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Graphical Abstract

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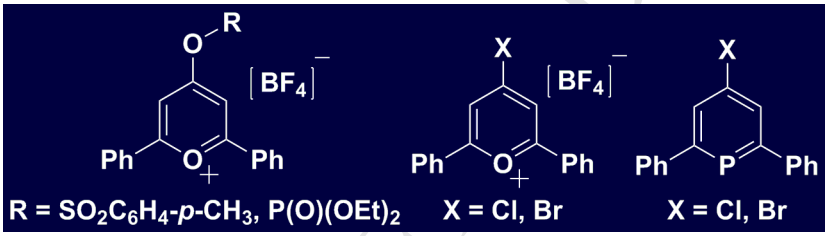
The reactions of a pyranone with sulfonic anhydride or chlorophosphate resulted in the formation of a series of new pyrylium salts that bear sulfonate and phosphonate groups, respectively, which were characterized spectroscopically. Moreover, the reactions of 4-chloro- and 4-bromopyrylium tetrafluoroborates with tris(trimethylsilyl)phosphine afforded the corresponding chloro- and bromophosphinines.



Synthetic Studies on a Series of Functionalized Pyrylium Salts, 4-Chloro- and 4-Bromophosphinines

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Abstract

A series of new pyrylium salts that bear sulfonate and phosphonate groups were obtained from the reactions between 2,6-diphenyl-4*H*-pyran-4-one, sulfonic anhydride, and chlorophosphates, and analyzed spectroscopically. Furthermore, treatment of 2,6-diphenyl-4*H*-pyran-4-one with phosphoryl chloride or bromide afforded the corresponding 4-chloro- and 4-bromopyrylium tetrafluoroborates in good yield. Subsequently, the synthesis of the corresponding 4-chloro- and 4-bromophosphinines was accomplished by treating the respective chloro- and bromopyrylium tetrafluoroborates with tris(trimethylsilyl)phosphine.

Key words

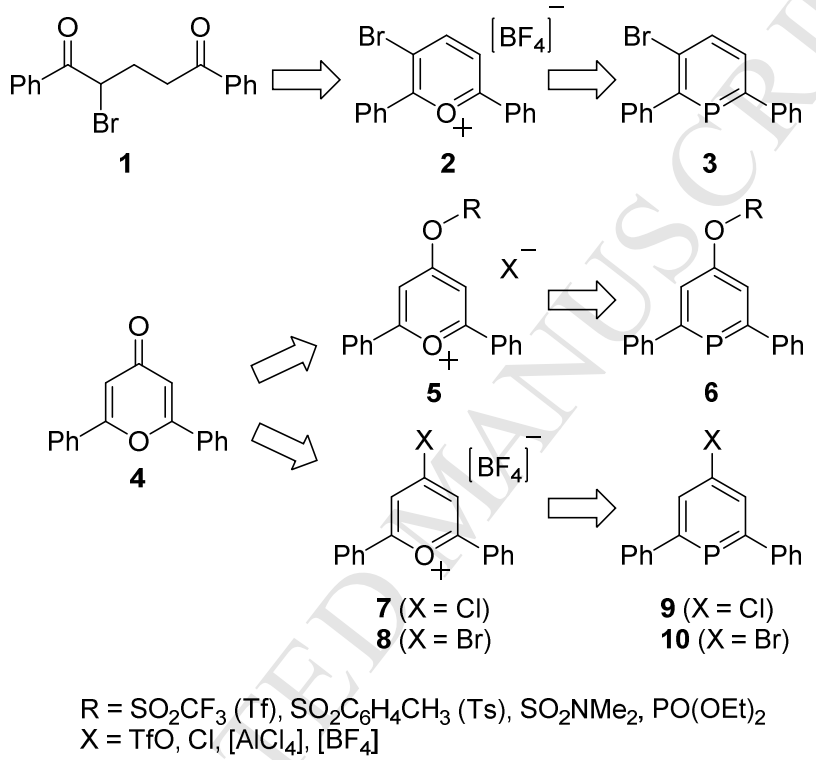
Pyrylium salt, Phosphinine, Chlorination, Bromination, Tris(trimethylsilyl)phosphine

Introduction

Since the pioneering synthesis of 2,4,6-triphenylphosphinine as the first stable phosphinine by Märkl,[1] the chemistry of heavier congeners of pyridine has been studied extensively over the last 50 years.[2] The chemistry of phosphinines has received much attention, as these compounds not only represent fascinating synthetic building blocks for phosphorus heterocycles, but potentially also offer fundamental insights into phosphorous-containing aromatics.[3] To date, it is known that phosphinines exhibit unique properties such as relatively low-lying π^* orbitals and a narrow HOMO–LUMO gap.[2] Phosphinine molecules are thus ideal prospectives for the development of functional materials such as organic electronic devices, and the development of advanced synthetic methods.

Meanwhile, chloro- and bromophosphinines are of interest due to their unique electronic structures and as potential new building blocks for phosphorous-containing aromatics. For example, 3-chloro- and 3-bromo-2-phenylphosphinine were synthesized by Märkl and Hock.[4] In 1990, the group of Mathey reported a [4+2] cycloaddition between dibromo(dibromomethyl)phosphine and buta-1,3-diene, which afforded 2-bromophosphinine after a dehydrobromination.[5] Thereafter, the synthesis of other 2-bromophosphinines has also been achieved.[6] Keglevich and co-workers reported the synthesis of 4-chlorophosphinines by taking advantage of ring expansion reactions of phosphabicyclo[3.1.0]hexane derivatives.[7] Although these reports describe synthetic routes to chloro- and bromophosphinines, the procedures involved are usually complicated and do not easily provide halogen-containing phosphinines.

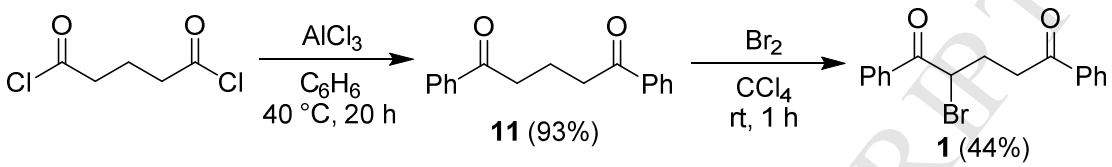
Meanwhile, Ni-catalyzed Suzuki-Miyaura coupling reactions of aryl sulfonamides or phosphonates have been developed,[8] and these results inspired us to explore the synthesis of new phosphinines bearing OSO_2NEt_2 or $OP(O)(OEt)_2$ groups in order to develop coupling reactions involving phosphinines. Although synthetic investigations into phosphinines that carry a sulfonamide or phosphonate group have not yet been conducted, they would represent an attractive research target. Therefore, we have designed a plausible synthetic route to a series of phosphinines (**3**, **6**, **9**, and **10**) based on reactions of the corresponding pyrylium salts with tris(trimethylsilyl)phosphine (Scheme 1).



