 193.5, 143.4, 139.1, 135.4, 133.7, 133.4, 131.1, 129.4, 129.3, 128.4, 126.0, 123.6 (d, J_{CP} = 92.9 Hz), 118.5, 43.9 (d, J_{CP} = 102 Hz), 27.3, 21.3. Anal. Calcd for C$_{34}$H$_{30}$IO$_4$PS: C, 58.97; H, 4.37; I, 18.32. Found C, 59.05; H, 4.34; I, 18.45.

Phenyliodonium[methyl(triphenylphosphoranylidene)acetate] Tosylate, 6b. In a similar procedure, the reaction of ylide **2b** (170 mg, 0.51 mmol) with reagent **5** (200 mg, 0.51 mmol) in dichloromethane afforded 170 mg (47%) of **6b** as white crystals: mp 118–119 °C; IR 3050, 2948, 1622, 1430, 1280, 1192, 1098, 1031, 1010 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.68–7.48 (m, 20H), 7.29 (d, 2H, J = 8 Hz), 7.09 (d, 2H, J = 8 Hz), 3.60 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 168.3, 143.8, 138.8, 135.0, 133.7, 132.1, 131.0, 129.5, 129.3, 128.3, 126.1, 123.8 (d, J_{CP} = 93.4 Hz), 119.9, 61.5 (d, J_{CP} = 103 Hz), 52.5, 21.3. Anal. Calcd for C$_{34}$H$_{30}$IO$_5$PS: C, 57.63; H, 4.27. Found: C, 58.02; H, 4.28.

Phenyliodonium[(triphenylphosphoranylidene)-acetonitrile] Tosylate, 6c. A solution of reagent **5** (200 mg, 0.51 mmol) in freshly distilled acetonitrile (20 mL) was added to the solution of ylide **2c** (153 mg, 0.51 mmol) in acetonitrile (5 mL) at 0 °C under nitrogen. The resulting clear yellow solution was stirred for 2 h at 0 °C and left overnight at room temperature. The resulting solution was concentrated in a vacuum, yielding a slightly yellow oil. The oil was recrystallized from acetonitrile and diethyl ester to afford 0.175 g (51%) of product **6c** as yellow crystals: mp 102–107 °C (dec); IR 3051, 2916, 2864, 2148, 1918, 1472, 1171, 1031 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.74–7.5 (m, 20H), 7.3 (d, 2H, J = 8 Hz), 7.07 (d, 2H, J = 8 Hz), 2.3 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 143.5, 138.9, 134.6, 133.7, 132.7, 131.3, 130.9, 129.8, 128.4, 125.9, 122.0 (d, J_{CP} = 93.4 Hz), 120.6, 33.8 (d, J_{CP} = 99 Hz), 21.2. Due to the compound's low stability, C, H, N analysis was not possible.

1-Iodo-1-(triphenylphosphoranylidene)-2-propanone, 7a (Typical Procedure). A solution of potassium iodide (240 mg, 1.4 mmol) in methanol (20 mL) was added to the solution of compound **6a** (200 mg, 0.29 mmol) in methanol (30 mL) under a nitrogen atmosphere at 0 °C. The resulting yellow mixture was stirred overnight at room temperature. The formation of a slightly yellow precipitate was observed. The precipitate was filtered and dried in a vacuum to yield

the yellow microcrystalline powder of product **7a** (103 mg, 80%): mp 96–98 °C; IR (KBr) 3049, 2991, 1676, 1524, 1362, 1156, 1102, 995 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.8–7.3 (m, 15H), 2.4 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 190.4, 133.5, 131.9, 128.6, 126.6 (d, J_{CP} = 92.9 Hz), 28.0, 10.0 (d, J_{CP} = 115 Hz, C=P); FAB HRMS m/z (%) 444.0165 (75) M$^+$, 445.0207 (100), [M + H]$^+$; calcd for C$_{21}$H$_{18}$IOP 444.0140; calcd for C$_{21}$H$_{19}$IOP 445.0218. Anal. Calcd for C$_{21}$H$_{18}$IOP·0.5H$_2$O: C, 55.65; H, 4.23. Found: C, 55.97, H, 4.30.

