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Hetaryl-Substituted Phosphonium-Iodonium Ylides in Synthesis of Heterocycles

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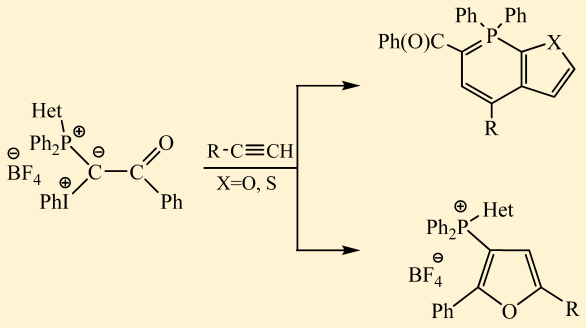
Supporting Information

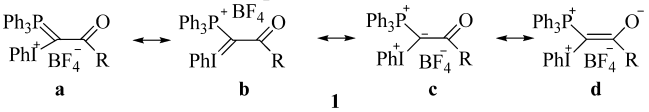
ABSTRACT: A series of hitherto unknown hetaryl-substituted (in phosphonium part) phosphonium−iodonium ylides were synthesized. The reaction of these mixed phosphonium−iodonium ylides with acetylenes opens a way to new furyl annelated phosphinolines or unusually substituted phosphininofurans.



INTRODUCTION

The work of Wittig et al., especially the discovery of carbonyl olefination by phosphonium ylides,[1,2] has spurred the development of the chemistry of these species and other ylides.[3,4] Some time ago, we focused our attention on mixed phosphonium−iodonium ylides, which reveal unusual reactivity. We have performed our studies mainly using carbonyl-stabilized mixed ylides **1**, $Ph_3P(IPh)=CHR$ (R=$COOC_2H_5$, COAr), which may be described by resonance structures **1a**−**d** (Scheme 1).[5,6]

Scheme 1. Resonance Structures (a−d) of Ylide 1



Our previous research on the chemistry of such phosphonium−iodonium ylides revealed several different pathways for the reactions of these compounds, which crucially depend on the possibility of the conjugation shown. The resonance structure **1d** clearly reveals the possibility for these ylides to play a role as nucleophile, having a negatively charged oxygen center. Indeed, we have shown that ylides **1** can be alkylated, silylated, or acetylated.[7,8] Moreover, we have found that phosphonium−iodonium ylides enter into photochemical reaction of 1,3-dipolar cycloaddition (probably via intermediacy of transient 1.3-dipoles) with a triple C≡N bond to afford triphenylphosphonium-substituted oxazoles **2**; their formation is obviously connected with a nucleophilic oxygen center of the ylides.[9,10] The mechanism of the photoinduced cycloaddition of acetonitrile to **1** was studied by steady-state and time-resolved methods.[11] It was found that the formation of the final products oxazole and phosphonium salt occurs in parallel processes starting by the heterolytic C−I^+−Ph cleavage followed by a 1,3-dipolar cycloaddition.

The analogous reactions with a C≡C triple bond proceed quite differently. In analogy with the C≡N triple bond one anticipates the formation of the corresponding furans **3**, which have been found experimentally.[12] However, the main pathway found for this reaction was the formation of phosphinolines **4**. In other words, interaction of acetylenes with ylides **1** using photochemical conditions led to a mixture of furans **3** and phosphinolines **4**, their ratio being dependent on the nature of the substituents at the triple bond of acetylenes (Scheme 2).[13,14]

Previously, we proposed a mechanism (Scheme 3) for the formation λ^5-phosphinolines and furans. Upon UV irradiation, the C−I bond is cleaved with the formation of an electrophilic intermediate, which interacts with the C≡C bond to give a carbocation **B**. Subsequent intramolecular ***electrophilic*** attack to the benzene ring attached to the phosphorus atom leads to the formation of six-membered phosphinoline[12] (path b, Scheme 3). In other words, this mechanistic scheme includes electrophilic aromatic substitution as key mechanistic step. This idea was supported using the corresponding ylide, in which one phenyl substituent was replaced by a thiophene ring.[14] In this case, the electrophilic substitution prefers the thiophene ring, known to be more inclined to undergo electrophilic

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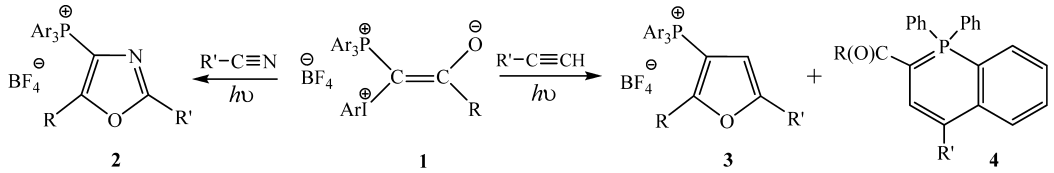
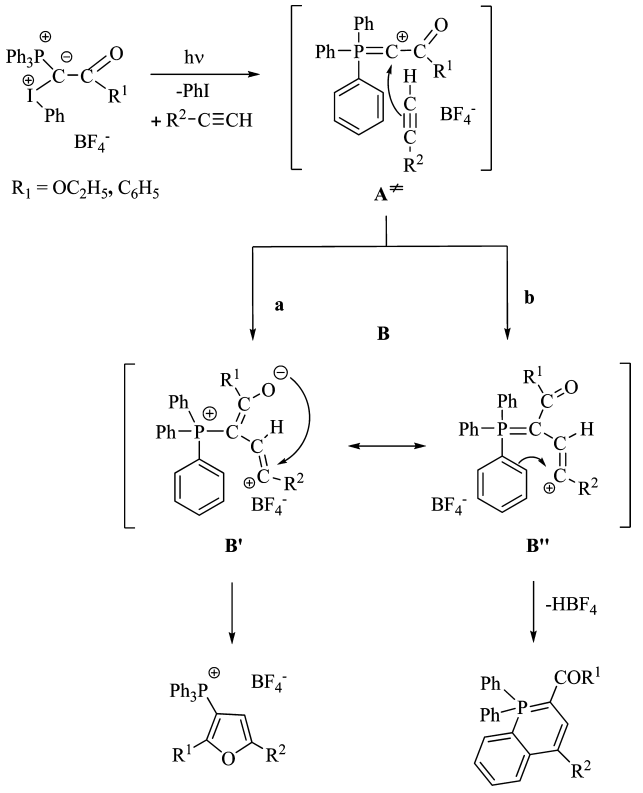
Scheme 2. Interaction of Acetylenes with Ylides 1