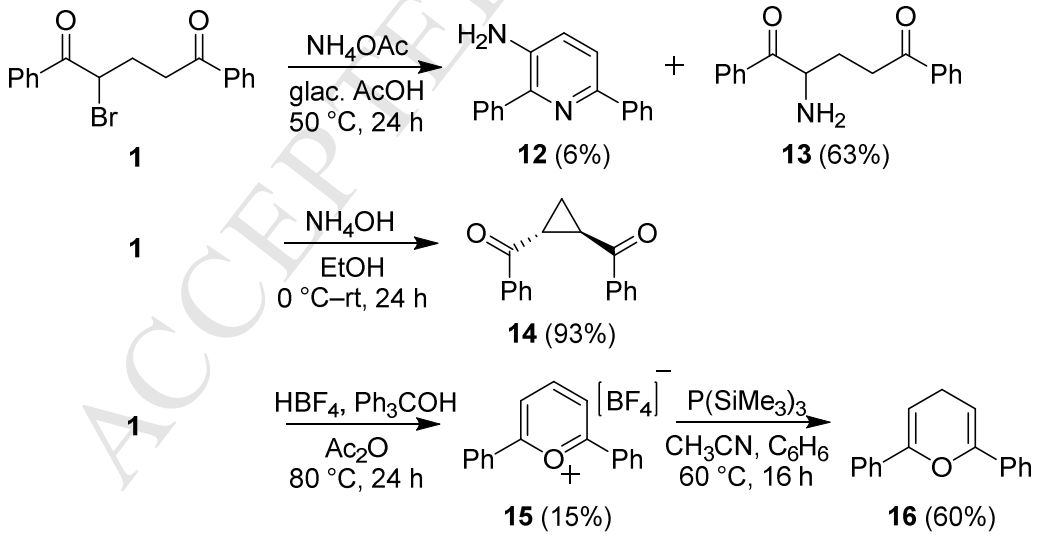
Scheme 1. Synthetic route to phosphinines **3**, **6**, **9**, and **10** via the corresponding pyrylium salts.

Results and Discussion

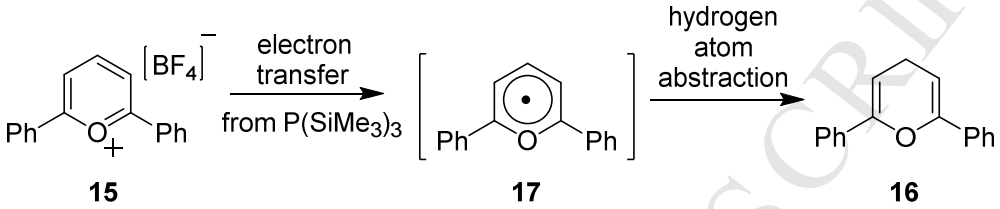
Attempted Synthesis of 3-Bromopyrylium Tetrafluoroborate 2. Initially, we attempted the synthesis of 3-bromopyrylium tetrafluoroborate **2** via 2-bromo-1,5-diphenylpentane-1,5-dione (**1**) (Scheme 2). A Friedel-Crafts reaction of glutaryl chloride with benzene in the presence of aluminum chloride afforded 1,5-diphenylpentane-1,5-dione (**11**) in 93% yield. A subsequent bromination of **11** in tetrachloromethane using Br_2 at room temperature furnished 2-bromo-1,5-diphenylpentane-1,5-dione (**1**) in 44% yield. Prior to inducing the formation of the pyrylium framework in 2-bromopentane-1,5-dione **1** with ammonium salts, we confirmed the formation of a pyridine ring according to previously reported methods.[9] Treating 2-bromopentane-1,5-dione **1** with ammonium acetate in glacial acetic acid at 50 °C for 24 h did not afford 3-bromo-2,6-diphenylpyridine but 3-amino-2,6-diphenylpyridine (**12**) in 6% yield together with 2-amino-2,5-diphenylpentane-2,5-dione (**13**) in 63% yield (Scheme 3). Treating an ethanol solution of **1** with ammonia resulted in the unexpected formation of *trans*-1,2-dibenzoylcyclopropane (**14**) in 93% yield. These results indicate that a nucleophilic substitution of **1** occurs in favor of the formation of a pyridine ring. Then, we investigated the formation of a 3-bromopyrylium ring from **1**. The reaction of **1** with $H[BF_4]$ and $Ph_3C[BF_4]$, which was prepared from $H[BF_4]$ and Ph_3COH, followed by the decantation using cold ether afforded 2,6-diphenylpyrylium tetrafluoroborate (**15**) in 15% yield together with a large amount of a complicated product mixture. These results indicate that a debromination of **1** occurred during the formation of the pyrylium ring. In order to synthesize 2,6-diphenylphosphinine, we attempted a reaction between pyrylium salt **15** and tris(trimethylsilyl)phosphine, which is efficient method for the synthesis of phosphinines.[10] Treatment of **15** with $P(SiMe_3)_3$ in acetonitrile/benzene (1:1, v/v) furnished the corresponding 2,6-diphenyl-4*H*-pyran (**16**) in 60% yield. One of the plausible reaction mechanism for the formation of **16** is shown in Scheme 4. Unfortunately, the formation of 2,6-diphenylphosphinine was not confirmed, which is comparable with the results in the literature.[11] These results indicate that a nucleophilic attack of $P(SiMe_3)_3$ to pyrylium tetrafluoroborate **15** is unlikely, and that an electron transfer from $P(SiMe_3)_3$ to **15** might occur, followed by abstraction of a hydrogen atom to afford **16** (Scheme 4).



Scheme 2. Synthesis of 2-bromo-1,5-diphenylpentane-1,5-dione (**1**).



Scheme 3. Reactions of 2-bromopentane-1,5-dione **1**.

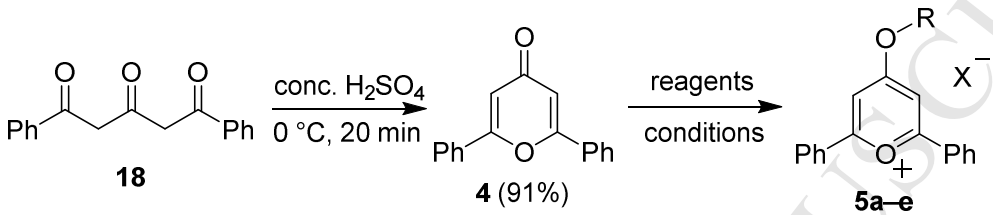


Scheme 4. Plausible reaction mechanism for the formation of 4*H*-pyran **16**.