1-Bromo-1-(triphenylphosphoranylidene)-2-propanone, 7b. In a similar procedure, the reaction of ylide **6a** (200 mg, 0.29 mmol) with potassium bromide (172 mg, 1.4 mmol) in methanol afforded 92 mg (81%) of **7b** as a white microcrystalline powder: mp 136–138 °C; IR 3050, 2981, 1682, 1505, 1377, 1156, 1102, 999 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.8–7.5 (m, 15H), 2.4 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 188.9, 133.6, 132.0, 128.5, 125.9 (d, J_{CP} = 92.9 Hz), 45.8 (d, J_{CP} = 117 Hz), 26.5. FAB HRMS m/z (%) 396.0275 (19), 398.0295 (23), M$^+$; calcd for C$_{21}$H$_{18}$^{79}BrOP 396.0278; calcd for C$_{21}$H$_{18}$^{81}BrOP 398.0258. Anal. Calcd for C$_{21}$H$_{18}$BrOP: C, 63.49; H, 4.57; Br, 20.11. Found: C, 63.41; H, 4.77; Br, 19.83.

Benzenesulfonyl[methyl(triphenylphosphoranylidene)-acetate], 8. A solution of sodium benzenesulfinate (232 mg, 1.4 mmol) in dimethyl sulfoxide (20 mL) was added to the solution of compound **6b** (200 mg, 0.29 mmol) in dichloromethane (20 mL) under a nitrogen atmosphere at 0 °C. The resulting mixture was stirred overnight at room temperature. Then mixture was washed with distilled water (3 × 15 mL), and the organic layer was dried with sodium sulfate and concentrated in a vacuum, yielding product **8** as a colorless oil (82 mg, 62%): IR (CCl$_4$) 3057, 2976, 1738, 1432, 1259, 1190, 1115, 1071 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.9–7.1 (m, 20H), 3.3 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 168.1, 147.9, 133.6, 132.4, 128.6, 127.8, 127.4, 124.9, 124.5 (d, J_{CP} = 90.0 Hz), 59.0 (d, J_{CP} = 112 Hz), 50.3, 29.5; FAB HRMS m/z 497.09524 [M + Na]$^+$, calcd for C$_{27}$H$_{23}$O$_4$PSNa 497.09658.

1-Phenylsulfanyl-1-(triphenylphosphoranylidene)-2-propanone, 9a (Typical Procedure). Butyllithium in hexane (0.11 mL of 2.5M solution) was mixed with benzenethiol (31 mg, 0.28 mmol) in dichloromethane (1 mL) under nitrogen at 0 °C. Then, a solution of ylide **6a** (194 mg, 0.28 mmol) in dichloromethane (10 mL) was added to this mixture. The resulting mixture was stirred for 5 h at 0 °C and then left overnight at room temperature. Then the mixture was filtered and the organic solution was concentrated in a vacuum to yield product **9a** in the form of a slightly yellow solid (106 mg, 89%): mp 214–218 °C;[18] ^{1}H NMR (CDCl$_3$) δ 7.8–7.0 (m, 20H), 2.35 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 196.8, 133.5, 133.1, 131.8, 129.2, 128.6, 127.2, 125.9, 126.6 (d, J_{CP} = 100 Hz), 55.5 (d, J_{CP} = 104 Hz), 25.5; FAB HRMS m/z 427.13188 (M + H)$^+$, calcd for C$_{27}$H$_{24}$OPS 427.12855. Ylide **9a** was further converted to the known[19] (Z)-4-phenyl-3-phenylsulfanyl-3-buten-2-one, **10a**, by treatment with benzaldehyde at room temperature.

Reaction of Compound 9b in Situ with Benzaldehyde. In a similar procedure, the reaction of ylide **6b** (200 mg, 0.28 mmol) with benzenethiol (31 mg, 0.28 mmol) in dichloromethane afforded 101 mg (85%) of crude **9b** as a yellow oil, which was further converted to the known[20] (Z)-methyl-2-(phenylsulfanyl) cinnamate, **10b**, by treatment with benzaldehyde at room temperature. Compound **10b** was isolated by column chromatography (silica gel, hexane/ethyl acetate, 10:1) to yield 49 mg (40%): ^{1}H NMR (CDCl$_3$) δ 8.1–7.1 (m, 11H), 3.7 (s, 3H);[19] CI HRMS m/z 271.0815 [M + H]$^+$, calcd for C$_{16}$H$_{15}$SO$_2$ 271.0793.