Scheme 3. Formation λ^5-Phosphinolines and Furans

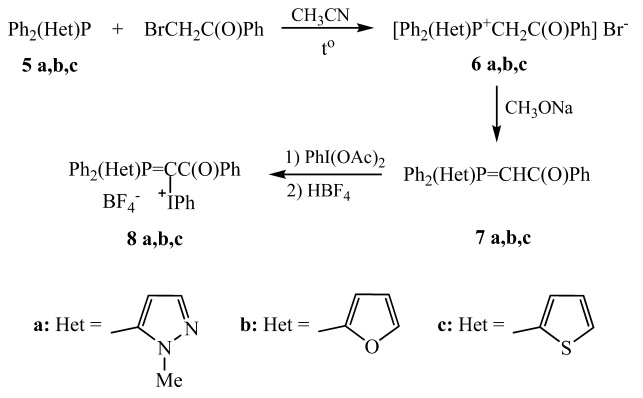


substitution than the phenyl ring. The present paper concerns the future development of this idea, using furyl and pyrazolyl derivatives, which are correspondingly more and less prone to undergo electrophilic substitution as compared with phenyl.

RESULTS AND DISCUSSION

We chose to use furyldiphenylphosphine **5b** and (pyrazolyl)-diphenylphosphine **5a** (Scheme 4) to prepare the corresponding ylides **8a** and **8b** because the heterocycle attached to the P center determines the tendency for electrophilic substitution. We expect in the case of **5a** less and in case of **5b** more tendency to electrophilic substitution as compared to the phenyl ring. These ylides **8a** and **8b** were not described previously in the literature, and Scheme 4 exhibits the synthetic pathways leading to them. The desired mixed ylides **8a** and **8b** were isolated in 80−95% yield as tetrafluoroborates.

Scheme 4. Preparation of the Ylides 8



The study of the photochemical reactions (2 h in CH_2Cl_2) of ylide **8a** with acetylenes reveals the data given in Scheme 5. In the photochemical reaction of ylide **8a** with phenylacetylene, we isolated only the corresponding phosphinoline **9** (R═Ph) in 10% yield. The isolation of this product demonstrates the higher activity of benzene as compared the pyrazole ring in the electrophilic substitution step. In contrast, the photochemical reaction of the ylide **8a** with 9-ethynylphenanthrene afforded only the corresponding furan **10** (R = $C_{14}H_9$) in 30% yield. The low yields are mostly due to the poor solubility of starting material in a CH_2Cl_2 as well as the enhanced decomposition of the ylide **8a** to give the corresponding phosphonium salt $[Ph_2PyrP^+CH_2COPh]\ BF_4^-$ **11** (up to 70%).[15]

These results have to be compared with our previous experiments on the thiophene series **8c**[14] which led only to phosphininothiophenes.

Our reactions of the ylide **8b** with various acetylenes such as phenylacetylene, 3-ethynylthiophene, 1-ethynyl-4-methoxybenzene, and 9-ethynylphenanthrene afforded either the furans **12** and **13** (Scheme 6) (yields 40−50%) or a new heterocyclic system: the phosphininofurans **14** and **15** (yields 50−65%). It is interesting to note that the reaction of ylide **8b** with phenylacetylene proceeds in seconds without UV irradiation.

A comparison between the triphenyl-substituted (**1**), pyrazolyldiphenyl-substituted (**8a**), and thienyl-substituted (**8c**) ylides with the furyl-substituted ylide **8b** shows the higher reactivity for the latter. The ylide **8b** reacts vigorously in daylight and even in the dark with high yields.

Thus, we found that interaction of benzoyl-substituted ylide **8b,c** with acetylenes depends on the aryl moiety at the acetylene unit and can lead to the selective formation of furans (**12** and **13**, daylight; **16**, with UV irradiation) or annelated phosphinines, phosphininothiophene and phosphininofurans (**14** and **15**, daylight; **17**,[14] with UV irradiation).

p-Methoxyphenylacetylene in reaction with the ylide (**8b**) in the dark leads to formation also the furan (**12**) with the same yield.

9-Ethynylphenanthrene in reaction with ylide **8b** in the dark affords two heterocyclic systems, furan (**13**) and phosphininofuran (**18**), with 30% and 40% yields, respectively (see Scheme 7).

All mentioned reactions are accompanied by the formation of the corresponding phosphonium salts $[Ph_2HetP^+CH_2COPh]$-BF_4^-. The isolation of iodobenzene confirms that the C−I bond in the ylide is cleaved.