Reactions of 2,6-Diphenyl-4*H*-pyran-4-one (4) with Sulfonic Acid, Sulfonic Anhydride, Chlorosulfonamide, and Chlorophosphate. In order to synthesize 2,6-diphenylpyrylium salts **5a**–**e**, we treated 2,6-diphenyl-4*H*-pyran-4-one (**4**) with sulfonic acid, sulfonic anhydrides, chlorosulfonamide, and chlorophosphate (Table 1). Treatment of 1,5-diphenylpentane-1,3,5-trione (**18**) with concentrated sulfuric acid at 0 °C afforded 2,6-diphenyl-4*H*-pyran-4-one (**4**) in 91% yield. The reaction of diphenylpyranone **4** with trifluoromethanesulfonic anhydride in dichloromethane did not afford the corresponding TfO-substituted pyrylium trifluoromethanesulfonate (**5a**), but HO-substituted pyrylium trifluoromethanesulfonate **5b** as yellow crystals in 84% yield (entry 1). This result can be rationalized in terms of a hydrolysis of **5a** during the purification, which would afford **5b**. The results stand in sharp contrast to the formation of a bipyrylium ether derivative during the reaction between 2,6-dimethyl-4*H*-pyran-4-one and Tf_2O reported by Stang and co-workers.[12] The reaction between pyranone **4** and TfOH also generated pyrylium trifluoromethanesulfonate **5b** (entry 2). Crystalline **5b** does not show any signs of decomposition under atmospheric conditions, and is moreover thermally stable (m.p. = 202.6–202.9 °C) under an atmosphere of argon. The molecular structure of **5b** was confirmed by a single-crystal X-ray diffraction analysis (Figure 1). The C(2)–C(3) and C(3)–C(4) bond lengths showed 1.406(4) and 1.403(4) Å, respectively, which are shorter than those of previously reported 4*H*-pyrans (1.50–1.52 Å)[13] and comparable to those of reported pyrylium salts (1.40–1.41 Å).[10b,14] The O–C bond lengths of **5b** fall in the range of 1.356(3)–1.360(3) Å, which is quite similar to those of reported pyrylium salts (1.35–1.36 Å).[10b,14] Subsequently, the reaction of **4** with *p*-toluenesulfonyl chloride and *p*-toluenesulfonic anhydride was examined (entries 3 and 4). Preliminarily, we confirmed that pyranone **4** did not react with TsCl at room temperature (entry 3). Upon treating **4** with Ts_2O at room temperature for 2 h, the signals for **4** disappeared in the ^{1}H NMR spectrum. Then, five equivalents of sodium tetrafluoroborate were added to the reaction mixture, which afforded pyrylium tetrafluoroborate **5c** as yellow crystals in 81% yield (entry 4). Under atmospheric conditions, crystalline pyrylium tetrafluoroborate **5f** did not show any decomposition or hygroscopy. An attempted reaction of **4** with chlorosulfonamide in the presence of aluminum chloride did not proceed, and exclusively the substrate was recovered (entry 5). 4-(Diethylphosphoryloxy)pyrylium salts **5d** and **5e** were also synthesized (entries 6–8). Although the reaction of **4** with

diethylchlorophosphate did not proceed (entry 6), pyranone **4** formed pyrylium salt **5d**, which bears a phosphoyloxy group, upon treatment with diethylchlorophosphate in the presence of aluminum chloride (entry 7). However, **5d** gradually decomposed in $CDCl_3$ to afford pyranone **4**. In order to exchange the counter anion to tetrafluoroborate, sodium tetrafluoroborate was added to the reaction mixture after the formation of **5d** (entry 8). Accordingly, pyrylium tetrafluoroborate **5e** was successfully obtained as pale yellow crystals that were relatively robust in solution and in the solid state.

Table 1. Reactions of 4*H*-pyran-4-one **4** with electrophiles.



entry	reagent(s)	solvent	conditions	results or product
1	Tf_2O	CH_2Cl_2	rt, 1.5 h	pyrylium salt **5b** (84%, R = H, X = TfO)
2	TfOH	CH_2Cl_2	rt, 2 h	pyrylium salt **5b** (79%)
3	TsCl	CH_2Cl_2	reflux, 48 h	no reaction
4	(1) Ts_2O, (2) $Na[BF_4]$	CH_2Cl_2	rt, 2 h	pyrylium salt **5c** (81%, R = Ts, X = BF_4)
5	Me_2NSO_2Cl, $AlCl_3$	CH_3NO_2	70 ºC, 24 h	no reaction
6	$(EtO)_2P(O)Cl$	CH_3NO_2	rt, 24 h	no reaction
7	$(EtO)_2P(O)Cl$, $AlCl_3$	CH_3NO_2	rt, 1.5 h	pyrylium salt **5d**[*] (R = $P(O)(OEt)_2$, X = Cl or $AlCl_4$)
8	(1) $(EtO)_2P(O)Cl$, $AlCl_3$, (2) $Na[BF_4]$	CH_3NO_2	rt, 1.5 h	pyrylium salt **5e** (72%, R = $P(O)(OEt)_2$, X = BF_4)

[*] Pyrylium salt **5d** gradually decomposed to afford 4*H*-pyran-4-one **4**.

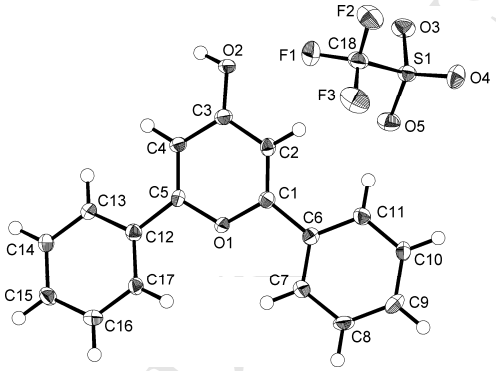
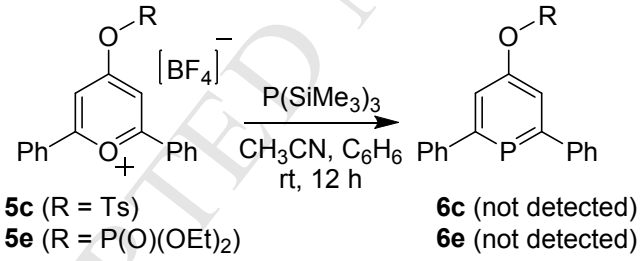


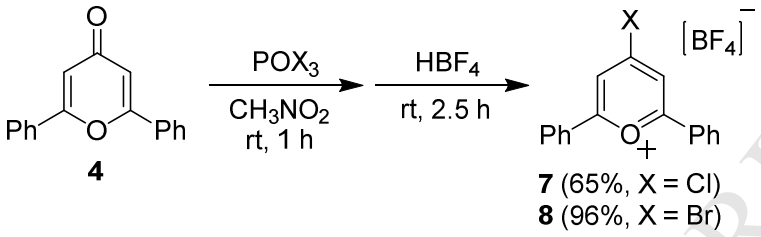
Fig. 1. Molecular structure of 4-hydroxypyrylium trifluoromethanesulfonate **5b** monohydrate with thermal ellipsoids set to 50% probability. One molecule of water was omitted for clarity. Selected bond lengths [Å] and angles [°] of **5b**: O(1)–C(5) 1.356(3), O(1)–C(1) 1.360(3), C(3)–O(2) 1.309(3), C(1)–C(7) 1.474(3), C(1)–C(2) 1.352(4), C(2)–C(3) 1.406(4), C(3)–C(4) 1.403(4), C(4)–C(5) 1.363(4), C(5)–O(1)–C(1) 121.8(2), O(2)–C(3)–C(2) 117.7(3), C(2)–C(1)–O(1) 120.0(3), C(1)–C(2)–C(3) 120.2(3), C(4)–C(3)–C(2) 118.3(3).

Finally, we attempted the synthesis of novel phosphinines from the stable pyrylium tetrafluoroborates **5c** and **5e**, which bear *p*-toluenesulfonate and phosphoyloxy groups, respectively (Scheme 5). After treating **5c** or **5e** for 12 h with $P(SiMe_3)_3$ at room temperature, an NMR spectroscopic analysis of the reaction mixtures revealed that the formation of the corresponding phosphinines had not occurred. Under these conditions, even the synthesis of phosphinines bearing a *p*-toluenesulfonate or phosphoyloxy group from the reaction of the corresponding pyrylium tetrafluoroborates with $P(SiMe_3)_3$ was found to be difficult.