**Typical Procedure for the Preparation of Phosphoranyl-Derived Benziodoxoles. 1-[2-Oxo-1-(triphenyl-λ^5-phosphanylidene)propyl]-1H-1λ^3-benzo[d][1,2]iodoxol-3-

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one, 12a. A sample of 1-acetoxybenziodoxole **11** (200 mg, 0.65 mmol) was dissolved in dichloromethane (3.5 mL) and stirred under nitrogen for 30 min, then trimethylsilyl triflate (145 mg, 0.65 mmol) was added, and after 10 min of stirring, a solution of pyridine (155 mg, 1.95 mmol) in dichloromethane (0.5 mL) was added. The reaction mixture was additionally stirred for 2 h at room temperature. A solution of ylide **2a** (207 mg, 0.65 mmol) in dichloromethane (0.1 mL) was then added to the reaction mixture. The mixture was stirred overnight at room temperature. The resulting clear solution was washed with distilled water and dried with anhydrous sodium sulfate. Solvents were removed in a vacuum to afford a colorless oil, which was recrystallized from dichloromethane and diethyl ether to yield 157 mg (43%) of **12a** in the form of white crystals: mp 175−176 °C; IR (KBr) 3048, 1635, 1610, 1535, 1361, 1303, 1010 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.38 (d, 1H, $J = 8$ Hz), 7.8 (d, 1H, $J = 8$ Hz), 7.8−7.4 (m, 17H), 2.47 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 194.6, 166.9, 134.1, 133.4, 133.2, 132.6, 132.5, 130.2, 129.4, 124.7 (d, $J_{CP} = 92.7$ Hz), 122.5, 117.4, 44.4 (d, $J_{CP} = 91.8$ Hz), 27.8; ES MS m/z (%) 565 (100), [M + H]$^+$, 317 (83), [M − IC$_6$H$_4$CO$_2$]$^+$. Anal. Calcd for C$_{28}$H$_{22}$IO$_3$P·H$_2$O: C, 57.75; H, 4.15; I, 21.79. Found: C, 57.81; H, 3.94; I, 22.05. For X-ray structure see ref 8.

(3-Oxo-3H-1λ3-benzo[d][1,2]iodoxol-1-yl)(triphenyl-λ^5-phosphanylidene)acetic Acid Methyl Ester, 12b. In a similar procedure, the reaction of 1-acetoxybenziodoxole **1** (200 mg, 0.65 mmol) with ylide **2b** (217 mg, 0.65 mmol) afforded 174 mg (46%) of product **12b** in the form of white crystals: mp 151−152 °C; IR (KBr) 3055, 1602, 1435, 1355, 1275, 1200 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.32 (d, 1H, J = 8 Hz), 7.81 (d, 1H, J = 8 Hz), 7.6−7.4 (m, 17H), 3.55 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 169.4 (d, $J_{CP} = 13$ Hz), 167.1, 134.1, 133.7, 133.2, 132.2, 130.2, 129.7, 129.2, 125.0 (d, $J_{CP} = 98.7$ Hz), 122.9, 117.3, 52.1, 26.7 (d, $J_{CP} = 98.2$ Hz). Anal. Calcd for C$_{28}$H$_{22}$IO$_4$P·H$_2$O: C, 56.20; H, 4.04; I, 21.21. Found: C, 56.30; H, 3.87; I, 20.72. For X-ray structure see ref 8.

Reaction of Compound 12a with Trifluoromethanesulfonic Acid. A sample of compound **12a** (200 mg, 0.35 mmol) was dissolved in dichloromethane (25 mL) and stirred under nitrogen at 0 °C for 30 min, then trifluoromethanesulfonic acid (53 mg, 0.35 mmol) was added. The reaction mixture was stirred overnight at room temperature, then the solvent was removed in a vacuum to afford 250 mg of colorless oil, which, according to ^{1}H and ^{13}C NMR spectra, was a mixture of phosphonium salt **13** and 1-hydroxybenziodoxole **14**. Careful crystallization of this oil from dichloromethane and diethyl ether afforded 137 mg (83%) of phosphonium salt **13** in the form of white crystals: mp 133−135 °C; IR (KBr) 3048, 2930, 2300, 1719, 1660, 1255, 1164 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.7 (m, 15H), 5.17 (d, $J_{CP} = 11.7$ Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 200.4 (C=O), 134.8 (CH), 133.5 (CH), 130.1 (CH), 120.1 (q, SO$_2$CF$_3$), 118.3 (d, $J_{CP} = 89.7$ Hz, CP), 38.9 (d, $J_{CP} = 59.9$ Hz, CH$_2$P); FAB MS m/z (%) 319 (100), [M − OTf]$^+$. Anal. Calcd for C$_{22}$H$_{20}$F$_3$O$_4$PS: C, 56.41; H, 4.30; S, 6.85. Found: C, 56.20; H, 4.36; S, 7.00.

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