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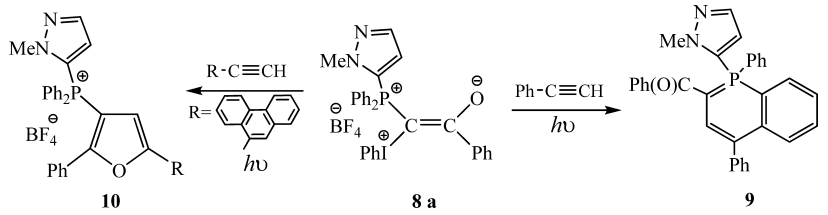
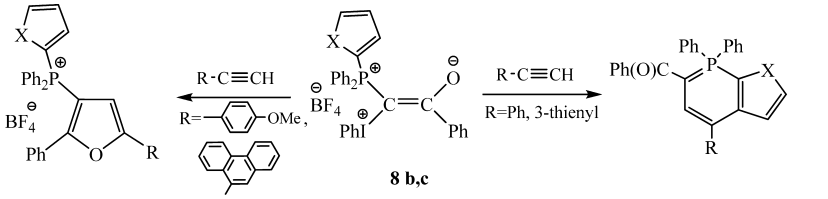
Scheme 5. Photochemical Reactions of Ylide 8a with Acetylenes



Scheme 6. Reactions of the Ylide 8b with Acetylenes



12: X=O, R=-C_6H_4-*p*OMe, 40%

13: X=O, R=9-Phenantryl, 50%

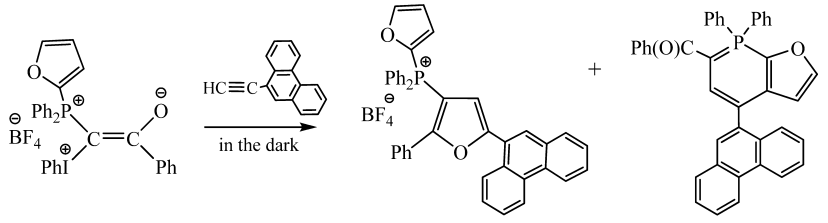
16: X=S, R=9-Phenantryl, 70%

14: X=O, R=Ph, 50%

15: X=O, R=3-Thienyl, 65%

17: X=S, R=Ph, 30%

Scheme 7. Reaction of the Ylide 8b with 9-Ethynylphenanthrene in the Dark



The structures of all obtained compounds were confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy (see the Supporting Information).

CONCLUSION

Our investigations revealed that the products of the reactions between benzoyl-substituted phosphonium−iodonium ylides and arylacetylenes depend on the aryl moiety and the substituents on the phosphonium group. It can either lead to the selective formation of furans or to annelated phosphinolines and phosphininofurans.

EXPERIMENTAL SECTION

General Methods. The ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, and CD_3CN with Me_4Si as the internal standard. ^{1}H NMR spectra were measured at 400 MHz and ^{13}C NMR at 100 MHz. The IR spectra were measured in CCl_4. The mass spectra were obtained on a quadrupole mass spectrometer (EI, 70 eV, direct inlet). The progress of the reactions and the purity after chromatographic separation were monitored by TLC on silica gel 60 plates. Chromatographic separation was carried out on columns with silica gel 60.

General Procedure for Preparation of Phosphonium Salts (6a,b). Bromoacetophenone 1.57 g (7.9 mmol) was dissolved in 8 mL of dry acetonitrile, and 7.52 mmol phosphine was added. The mixture was stirred for 30 min, and the precipitate was filtered, washed with acetonitrile (3 × 5 mL) and diethyl ether (5 mL), and dried at room temperature.

*(1-Methyl-1H-pyrazol-5-yl)(2-oxo-2-phenylethyl)-diphenylphosphonium Bromide (**6a**).* Yield: 2.70 g (80%). Mp: 219 °C. ^{1}H NMR ($CDCl_3$), δ: 3.71 (s, 3H), 6.43 (d, 2H, J = 12.4 Hz); 7.18 (dd, 1H, J = 2.0 Hz, J = 2.3 Hz); 7.43 (dd, 2H, J = 7.8 Hz, J = 7.5 Hz); 7.56 (dd, 1H, J = 7.3 Hz, J = 7.3 Hz); 7.64−7.69 (m, 4H); 7.71 (dd, 1H, J = 2.0 Hz, J = 1.5 Hz); 7.75−7.79 (m, 2H); 7.96 (ddd, 4H, J = 7.3 Hz, J = 14.1 Hz, J = 1.0 Hz); 8.31 (d, 2H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 39.7 (d, J_{CP} = 63.6 Hz); 40.9; 117.2 (d, J_{CP} = 92.2 Hz); 120.7 (d, J_{CP} = 106.9 Hz); 121.6 (d, J_{CP} = 16.9 Hz); 129.0; 130.0; 130.5 (d, J_{CP} = 13.9 Hz); 133.77 (d, J_{CP} = 11.0 Hz); 134.82 (d, J_{CP} = 5.1 Hz); 135.0; 135.5; 140.0 (d, J_{CP} = 15.4 Hz); 191.9 (d, J_{CP} = 5.9 Hz). ^{31}P NMR ($CDCl_3$), δ: 8.61. IR, $\tilde{\nu}$ /cm^{-1}: 1660 (C═O), 730−770, 1480 (Ar). Anal. Calcd for $C_{24}H_{22}BrN_2OP$: C, 61.95; H, 4.77; N, 6.02. Found: C, 61.77; H, 4.76; N, 6.03.