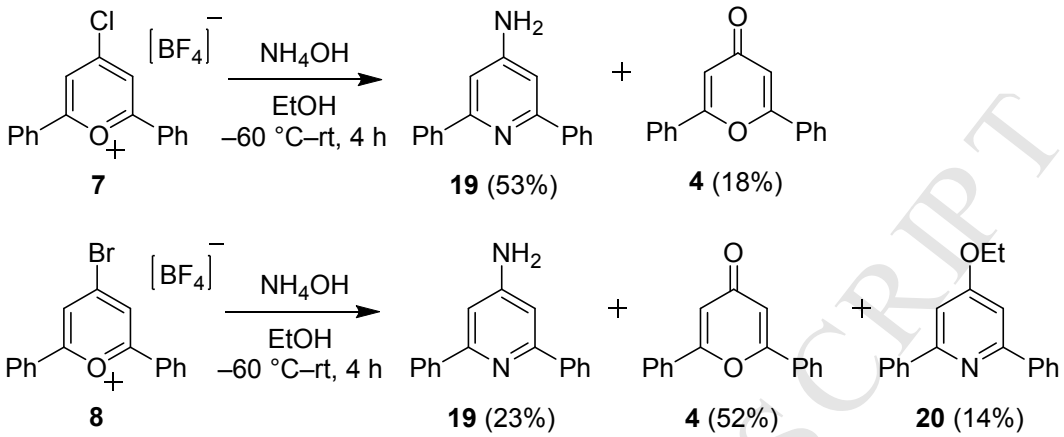
Scheme 5. Attempted reaction of **5c** or **5e** with $P(SiMe_3)_3$.

Synthesis of 4-Chloro- and 4-Bromopyrylium Tetrafluoroborates. The first synthesis of 4-chloropyrylium perchlorate and hexachloroantimonate was accomplished by the reaction of 4*H*-pyran-4-one with phosgene, reported by Föhlisch and Krockenberger.[15] Later on, Razus and co-workers synthesized 4-chloropyrylium perchlorate from the reaction of pyranone with PCl_5 or $POCl_3$ followed by treatment with $HClO_4$.[16] Following to the literature reports for the synthesis of chloropyrylium salts, we initially tried to synthesize 4-chloro- and 4-bromopyrylium tetrafluoroborates via the synthetic route shown in Scheme 6. Treating pyranone **4** for 1 h with phosphoryl chloride at room temperature, followed by the addition of $H[BF_4]$ afforded 4-chloro-2,6-diphenylpyrylium tetrafluoroborate (**7**) as yellow crystals in 65% yield. Similarly, 4-bromopyrylium tetrafluoroborate **8** was obtained from the reaction of **4** with phosphoryl bromide followed by the addition of $H[BF_4]$. Purification by decantation of the reaction mixture afforded pure yellow crystalline of **8** in 96% isolated yield. However, we did not detect any formation of 4-bromopyrylium tetrafluoroborate **8** in the reaction between **4** and phosphorus tribromide instead of phosphoryl bromide. Pyrylium salts **7** and **8** are thermally stable (**7**: m.p. = 167 °C (decomp.); **8**: m.p. = 181 °C (decomp.)) under atmospheric conditions.



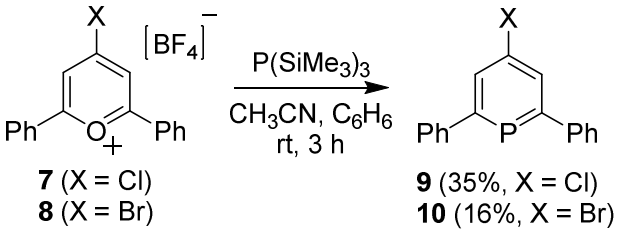
Scheme 6. Synthesis of 4-chloro- (**7**) and 4-bromopyrylium tetrafluoroborates (**8**).

Reactions of 4-Chloro- and 4-Bromopyrylium Tetrafluoroborates. In order to examine their reactivity, we treated 4-chloro and 4-bromopyrylium salts with nucleophiles that contain a nitrogen or phosphorus atom (Scheme 7). The reaction of 4-chloropyrylium tetrafluoroborate **7** with an ethanolic solution of ammonia furnished 4-aminopyridine **19** and 4*H*-pyran-4-one **4** in 53% and 18% yield, respectively. These results are comparable with the formation of 3-aminopyridine **12** from the reaction of 2-bromopentane-1,5-dione **1** with ammonia, which can be rationalized in terms of a nucleophilic substitution of the chlorine atom in **7**. In the case of 4-bromopyrylium tetrafluoroborate **8**, the reaction with ammonia afforded 4-aminopyridine **19** in 23%, together with 4*H*-pyran-4-one **4** (52%) and 4-ethoxypyridine **20** (14%), which should be the hydrolysis and solvolysis product, respectively. Also, the formation of a 4-bromopyridine derivative could be detected in the reaction mixture. It should be noted that chloro- and bromopyrylium tetrafluoroborates **7** and **8** exhibit high reactivity toward ammonia, water, and ethanol.



Scheme 7. Reactions of chloro- and bromopyrylium tetrafluoroborates **7** and **8** with ammonia.

We also attempted the formation of a phosphinine framework using $P(SiMe_3)_3$ as a phosphorus source. The reactions of **7** and **8** with $P(SiMe_3)_3$ in acetonitrile/benzene (1:1, v/v) proceeded at room temperature, and furnished 4-chloro- (**9**) and 4-bromophosphines (**10**) in 35% and 16% isolated yield, respectively, after chromatographic purification (Scheme 8). The ^{1}H NMR spectra of **9** and **10** in $CDCl_3$ showed doublet signals at 7.98 ($^3J_{PH}$ = 5.2 Hz) and 8.12 ($^3J_{PH}$ = 5.8 Hz) ppm, respectively, which can be feasibly attributed to hydrogen atoms at the 3-position of the phosphinine rings. The ^{31}P NMR spectra of **9** and **10** exhibited signals at +184.2 and +186.1 ppm, respectively, which are slightly up-field shifted relative to those of previously reported 2,4,6-triarylphosphinines (171–172 ppm),[2d,10b] reflecting the electronic perturbations when connecting the halogens of **9** and **10**. These results should be of great interest for the synthesis of chloro- and bromophosphinines **9** and **10** from the reaction of chloro- and bromopyrylium tetrafluoroborates **7** and **8** with $P(SiMe)_3$, as compared to more traditional synthetic methods.[4–7] Cl- and Br-containing **9** and **10** thus represent fascinating potential synthetic building blocks for new phosphorous-containing aromatics.



7 (X = Cl)
8 (X = Br)

9 (35%, X = Cl)
10 (16%, X = Br)

Scheme 8. Reactions of **7** and **8** with $P(SiMe_3)_3$.