*Furan-2-yl(2-oxo-2-phenylethyl)diphenylphosphonium Bromide (**6b**).* Yield: 3.40 g (80%). Mp: 239−240 °C. ^{1}H NMR ($CDCl_3$), δ: 6.39 (d, 2H, J = 12.4 Hz); 6.77−6.79 (m, 1H); 7.51 (t, 2H, J = 7.4 Hz); 7.60−7.68 (m, 5H); 7.74−7.79 (m, 2H); 7.92 (m, 1H); 7.96−8.02 (m, 4H); 8.14 (dd, 1H, J = 1.0 Hz, J = 3.8 Hz); 8.39 (d, 2H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 38.5 (d, J_{CP} = 65.1 Hz); 113.1 (d, J_{CP} = 8.8 Hz); 117.6 (d, J_{CP} = 94.4 Hz); 129.0; 130.0; 130.1 (d, J_{CP} = 13.9 Hz); 130.8 (d, J_{CP} = 19.8 Hz); 133.7 (d, J_{CP} = 130.3 Hz); 133.9 (d, J_{CP} = 11.7 Hz); 134.9; 135.0 (d, J_{CP} = 1.5 Hz); 152.3 (d, J_{CP} = 8.1 Hz); 191.8 (d, J_{CP} = 5.9 Hz). ^{31}P NMR ($CDCl_3$), δ: 9.87. IR, $\tilde{\nu}$/cm^{-1}: 1660 (C═O), 730−760, 1470 (Ar). Anal. Calcd for $C_{24}H_{20}BrO_2P$: C, 64.18; H, 4.58. Found: C, 63.87; H, 4.47.

General Procedure for Preparation of Phosphoranes (7a,b). A solution of 118 mg of sodium methylate (2.2 mmol) in 1 mL of dry methanol was added gradually to a solution of 2.15 mmol phosphonium salt **8** in 5 mL of dry methanol at 0 to +5 °C. The mixture was stirred for 1 h and then evaporated in vacuo, and the residue was dissolved in 10 mL of methylene chloride. The precipitate of sodium bromide was separated from the solution of ylides **9** by

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filtration, washed on the filter with methylene chloride (3 × 10 mL). The residue was evaporated in vacuo.

*1-[(1-Methyl-1H-pyrazol-5-yl)(diphenyl)phosphonio]-2-oxo-2-phenylethanide (**7a**).* Yield: 0.67 g (80%). Mp: 115−116 °C. ^{1}H NMR ($CDCl_3$), δ: 3.79 (s, 3H); 4.58 (d, 1H, J = 27.3 Hz); 6.24 (s, 1H); 7.36−7.38 (m, 3H); 7.60−7.75 (m, 11H); 7.90−7.92 (m, 2H). ^{13}C NMR ($CDCl_3$), δ: 40.3, 47.7 (d, J_{CP} = 113.4 Hz); 118.3 (d, J_{CP} = 15.3 Hz); 126.5 (d, J_{CP} = 95.1 Hz); 127.2; 128.3; 128.8 (d, J_{CP} = 104.6 Hz); 129.8 (d, J_{CP} = 13,2 Hz); 130.1; 132.8 (d, J_{CP} = 10.2 Hz); 133.2; 138.9 (d, J_{CP} = 13.1 Hz); 140.8 (d, J_{CP} = 14.6 Hz); 180.2. ^{31}P NMR ($CDCl_3$), δ: 1.44. IR, $\tilde{\nu}$/cm^{-1}: 1590 (C═O), 700−740, 1460 (Ar). Anal. Calcd for $C_{24}H_{21}NOP$: C, 74.99; H, 5.51; N, 7.29. Found: C, 75.26; H, 5.31; N, 7.05.

*1-[Furan-2-yl(diphenyl)phosphonio]-2-oxo-2-phenylethanide (**7b**).* Yield: 0,74 g (95%). Mp: 167−168 °C. ^{1}H NMR (CD_2Cl_2), δ: 4.40 (d, 1H, J = 23.5 Hz); 6.63−6.64 (m, 1H); 7.21−7.22 (m, 1H); 7.39−7.40 (m, 3H); 7.40 (d, 1H, J = 1.8 Hz) 7.51−7.55 (m, 4H, J = 18.3 Hz); 7.61−7.65 (m, 2H); 7.76−7.83 (m, 5H); 7.92−7.95 (m, 2H). ^{13}C NMR ($CDCl_3$), δ: 47.8 (d, J_{CP} = 117.8 Hz); 111.5 (d, J_{CP} = 8.0 Hz); 124.8 (d, J_{CP} = 18.3 Hz); 126.3 (d, J_{CP} = 96.6 Hz); 127.0; 127.8; 128.8 (d, J_{CP} = 13.2 Hz); 129.6; 132.2; 132.9 (d, J_{CP} = 11.0 Hz); 140.7 (d, J_{CP} = 14.6 Hz); 149.0 (d, J_{CP} = 4.9 Hz); 185.5. ^{31}P NMR ($CDCl_3$), δ: 2.93. IR, $\tilde{\nu}$/cm^{-1}: 1590 (C═O), 700−730, 1450 (Ar). Anal. Calcd for $C_{24}H_{19}O_2P$: C, 77.83; H, 5.17. Found: C, 77.65; H, 5.25.

General Procedure for Preparation of Phosphonium−Iodonium Ylides (8a,b). A solution of 1.3 mmol of diacetoxyiodobenzene in 3 mL of methanol was added to the solution of 1.3 mmol ylide **7** in 2 mL of methanol at 0−5 °C, and then 1.3 mmol of a solution of HBF_4 (40%) was added at 0−5 °C. The mixture was stirred for 1 h, 10 mL of diethyl ether was added, and the mixture was stirred for 1 h. The precipitate was filtered and washed with diethyl ether.