Conclusions

A series of new pyrylium salts was obtained from the reactions of 2,6-diphenylpyranone **4**. Pyrylium salts bearing sulfonate and phosphonate groups were synthesized by the reactions of pyranone **4** with sulfonic anhydride and chlorophosphate, respectively. We found that the consecutive treatment of pyranone **4** with phosphoryl chloride or bromide and sodium tetrafluoroborate afforded the corresponding 4-chloro- and 4-bromopyrylium tetrafluoroborates as stable crystalline solids in good yield. Furthermore, we succeeded in synthesizing 4-chloro- and 4-bromo-2,6-diphenylphosphinines from the reactions of the corresponding chloro- and bromopyrylium tetrafluoroborates with $P(SiMe_3)_3$. The unprecedented formation of 4-chloro- and 4-bromo-2,6-diphenylphosphinines is noteworthy not only with respect to the construction of phosphinine frameworks from pyrylium salts and $P(SiMe_3)_3$, but also with regard to the development of synthetic methods for halogenated phosphinines.

Experimental section

General Comments. All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were purified by standard methods. Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 Hz) spectra were measured in $CDCl_3$ or CD_3CN with a Varian Mercury 400 plus or a Bruker Avance III spectrometer using $CHCl_3$ (δ_H = 7.26) and $CDCl_3$ (δ_C = 77.0), or CHD_2CN (δ_H = 1.94) and CD_3CN (δ_C = 1.32) as internal standards for ^{1}H and ^{13}C NMR spectra, respectively. ^{31}P NMR (161 MHz) and ^{19}F NMR (376 MHz) spectra were measured in $CDCl_3$ or CD_3CN with a Varian Mercury 400 plus or a Bruker Avance III spectrometer using 85% H_3PO_4 in water (δ_P = 0.00) and $CFCl_3$ (δ_F = 0.00) as an external standard, respectively. An assignment of the signals was usually used by 1D (homodecoupling and DEPT) and 2D (COSY, HMQC, and HMBC) NMR techniques. All ^{13}C, ^{19}F, and ^{31}P NMR experiments were performed with broad-band ^{1}H decoupling unless otherwise noted. EI and ESI-TOF mass spectral data were obtained on a JEOL JMS-GCmateII and a JEOL JMS-T100CS spectrometer, respectively. Elemental analyses were performed by a Yanaco MT-5 CHN corder. All melting points were determined on a Yanaco micro melting point apparatus or a Mettler Toledo MP90 melting point system, and were uncorrected.

Materials. All materials were purchased from chemical suppliers and used without further purification unless otherwise noted. 1,5-Diphenylpentane-1,3,5-trione (**18**) and 2,6-diphenyl-4*H*-pyran-4-one (**4**) were prepared according to the procedures reported in the literatures.[17]

Preparation of 1,5-Diphenylpentane-1,5-dione (11). To a solution of glutaryl chloride (6.704 g, 39.67 mmol) in benzene (300 mL) was added aluminum chloride (11.54 g, 79.42 mmol) at room temperature. After the solution was stirred at 40 ºC for 20 h, saturated ammonium chloride solution was added to the solution. An organic layer was extracted with hexane, dried over anhydrous sodium sulfate, filtered, evaporated to afford 1,5-diphenylpentane-1,5-dione (9.347 g, 37.05 mmol, 93%) as orange solid. **11**: ^{1}H NMR (400 MHz, $CDCl_3$) δ8.00–7.96 (m, 4H, ArH), 7.58–7.52 (m, 2H, ArH), 7.49–7.43 (m, 4H, ArH), 3.13 (t, J = 7.0 Hz, 4H, CH_3), 2.21 (quint, J = 7.0 Hz, 2H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ199.8, 136.8, 133.0, 128.6, 128.0, 37.5, 18.7; MS (EI^+) *m/z* 252 (M^+).

Bromination of 1,5-Diphenylpentane-1,5-dione (11). To a solution of

1,5-diphenylpentane-1,5-dione (0.503 g, 1.99 mmol) in carbon tetrachloride (15 mL) was added molecular bromine (0.317 g, 1.98 mmol) at room temperature. After the solution was stirred at room temperature for 1 h, water was added to the reaction mixture. An organic layer was extracted with dichloromethane, dried over anhydrous sodium sulfate, filtered, evaporated to give orange oil. Purification of the reaction mixture by column chromatography on silicagel (eluting with hexane:dichloromethane = 1:1) afforded 2-bromo-1,5-diphenylpentane-1,5-dione (0.287 g, 0.857 mmol, 44%) as orange oil. **1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.05 (m, 2H, ArH), 8.01–7.98 (m, 2H, ArH), 7.63–7.55 (m, 2H, ArH), 7.52–7.46 (m, 4H, ArH), 5.49 (q, *J* = 7.2 Hz, 1H, CH), 3.41–3.33 (m, 1H, CH), 3.26–3.19 (m, 1H, CH), 2.70–2.63 (m, 1H, CH), 2.61–2.49 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 193.2, 136.5, 134.2, 133.8, 133.4, 129.0, 128.8, 128.7, 128.0, 47.1, 35.6, 27.8; HRMS (ESI^+) *m/z* found 330.0248 [M^+], calcd for $C_{17}H_{15}{}^{79}BrO_2$: 330.0255.

Reaction of 2-Bromo-1,5-diphenylpentane-1,5-dione (1) with Ammonium Acetate. To a solution of 2-bromopentane-1,5-dione **1** (0.089 g, 0.27 mmol) in glacial acetic acid (10 mL) was added ammonium acetate (0.042 g, 0.54 mmol) at room temperature. The solution was stirred at 50 ºC for 24 h, and cooled to room temperature. An organic layer was extracted with ether, dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. Separation of the reaction mixture by column chromatography on silicagel (eluent with dichloromethane) gave 2-amino-1,5-diphenylpentane-1,5-dione (**13**) (0.054 g, 0.20 mmol, 63%) as orange oil and 3-amino-2,6-diphenylpyridine (**12**) (0.010 g, 0.025 mmol, 6%) as yellow solid. **13**: orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.2 Hz, 2H, ArH), 7.86 (d, *J* = 7.6 Hz, 2H, ArH), 7.67–7.63 (m, 1H, ArH), 7.59–7.53 (m, 3H, ArH), 7.49–7.43 (m, 2H, ArH), 5.23–5.18 (m, 1H, CH), 3.51–3.42 (m, 1H, CH_2), 3.13–3.06 (m, 1H, CH_2), 2.55–2.47 (m, 1H, CH_2), 1.78–1.69 (m, 1H, CH_2); HRMS (EI^+) *m/z* found 267.1246 [M^+], calcd for $C_{17}H_{17}NO_2$: 267.1259. **12**: yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.8 Hz, 2H, ArH), 7.86 (d, *J* = 6.8 Hz, 2H, ArH), 7.64 (d, *J* = 7.64 Hz, 1H, CH), 7.56–7.52 (m, 2H, ArH), 7.48–7.43 (m, 3H, ArH), 7.38–7.36 (m, 1H, ArH), 7.33 (d, *J* = 8.4 Hz, 1H, CH) 5.47 (s, 1H, NH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 149.3, 138.9, 136.7, 129.0, 128.55, 128.52, 128.48, 128.08, 126.6, 124.7, 120.6; HRMS (EI^+) *m/z* found 246.1142 [M^+], calcd for $C_{17}H_{14}N_2$: 246.1157.