*1-[(1-Methyl-1H-pyrazol-5-yl)(diphenyl)phosphonio]-2-oxo-2-phenyl-1-(phenyliodonio)ethanide tTetrafluoroborate (**8a**).* Yield: 0,69 g (80%). Mp: 158 °C. ^{1}H NMR (CD_3CN), δ: 3.50 (s, 3H); 6.50 (dd, 1H, J = 2.0 Hz, J = 2.3 Hz); 7.20 (d, 2H, J = 7.8 Hz); 7.43 (dd, 2H, J = 7.9 Hz, J = 8.0 Hz); 7.51−7.57 (m, 3H); 7.61−7.68 (m, 11H); 7.70 (dd, 1H, J = 2.0 Hz, J = 1.5 Hz); 7.78−7.83 (m, 2H). ^{13}C NMR (CD_3CN), δ: 40.3; 120.4 (d, J_{CP} = 17.5 Hz); 122.1 (d, J_{CP} = 96.5 Hz); 125.8 (d, J_{CP} = 108.3 Hz); 127.6; 128.6; 129.9 (d, J_{CP} = 13.2 Hz); 130.8; 131.9; 132.6; 133.2 (d, J_{CP} = 8.0 Hz); 133.2; 134.3; 138.8 (d, J_{CP} = 8.1 Hz); 139.5 (d, J_{CP} = 15.4 Hz); 192.1 (d, J_{CP} = 6.6 Hz). ^{31}P NMR (CD_3CN), δ: 12.89. IR, $\tilde{\nu}$/cm^{-1}: 1600 (C═O), 1080 (BF_4^-), 740−750, 1470 (Ar). Anal. Calcd for $C_{30}H_{26}BF_4IN_2OP$: C, 53.36; H, 3.88; N, 4.15. Found: C, C, 53.29; H, 3.93, N, 3.95.

*1-[Furan-2-yl(diphenyl)phosphonio]-2-oxo-2-phenyl-1-(phenyliodonio)ethanide Tetrafluoroborate (**8b**).* Yield: 0,82 g (95%). Mp: 155 °C. ^{1}H NMR(CD_3CN), δ: 6.84−7.86 (m, 1H); 7.14−7.18 (m, 1H); 7.36−7.40 (m, 6H); 7.46−7.76 (m, 14H); 8.11−8.14 (m., 1H). ^{13}C NMR (CD_3CN), δ: 113.8 (d, 8J_{CP} = 8.8 Hz); 123.5 (d, J_{CP} = 98.1 Hz); 128.9; 129.8; 129.9 (d, J_{CP} = 19.0 Hz); 130.9 (d, J_{CP} = 13.9 Hz); 131.9; 133.0; 133.4; 134.6 (d, J_{CP} = 11.0 Hz); 135.5; 140.1 (d, J_{CP} = 131.0 Hz); 140.1 (d, J_{CP} = 6.6 Hz); 153.3 (d, J_{CP} = 7.3 Hz); 192.9. ^{31}P NMR (CD_3CN), δ: 14.60. IR, $\tilde{\nu}$/cm^{-1}: 1540 (C═O), 1070−1110 (BF_4^-), 740, 1470 (Ar). Anal. Calcd for $C_{30}H_{23}BF_4IO_2P$: C, 54.58; H, 3.51. Found: C, 54.81; H, 3.73.

General Procedure for the Reaction of Ylides (8a) with Alkynes. The ylide (0.3 mmol) was added gradually to a solution of alkynes (0.9 mmol) in anhydrous dichloromethane. The reactions were irradiated in a quartz flask with a mercury lamp (366 nm) source under argon atmosphere. The progress of the reaction was monitored by TLC. After the end of the reaction, the mixtures were concentrated in vacuo. The residue was dissolved in a minimum of CH_2Cl_2 and chromatographed on silica gel. Benzene was used to elute phenylacetylene and PhI; the corresponding phosphinoline was eluted by using a CH_2Cl_2/MeOH mixture in a ratio of 200:1, the furan was eluted by using a CH_2Cl_2/CH_3CN mixture in a ratio of 5:1.

*[1-(1-Methyl-1H-pyrazol-5-yl)-1,4-diphenyl-1λ^5-phosphinolin-2-yl](phenyl)methanone (**9**).* Yield: 15 mg (10%). Red oil. ^{1}H NMR($CDCl_3$), δ: 3.86 (s, 3H); 6.69 (dd, 1H, J = 2.0 Hz, J = 2.0 Hz); 7.17 (d, 1H, J = 33.1 Hz); 7.36 (d, 1H, J = 1.8 Hz); 7.34−7.44 (m, 11H); 7.53−7.57 (m, 3H); 7.62 (dd 1H, J = 2.0 Hz, J = 1.5 Hz); 7.64−7.67 (m, 2H); 7.98 (ddd, 2H, J = 6.9 Hz, J = 13.9 Hz, J = 1.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 30.3 (d, J_{CP} = 120.0 Hz); 39.8; 118.0 (d, J_{CP} = 16.8 Hz); 124.9 (d, J_{CP} = 11.0 Hz); 126.3 (d, J_{CP} = 8.1 Hz); 126.5; 126.8 (d, J_{CP} = 5.8 Hz); 127.6 (d, J_{CP} = 94.4 Hz); 128.4 (d, J_{CP} = 85.6 Hz); 128.4; 128.7; 129.0; 129.1; 129.1; 130.2 (d, J_{CP} = 7.3 Hz); 132.4; 132.6; 133.0 (d, J_{CP} = 99.5 Hz); 133.1; 133.4 (d, J_{CP} = 11.7 Hz); 135.0 (d, J_{CP} = 6.5 Hz); 138.5 (d, J_{CP} = 14.6 Hz); 140.1; 190.3. ^{31}P NMR ($CDCl_3$), δ: −12.03.