Reaction of 2-Bromo-1,5-diphenylpentane-1,5-dione (1) with Ammonia. To a solution of

2-bromopentane-1,5-dione **1** (0.105 g, 0.319 mmol) in ethanol (10 mL) was added a solution of 26% ammonia (13.8 mol/L, 0.23 mL, 3.2 mmol) at 0 ºC. The solution was stirred at room temperature for 24 h, and then an organic layer was extracted with ethyl acetate. The solution was washed with calcium chloride solution, dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure to afford *trans*-1,2-dibenzoylcyclopropane[18] (**14**) (0.075 g, 0.30 mmol, 93%) as pale red solid. **14**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.04 (m, 2H, ArH), 7.62–7.57 (m, 4H, ArH), 7.51–7.45 (m, 2H, ArH), 3.43 (t, J = 7.2 Hz, 1H, CH), 1.82 (t, J = 7.2 Hz, 2H, CH); HRMS (EI$^+$) *m/z* found 250.0980 [M^+], calcd for $C_{17}H_{14}O_2$: 250.0994.

Reaction of 2-Bromo-1,5-diphenylpentane-1,5-dione (1) with Tetrafluoroboric Acid and Triphenylmethanol. To a solution of 2-bromopentane-1,5-dione **1** (0.808 g, 2.44 mmol) in acetic anhydride (80 mL) was added a solution of tetrafluoroboric acid (1.930 g, 10.98 mmol) in acetic anhydride (30 mL) at room temperature. The solution was stirred at 80 ºC for 24 h, and cooled to room temperature. The reaction mixture was slowly added to a solution of cooled ether, green precipitate generated in the cooled etheral solution. After supernatant of the suspension was separated, the resulting brown precipitate was dried under reduced pressure to afford 2,6-diphenylpyrylium tetrafluoroborate (0.112 g, 0.34 mmol, 15%) as brown solids. **15**: ^{1}H NMR (400 MHz, CD_3CN) δ8.94 (t, J = 8.4 Hz, 2H, CH), 8.49 (d, J = 8.4 Hz, 2H, CH), 8.36–8.34 (m, 4H, ArH), 7.89–7.86 (m, 2H, ArH), 7.79–7.75 (m, 4H, ArH); ^{19}F NMR (376 MHz, CD_3CN) δ –152.3; HRMS (ESI$^+$) *m/z* 233.0982 ([M–BF_4]$^+$), calcd for $C_{17}H_{13}O$: 233.0961.

Reaction of 2,6-Diphenylpyrylium Tetrafluoroborate (15) with Tris(trimethylsilyl)phosphine. To a solution of 2,6-diphenylpyrylium tetrafluoroborate (0.261 g, 0.815 mmol) in acetonitrile (5 mL) was added a solution of tris(trimethylsilyl)phosphine (0.205 g, 0.818 mmol) in benzene (3 mL) at room temperature. The solution was stirred at 60 ºC for 16 h, and then cooled to room temperature. After the solution was evaporated under reduced pressure, separation of the reaction mixture by column chromatography on silica gel (eluting with dichloromethane) afforded 2,6-diphenyl-4*H*-pyran (0.114 g, 0.459 mmol, 60%) as brown solids. **16**: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.68–7.66 (m, 4H, ArH), 7.40–7.37 (m, 4H, ArH), 7.34–7.32 (m, 2H, ArH), 5.43 (t, J = 3.6 Hz, 2H, CH), 3.09 (t, J = 3.6 Hz 2H, CH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 134.7, 128.26, 128.14, 124.3, 96.5, 21.8; HRMS (EI$^+$) *m/z* 234.1060 (M^+), calcd for

$C_{17}H_{14}O$: 234.1045.

Preparation of 1,5-Diphenylpentane-1,3,5-trione (18). To a solution of benzoylacetone (0.505 g, 3.08 mmol) in 1,2-dimethoxyethane (18 mL) was added sodium hydride (0.592 g, 14.8 mmol) at room temperature. Methyl benzoate (0.540 g, 3.70 mmol) was added to the mixture at room temperature, the solution was refluxed for 48 h, and then allowed to be cool to room temperature. After saturated ammonium chloride solution was added to the solution, an organic layer was extracted with ether. The layer was dried over anhydrous sodium sulfate, filtered, and dried under reduced pressure to afford 1,5-diphenylpentane-1,3,5-trione (0.812 g, 3.05 mmol, 99%) as yellow crystals. **18**: mp 106–108 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.8 (br, 1H), 7.87–7.84 (dd, J = 7.2, 1.2 Hz, 4H), 7.51–7.43 (m, 6H), 6.02 (s, 2H), 4.11 (s, 1H); MS (EI^+) *m/z* 266 (M^+).

Preparation of 2,6-Diphenyl-4*H*-pyran-4-one (4). 1,5-Diphenylpentane-1,3,5-trione (**18**) was added to concentrated sulfuric acid at 0 ºC, the solution was stirred at 0 ºC for 20 min. The solution was poured into a mixture of crushed ice and water. The resulting precipitate were filtered and dried under reduced pressure to afford 2,6-diphenyl-4*H*-pyran-4-one (0.340 g, 1.37 mmol, 91%) as colorless crystals. **4**: mp 138.0–140.8 ºC (lit.[17] mp 139–140 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.86 (m, 4H), 7.56–7.52 (m, 6H), 6.84 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 163.4, 131.4, 129.1, 125.9, 111.3, 29.6; MS (EI^+) *m/z* 248 (M^+).

Reaction of 4*H*-Pyran-4-one 4 with Trifluoromethanesulfonic Anhydride (Tf_2O). To a solution of 4*H*-pyran-4-one **4** (0.829 g, 3.34 mmol) in dichloromethane (30 mL) was added Tf_2O (1.09 g, 3.86 mmol) at room temperature. The solution was stirred at room temperature for 1.5 h, volatile substances were removed under reduced pressure. The resulting yellow solid was washed with ether, and the ethereal solution was dried under reduced pressure to afford 4-hydroxypyrylium trifluoromethanesulfonate **5b** (1.44 g, 2.71 mmol, 84%) as yellow solid. **5b**: mp 202.6–202.9 ºC; ^{1}H NMR (400 MHz, CD_3CN) δ 8.19 (d, J = 8.4 Hz, 4H, ArH), 7.80–7.67 (m, 6H, ArH), 7.76 (s, 2H, pyrylium ring); ^{13}C NMR (101 MHz, CD_3CN) δ 179.7, 171.4, 134.8, 130.1, 129.2, 128.1, 120.3 (quartet, J_{FC} = 157.4 Hz, $CF_3SO_3^-$), 117.6, 107.4; ^{19}F NMR (376 MHz, CD_3CN) δ –79.82 (s); MS (ESI^+) *m/z* 249 ($[M–TfO]^+$); Anal. Calcd for $C_{18}H_{13}F_3O_5S$: C, 54.27; H, 3.29%. Found C, 54.09; H, 3.56%.

Reaction of 4*H*-Pyran-4-one 4 with *p*-Toluenesulfonic Anhydride (Ts_2O) and Sodium

Tetrafluoroborate. To a solution of 4*H*-pyran-4-one **4** (0.504 g, 2.03 mmol) in dichloromethane (15 mL) was added Ts_2O (0.796 g, 2.44 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 2 h, sodium tetrafluoroborate (1.115 g, 10.15 mmol) was added to the reaction mixture. The suspension was stirred for 1 h, and then volatile materials were removed under reduced pressure. The resulting yellow solid was washed with ether, then the ethereal solution was dried under reduced pressure to afford 4-(*p*-toluenesulfonyloxy)pyrylium tetrafluoroborate **5c** (0.673 g, 1.64 mmol, 81%) as pale yellow solid. **5c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.2 Hz, 4H, ArH), 7.86 (d, J = 8.4 Hz, 2H, ArH), 7.85 (s, 2H, ArH), 7.70 (t, J = 7.2 Hz, 2H, ArH), 7.66 (t, J = 7.2 Hz, 4H, ArH), 7.22 (d, J = 8.4, 2H, ArH), 2.37 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.8 (C), 169.7 (C), 141.5 (C), 139.6 (C), 134.1 (CH), 129.9 (CH), 129.0 (CH), 129.0 (C), 127.3 (CH), 126.3 (CH), 107.8 (CH), 21.38 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –150.3 (s); HRMS (ESI$^+$) *m/z* 403.1013 ([M–BF_4]$^+$), calcd for $C_{24}H_{19}O_4S$: 403.0999; Anal. Calcd for $C_{24}H_{19}BF_4O_4S$: C, 58.80; H, 3.91%. Found C, 59.12; H, 4.10%.

Reaction of 4*H*-Pyran-4-one 4 with Diethyl Chlorophosphate and Sodium Tetrafluoroborate. To a solution of 4*H*-pyran-4-one **4** (0.504 g, 2.03 mmol) in nitromethane (15 mL) was added diethyl chlorophosphate (0.720 g, 4.17 mmol) and aluminum chloride (0.544 g, 4.08 mmol) at room temperature. After the solution was stirred at room temperature for 1.5 h, signals for 4*H*-pyran-4-one **4** disappeared in the ^{1}H NMR spectrum. Sodium tetrafluoroborate (0.890 g, 8.11 mmol) was added to the reaction mixture at room temperature. The solution was stirred at room temperature for 24 h, and then volatile materials were removed under reduced pressure. After the resulting yellow solid was washed with ether, the ethereal solution was dried under reduced pressure to afford 4-(diethylphosphoryloxy)pyrylium tetrafluoroborate **5e** (0.689 g, 1.46 mmol, 72%) as pale yellow solid. **5e**: mp 97.5–99.0 ºC; ^{1}H NMR (400 MHz, CD_3CN) δ 8.15 (d, J = 8.0 Hz, 4H, ArH), 7.75 (t, J = 7.2 Hz, 2H, ArH), 7.68 (t, J = 7.2, 4H, ArH), 7.61 (s, 2H, ArH), 4.27–4.23 (m, 4H, CH_2), 2.45 (td, J = 7.6 Hz, 6H, CH_3); ^{13}C NMR (101 MHz, CD_3CN) δ 171.1, 134.9, 130.8, 130.5, 130.1, 128.5, 109.6, 67.4 (d, J_{PC} = 7.1 Hz), 16.0 (d, J_{PC} = 7.0 Hz); ^{19}F NMR (376 MHz, CD_3CN) δ –152.5 (s); ^{31}P NMR (162 MHz, CD_3CN) δ 3.50 (s); HRMS (ESI$^+$) *m/z* 385.1189 ([M–BF_4]$^+$), calcd for $C_{21}H_{22}O_5P$: 385.1199.

Preparation of 4-Chloropyrylium Tetrafluoroborate 7. To a solution of 4*H*-pyran-4-one **4** (1.036

g, 4.17 mmol) in nitromethane (30 mL) was added phosphoryl chloride (0.76 mL, 8.2 mmol) at room temperature. After the solution was stirred at room temperature for 1 h, tetrafluoroboric acid in ether solution (1.18 g/mL, 1.30 mL, 10.3 mmol) was added to the reaction mixture. The solution was stirred at room temperature for 1 h, and then dropwisely poured into cooled ether. The resulting precipitate was filtered, washed with cooled ether, and dried under reduced pressure to afford 4-chloropyrylium tetrafluoroborate **7** (0.961 g, 2.71 mmol, 65%) as yellow crystals. **7**: mp 166.9 ºC (decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 8.60 (s, 2H), 8.33 (d, J = 7.8 Hz, 4H), 7.90 (t, J = 7.6 Hz, 2H), 7.77 (t, J = 7.8 Hz, 4H); ^{19}F NMR (376 MHz, CD_3CN) δ –152.2 (s); ^{13}C NMR (101 MHz, CD_3CN) δ 172.74, 167.56, 137.4, 131.3, 130.1, 128.8, 121.1; MS (ESI$^+$) *m/z* 267 ([M–BF_4]$^+$); Anal. Calcd for $C_{17}H_{12}BClF_4O$: C, 57.59; H, 3.41%. Found C, 57.35; H, 3.58%.

Preparation of 4-Bromopyrylium Tetrafluoroborate 8. To a solution of 4*H*-pyran-4-one **4** (0.202 g, 0.814 mmol) in nitromethane (15 mL) was added phosphoryl bromide (0.469 g, 1.64 mmol) at room temperature. After the solution was stirred at room temperature for 2 h, tetrafluoroboric acid in ether solution (1.18 g/mL, 0.50 mL, 3.4 mmol) was added to the reaction mixture. The solution was stirred at room temperature for 18 h, and then dropwisely poured into cooled ether. The resulting precipitate was filtered, washed with cooled ether, and dried under reduced pressure to afford 4-bromopyrylium tetrafluoroborate **8** (0.308 g, 0.772 mmol, 96%) as yellow crystals. **8**: mp 181 ºC (decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 8.81 (s, 2H, pyrylium ring), 8.34 (d, J = 7.4 Hz, 4H, ArH), 7.89 (t, J = 7.4 Hz, 2H, ArH), 7.79 (t, J = 7.4 Hz, 4H, ArH); ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.0, 162.5, 131.5, 131.0, 129.2, 126.1, 110.9; ^{19}F NMR (376 MHz, CD_3CN) δ –152.2 (s); HRMS (ESI$^+$) *m/z* 331.0055 ([M–BF_4]$^+$), calcd for $C_{17}H_{12}{}^{79}BrO$: 331.0066.

Reaction of 4-Chloropyrylium Tetrafluoroborate 7 with Ammonia. To a solution of 4-chloropyrylium tetrafluoroborate **7** (0.300 g, 0.846 mmol) in ethanol (16 mL) was added 26% ammonia solution (13.8 mol/L, 0.61 mL, 8.5 mmol) at –60 ºC. The solution was stirred at –60 ºC to room temperature for 16 h. An organic layer was extracted with ethyl acetate, washed with brain, dried over anhydrous sodium sulfate, and filtered. The layer was evaporated and purified by PTLC (eluent with hexane and dichloromethane) to afford 4*H*-pyran-4-one **4** (0.038 g, 0.15 mmol, 18%) and 4-aminopyridine **19** (0.111 g, 0.451 mmol, 53%). **19** (4-aminopyridine): ^{1}H NMR (400 MHz,

$CDCl_3$) δ8.06 (d, *J* = 7.2 Hz, 4H, ArH), 7.46 (t, *J* = 7.4 Hz, 4H, ArH), 7.40 (t, *J* = 7.4 Hz, 2H, ArH), 6.96 (s, 2H, ArH), 4.34 (br, 2H, NH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.64, 154.13, 139.67, 128.76, 128.48, 126.95, 105.07; HRMS (EI^+) *m/z* 246.1170 (M^+), calcd for $C_{17}H_{14}N_2$: 246.1162.