*(1-Methyl-1H-pyrazol-5-yl)[5-(phenanthren-9-yl)-2-phenylfuran-3-yl]diphenylphosphonium Tetrafluoroborate (**10**).* Yield: 60 mg (30%). Colorless oil. ^{1}H NMR(CD_2Cl_2), δ: 3.50 (s, 3H); 6.80 (dd, 1H, J = 2.2 Hz, J = 2.7 Hz); 6.82 (d, 1H, J = 3.9 Hz); 7.13−7.17 (m, 2H); 7.13−7.17 (m, 2H); 7.25−7.32 (m, 3H); 7.57−7.64 (m, 2H); 7.66−7.75 (m, 11H); 7.80−7.85 (m, 2H); 7.92 (dd, 1H, J = 8.0 Hz, J = 7.9 Hz); 8.08 (s, 1H); 8.20 (dd, 1H, J = 7.9 Hz, J = 1.1 Hz); 8.65 (d, 1H, J = 7.9 Hz); 8.74 (ddd, 1H, J = 7.5 Hz, J = 8.3 Hz, J = 1.4 Hz). ^{13}C NMR (CD_2Cl_2), δ: 42.3; 98.9 (d, J_{CP} = 114.0 Hz); 114.8 (d, J_{CP} = 12.9 Hz); 118.5 (d, J_{CP} = 96.0 Hz); 122.1 (d, J_{CP} = 112.8 Hz); 123.3 (d, J_{CP} = 18.5 Hz); 124.3; 125.1; 125.7; 126.8; 128.6; 129.0; 129.1 (d, J_{CP} = 3.2 Hz); 129.80; 130.0; 130.3; 130.5; 130.9; 131.3; 132.3; 132.4; 132.5; 132.8 (d, J_{CP} = 13.6 Hz); 132.9 (d, J_{CP} = 4.0 Hz); 135.2 (d, J_{CP} = 11.6 Hz); 138.0 (d, J_{CP} = 2.8 Hz); 142.2 (d, J_{CP} = 16.5 Hz); 158.5 (d, J_{CP} = 15.7 Hz); 164.9 (d, 9J_{CP} = 18.5 Hz). ^{31}P NMR (CD_2Cl_2), δ: 2.49. IR, $\tilde{\nu}$/cm^{-1}: 1070 (BF_4^-), 700−760, 1470 (Ar). HRMS: calcd for $C_{40}H_{30}N_2OP$ (M^+) m/z 585.2090, found 585.2077.

General Procedure for the Reaction of Ylides (8b,c[14]) with Alkynes. The alkyne was added to a solution of ylide **8b,c** (0.3 mmol) in anhydrous methylene chloride. The mixture was stirred under argon atmosphere. The progress of the reaction was monitored by TLC. After the end of the reaction, the mixture was concentrated in vacuo. The residue was dissolved in a minimum of CH_2Cl_2 and chromatographed on silica gel. Benzene was used to elute the residual alkynes and PhI; the corresponding phosphinoline was eluted by using a CH_2Cl_2/MeOH mixture in a ratio of 200:1, the furans were eluted by using a CH_2Cl_2/CH_3CN mixture in a ratio of 5:1.

*2,3-Dihydrofuran-2-yl[5-(4-methoxyphenyl)-2-phenylfuran-3-yl]-diphenylphosphonium Tetrafluoroborate (**12**).* Yield: 70 mg (40%). Colorless oil. ^{1}H NMR ($CDCl_3$), δ: 3.86 (s, 3H); 6.63 (d, 1H, J = 4.0 Hz); 6.76−6.77 (m, 1H.); 6.98 (d, 2H, J = 8.8 Hz); 7.13−7.17 (m, 2H); 7.22−7.23 (m, 2H); 7.26−7.30 (m, 1H); 7.34−7.35 (m, 1H); 7.68−7.78 (m, 10H); 7.82−7.86 (m, 2H); 8.01−8.02 (m, 1H). ^{13}C NMR (CD_2Cl_2), δ: 57.0; 98.8 (d, J_{CP} = 115.7 Hz); 109.0 (d, J_{CP} =12.5 Hz); 114.6 (d, J_{CP} = 9.6 Hz); 116.2; 118.5 (d, J_{CP} = 97.6 Hz); 122.3; 127.8; 128.9; 129.8; 130.2; 132.3 (d, J_{CP} = 13.7 Hz); 132.3; 132.6 (d, J_{CP} = 20.5 Hz); 135.1 (d, J_{CP} = 135.7 Hz); 135.3 (d, J_{CP} = 11.6 Hz); 137.65 (d, J_{CP} = 3.21 Hz); 155.5 (d, J_{CP} = 8.0 Hz); 158.6 (d, J_{CP} =15.3 Hz); 162.5; 164.0 (d, J_{CP} =19.3 Hz). ^{31}P NMR (CD_2Cl_2), δ: 3.39. IR, $\tilde{\nu}$/cm^{-1}: 1030−1100 (BF_4^-), 710−740, 1450 (Ar). HRMS: calcd for $C_{33}H_{26}O_3P$ (M^+) m/z 501.1614, found 501.1611.

*Furan-2-yl[5-(phenanthren-9-yl)-2-phenylfuran-3-yl]-diphenylphosphonium Tetrafluoroborate (**13**).* Yield: 98 mg (50%). Colorless oil. ^{1}H NMR (CD_2Cl_2), δ: 6.81 (m, 1H); 6.93 (d, 1H, J = 4.1 Hz); 7.22−7.26 (m, 2H); 7.37−7.40 (m, 4H); 7.70−7.95 (m, 14H); 8.04 (d, 1H, J = 7.9 Hz); 8.08−8.09 (m, 1H); 8.20 (s, 1H); 8.37 (dd, 1H, J = 8.1 Hz, J = 8.4 Hz); 8.77 (d, 1H, J = 8.4 Hz); 8.85 (d, 1H, J = 8.1 Hz). ^{13}C NMR (CD_2Cl_2), δ: 97.8 (d, J_{CP} = 115.6 Hz); 113.6 (d, J_{CP} = 9.6 Hz); 114.1 (d, J_{CP} = 12.5 Hz); 117.4 (d, J_{CP} = 97.6 Hz); 123.3; 124.0; 124.9; 125.9; 127.8; 127.9; 128.0 (d, J_{CP} = 4.1 Hz); 128.9; 129.0; 129.3; 129.3; 129.9 (d, J_{CP} = 13.2 Hz); 131.3 (d, J_{CP} = 14.0 Hz); 131.4 (d, J_{CP} = 7.7 Hz); 131.5; 131.7; 131.9; 134.1 (d, J_{CP} = 136.1 Hz); 134.3 (d, J_{CP} = 11.6 Hz); 136.7 (d, J_{CP} = 2.8 Hz); 154.5 (d, J_{CP} = 8.0 Hz); 156.9 (d, J_{CP} = 15.3 Hz); 164.3 (d, J_{CP} = 18.8 Hz). ^{31}P NMR (CD_2Cl_2), δ: 1.41. IR, $\tilde{\nu}$/cm^{-1}: 1070 (BF_4^-), 730−760, 1470 (Ar). HRMS: calcd for $C_{40}H_{28}O_2P$ (M^+) m/z 571.1821, found 571.1817.

*Phenyl(4,7,7-triphenyl-7λ^5-phosphinino[2,3-b]furan-6-yl)-methanone (**14**).* Yield: 71 mg (50%). Red oil. ^{1}H NMR ($CDCl_3$), δ: 6.51 (dd, 1H, J = 2.3 Hz, J = 2.2 Hz); 7.22−7.26 (m, 1H); 7.42 (d, 1H,

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J = 34.1 Hz); 7.35−7.39 (m, 2H); 7.42−7.47 (m, 3H); 7.46 (dd, 1H, J = 2.2 Hz, J = 2.3 Hz); 7.50−7.57 (m, 8H); 7.67−7.69 (m, 2H); 7.86 (dd, 4H, J = 7.6 Hz, J = 13.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 78.9 (d, J_{CP} = 103.9 Hz); 91.5 (d, J_{CP} = 104.7 Hz); 107.0 (d, J_{CP} = 2.9 Hz); 110.7 (d, J_{CP} = 7.3 Hz); 125.8; 127.2 (d, J_{CP} = 98.1 Hz); 127.6; 128.1; 128.3; 128.5 (d, J_{CP} = 13.2 Hz); 128.7; 129.7; 131.6; 132.9 (d, arom., $^2J_{CP}$ = 11.7 Hz); 133.4 (d, J_{CP} = 8.1 Hz); 138.1; 140.2 (d, J_{CP} = 8.8 Hz); 141.2 (d, J_{CP} = 13.2 Hz); 161.4 (d, J_{CP} = 12.5 Hz); 191.6 (d, J_{CP} = 5.9 Hz). ^{31}P NMR ($CDCl_3$), δ: 2.09. IR, $\tilde{\nu}$/cm^{-1}: 1520−1590 (C═O), 710−740, 1470 (Ar). HRMS: calcd for $C_{32}H_{23}O_2P$ (M^+) m/z 470.1436, found 470.1418.

*[7,7-Diphenyl-4-(thiophene-3-yl)-7λ^5-phosphinino[2,3-b]furan-6-yl](phenyl)methanone (**15**).* Yield: 93 mg (65%). Red oil. ^{1}H NMR (CD_2Cl_2), δ: 6.42 (dd, 1H, J = 2.0 Hz, J = 2.6 Hz); 7.15−7.19 (m, 2H); 7.42 (d, 1H, J = 36.2 Hz); 7.32−7.36 (m, 3H); 7.40 (dd, 1H, J = 3.43 Hz, J = 1.87 Hz); 7.41−7.49 (m, 7H); 7.51−7.54 (m, 2H); 7.72 (dddd, 4H, J = 6.7 Hz, J = 14.0 Hz, J = 1.4 Hz, J = 1.7 Hz). ^{13}C NMR (CD_2Cl_2), δ: 80.1 (d, J_{CP} = 104.0 Hz); 93.0 (d, J_{CP} = 104.0 Hz); 103.8 (d, J_{CP} = 4.4 Hz); 112.2 (d, J_{CP} = 7.3 Hz); 119.9; 126.2; 128.3; 128.9 (d, J_{CP} = 97.6 Hz); 129.7; 130.1; 130.1 (d, J_{CP} = 13.0 Hz); 131.3; 133.3 (d, J_{CP} = 3.2 Hz); 133.8 (d, J_{CP} = 8.8 Hz); 134.45 (d, J_{CP} = 11.6 Hz); 139.8; 141.9 (d, J_{CP} = 8.8 Hz); 143.1 (d, J_{CP} = 13.2 Hz); 162.9 (d, J_{CP} = 12.9 Hz); 192.7 (d, J_{CP} = 5.6 Hz) ^{31}P NMR ($CDCl_3$), δ: 1.54. IR, $\tilde{\nu}$/cm^{-1}: 1520−1580 (C═O), 710−760, 1470 (Ar). HRMS: calcd for $C_{30}H_{21}O_2PS$ (M^+) m/z 476.0999, found 476.0985.