Reaction of 4-Bromopyrylium Tetrafluoroborate 8 with Ammonia. To a solution of 4-bromopyrylium tetrafluoroborate **8** (0.206 g, 0.516 mmol) in ethanol (10 mL) was added 26% ammonia solution (13.8 mol/L, 0.18 mL, 2.5 mmol) at –60 ºC. The solution was stirred at –60 ºC to room temperature for 24 h. An organic layer was extracted with ethyl acetate, washed with brain, dried over anhydrous sodium sulfate, and filtered. The layer was evaporated and purified by PTLC (eluent with hexane and dichloromethane) to afford 4-ethoxypyridine **20** (0.017 g, 0.073 mmol, 14%), 4*H*-pyran-4-one **4** (0.070 g, 0.27 mmol, 52%), and 4-aminopyridine **19** (0.029 g, 0.12 mmol, 23%). **20**: brown crystals; mp 73.6–74.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.12 (d, *J* = 6.8 Hz, 4H, ArH), 7.49 (t, *J* = 7.2 Hz, 4H, ArH), 7.42 (t, *J* = 7.2 Hz, 2H, ArH), 7.21 (s, 2H, ArH), 4.23 (q, *J* = 7.2 Hz, 2H, OEt), 1.51 (t, *J* = 7.2 Hz, 3H, OEt); ^{13}C NMR (101 MHz, $CDCl_3$) δ166.6 , 158.5, 139.7, 128.9, 128.6, 127.0, 105.3, 63.58, 14.60; HRMS (EI^+) *m/z* 275.1302 (M^+), calcd for $C_{19}H_{17}NO$: 275.1310.

Preparation of Tris(trimethylsilyl)phosphine.[19] Sodium (3.96 g, 172 mmol) and potassium (5.26 g, 135 mmol) were added to 1,2-dimethoxyethane (200 mL) at room temperature, and the suspension was refluxed for 1 h (Color of the suspension was changed to purple). After the suspension allowed to be cool to room temperature, red phosphorus (3.12 g, 101 mmol) was added to the suspension at room temperature. The reaction mixture was refluxed for 4.5 h, and then cooled down to room temperature. After a solution of Me_3SiCl (42.0 mL, 330 mmol) in 1,2-dimethoxyethane (50 mL) was added to the reaction mixture at room temperature (Color of the suspension was changed to gray), the resulting suspension was refluxed for 1 h. After the suspension allowed to cool to room temperature, volatile substances were removed under reduced pressure. Hexane (3 x 50 mL) was added to the reaction mixture, and the hexane solution was filtered through a pad of celite. Volatile substances was removed under reduced pressure to afford $P(SiMe_3)_3$ (13.9 g, 55.5 mmol, 55%) as colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ0.31 (d, $^3J_{HP}$ = 4.4 Hz, CH_3); ^{31}P NMR (162 MHz, C_6D_6) δ –252.3 (s). Caution: $P(SiMe_3)_3$ ignites spontaneously under atmospheric conditions.

Preparation of 4-Chlorophosphinine 9. To a solution of 4-chloropyrylium tetrafluoroborate **7** (0.502 g, 1.42 mmol) in acetonitrile (50 mL) was added a solution of tris(trimethylsilyl)phosphine (0.530 g, 2.12 mmol) in benzene (5 mL) at room temperature. The solution was stirred at room temperature for 3 h. Purification of the reaction mixture by column chromatography on silicagel (eluent with dichloromethane:hexane = 1:1) gave 4-chlorophosphinine **9** (0.014 g, 0.050 mmol, 35%) as yellow crystals. **9**: mp 213–214 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J_{PH} = 5.2 Hz, 2H, phosphinine ring) 7.68 (d, J_{HH} = 7.6 Hz, 4H, ArH) 7.50–7.43 (m, 6H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8 (d, J_{PC} = 54.3 Hz), 142.1 (d, J_{PC} = 24.2 Hz), 137.1 (d, J_{PC} = 15.1 Hz), 132.0 (d, J_{PC} = 12.8 Hz), 129.0 (s), 128.4 (d, J_{PC} = 1.0 Hz), 126.1 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 184.2 (s); HRMS (EI$^+$) *m/z* 282.0382 (M^+), calcd for $C_{17}H_{12}ClP$: 282.0375.

Preparation of 4-Bromophosphinine 10. To a solution of 4-bromopyrylium tetrafluoroborate **8** (0.213 g, 0.534 mmol) in acetonitrile (40 mL) was added a solution of tris(trimethylsilyl)phosphine (0.251 g, 1.00 mmol) in benzene (5 mL) at room temperature. The solution was stirred at room temperature for 3 h. Purification of the reaction mixture by column chromatography on silicagel (eluent with dichloromethane) afforded 4-bromophosphinine **10** (0.028 g, 0.086 mmol, 16%) as brown crystals. **10**: 110.5 ºC (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J_{PH} = 5.8 Hz, 2H, phosphinine ring), 7.73 (d, J_{HH} = 8.0 Hz, 4H, ArH), 7.54–7.49 (m, 4H, ArH), 7.47–7.44 (m, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2 (d, J_{PC} = 52.3 Hz), 143.2 (d, J_{PC} = 24.2 Hz), 142.9 (d, J_{PC} = 13.1 Hz), 131.3 (d, J_{PC} = 12.1 Hz), 129.0 (s), 128.1 (d, J_{PC} = 1.0 Hz), 126.1 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 186.1 (s); HRMS (EI$^+$) *m/z* 325.9869 (M^+), calcd for $C_{17}H_{12}{}^{79}BrP$: 325.9860.

X-Ray Crystallographic Analysis of 4-Hydroxypyrylium Trifluoromethanesulfonate 5b. Single crystals of 4-hydroxypyrylium trifluoromethanesulfonate **5b** were obtained by slow recrystallization from dichloromethane solution at room temperature. The intensity data were collected on a Rigaku Saturn CCD system with graphite-monochromated Mo K_α radiation (λ = 0.71070 Å). Selected structural parameters and crystal data of **5b** are shown in Tables 2 and S1–S3 (in the Supplementary Data), respectively. The structure was solved by direct method (SHELXS-97)[20] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[21] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. Crystallographic data reported in this manuscript have been

deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-1532041. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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Supplementary data

Supplementary data related to this article can be found at XXX.

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Table 2. Crystallographic Data and Experimental Parameters for the Crystal Structure Analysis of 4-Hydroxypyrylium Trifluoromethanesulfonate **5b** Monohydrate

	5b H_2O
Formula	$C_{18}H_{13}F_3O_6S\ H_2O$
Formula weight	416.36
Crystal dimensions/mm	0.35 × 0.20 × 0.10
Collection temperature/K	113(2)
Crystal system	triclinic
Space group	*P*–1 (#2)
a/Å	10.1827(17)
b/Å	10.3268(18)
c/Å	10.795(2)
α/°	66.49(2)
β/°	64.51(2)
γ/°	63.65(2)
Volume/Å^3	887.4(3)
Z	2
Density/gcm^{-3}	1.558
Independent reflections	3468
No. of parameters	262
R_1 [I>2σ(I)]	0.0532
wR_2 [I>2σ(I)]	0.0996
R_1 (all data)	0.0933
wR_2 (all data)	0.1149
Goodness of fit	1.066
Largest diff. peak/hole/e Å^{-3}	0.302/–0.358