*[5-(Phenanthren-9-yl)-2-phenylfuran-3-yl](diphenyl)thiophene-2-ylphosphonium Tetrafluoroborate (**16**).* Yield: 142 mg (70%). Colorless oil (reaction with UV irradiation with a mercury lamp (366 nm)). ^{1}H NMR (CD_2Cl_2), δ: 6.82 (d, 1H, J = 4.0 Hz); 7.18 (dd, 2H, J = 7.3 Hz, J = 8.1 Hz); 7.32−7.35 (m, 3H); 7.43−7.45 (m, 1H);7.66−7.90 (m, 15H); 8.00 (d, 1H, J = 7.8 Hz); 8.15 (s, 1H); 8.22 (dt, 1H, J = 4.8 Hz, J = 1.3 Hz); 8.31 (dd, 1H, J = 8.1 Hz, J = 1.5 Hz); 8.74 (d, 1H, J = 8.3 Hz); 8.83 (d, 1H, J = 8.3 Hz). ^{13}C NMR (CD_2Cl_2), δ: 99.1 (d, J_{CP} = 114.1 Hz); 113.8 (d, J_{CP} = 12.5 Hz); 116.6 (d, J_{CP} = 98.8 Hz); 118.6 (d, J_{CP} = 96.6 Hz); 122.7; 123.4; 124.3; 125.3; 127.3; 127.5; 128.3; 128.7; 129.3; 130.0; 130.7 (d, J_{CP} = 13.9 Hz); 130.7 (d, J_{CP} = 16.1 Hz); 130.9; 133.7 (d, J_{CP} = 11.0 Hz); 136.0; 140.5 (d, J_{CP} = 5.1 Hz); 143.0 (d, J_{CP} = 11.0 Hz); 156.1 (d, J_{CP} = 16.1 Hz); 163.1 (d, J_{CP} = 17.6 Hz). ^{31}P NMR (CD_2Cl_2), δ: 7.95. IR, $\tilde{\nu}$/cm^{-1}: 1070 (BF_4^-), 730−760, 1470 (Ar). HRMS: calcd for $C_{40}H_{28}OPS$ (M^+) m/z 587.1593, found 587.1593.

*Phenyl(4,7,7-triphenyl-7λ^5-phosphinino[2,3-b]thiophene-6-yl)-methanone (**17**).* Yield: 44 mg (30%). Red oil (reaction with UV irradiation with a mercury lamp (366 nm)). ^{1}H NMR (CD_2Cl_2), δ: 7.04 (dd, 1H, J = 5.3 Hz, J = 3.6 Hz); 7.10 (dd, 1H, J = 5.3 Hz, J = 2.8 Hz); 7.17 (d, 1H, J = 34.0 Hz); 7.24−7.28 (m, 1H); 7.34−7.38 (m, 2H); 7.40−7.43 (m, 3H); 7.50−7.60 (m, 8H); 7.62−7.64 (m, 2H); 7.82−7.87 (m, 4H). ^{13}C NMR (CD_2Cl_2), δ: 78.5 (d, J_{CP} = 103.4 Hz); 107.0 (d, J_{CP} = 90.8 Hz); 113.5 (d, J_{CP} = 8.1 Hz); 122.1 (d, J_{CP} = 16.5 Hz); 127.1; 128.1 (d, J_{CP} = 98.8 Hz); 128.6; 128.8; 129.1; 129.1 (d, J_{CP} = 13.3 Hz); 129.1; 129.2 (d, J_{CP} = 11.1 Hz); 130.2; 132.2 (d, J_{CP} = 7.6 Hz); 132.3 (d, J_{CP} = 3.2 Hz); 133.6 (d, J_{CP} = 11.2 Hz); 141.2 (d, J_{CP} = 9.3 Hz); 142.8; 154.2 (d, J_{CP} = 8.0 Hz); 191.5 (d, J_{CP} = 5.6 Hz) ^{31}P NMR (CD_2Cl_2), δ: 1.97. MS, m/z: 486 $[M]^+$, 409 $[M - C_6H_5]^+$, 381 $[M - PhCO]^+$, 183 $[Ph_2P - 2H]^+$.

*[4-(Phenanthren-9-yl)-7,7-diphenyl-7λ^5-phosphinino[2,3-b]-furan-6-yl](phenyl)methanone (**18**).* Yield: 68 mg (40%). Red oil. ^{1}H NMR (CD_2Cl_2), δ: 6.45 (dd, 1H, J = 2.2 Hz, J = 2.3 Hz); 7.23 (d, 1H, J = 36.4 Hz); 7.21 (dd, 1H, J = 2.4 Hz, J = 2.1 Hz); 7.22−7.25 (m, 3H); 7.42−7.58 (m, 12H); 7.66 (s, 1H); 7.76−7.87 (m, 6H); 8.61 (d, 1H, J = 8.3 Hz); 8.66 (d, 1H, J = 8.3 Hz). ^{13}C NMR (CD_2Cl_2), δ: 80.1 (d, J_{CP} = 104.0 Hz); 92.6 (d, J_{CP} = 104.0 Hz); 107.2 (d, J_{CP} = 1.6 Hz); 112.2 (d, J_{CP} = 6.8 Hz); 124.1; 124.4; 127.9; 128.0; 128.; 128.7; 129.6; 129.7; 130.0; 130.2 (d, J_{CP} = 13.6 Hz); 131.2 (d, J_{CP} = 92.4 Hz); 131.2; 131.6; 133.4 (d, J_{CP} = 3.3 Hz); 133.5; 133.9; 134.6 (d, J_{CP} = 11.6 Hz); 135.7 (d, J_{CP} = 8.1 Hz); 136.5; 139.6 (d, J_{CP} = 7.7 Hz); 141.6 (d, J_{CP} = 8.8 Hz); 143.5 (d, J_{CP} = 13.7 Hz); 163.8; 192.4. ^{31}P NMR (CD_2Cl_2), δ: 4.37. IR, $\tilde{\nu}$/cm^{-1}: 1520−1580 (C═O), 700−800, 1470 (Ar). HRMS: calcd for $C_{40}H_{27}O_2P$ (M^+) m/z 570.1743, found 570.1722.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{31}P, and ^{13}C NMR spectra of the new compounds **6**−**10**, **12**−**16**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(15) The decomposition of ylides to give the corresponding phosphonium salt is the common phenomenon, which we have observed in many different related photochemical processes. This reaction is under careful investigation, using deuterium labeling, because the source of two hydrogens is not absolutely clear yet.