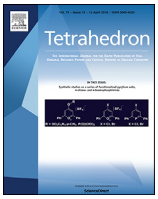
Tetrahedron 74 (2018) 1880–1887

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet



# Synthetic studies on a series of functionalized pyrylium salts, 4-chloro- and 4-bromophosphinines

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## ARTICLE INFO

*Article history:*
Received 23 January 2018
Received in revised form
19 February 2018
Accepted 21 February 2018
Available online 25 February 2018

*Keywords:*
Pyrylium salt
Phosphinine
Chlorination
Bromination
Tris(trimethylsilyl)phosphine

## 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.

## 1. 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 $\pi^*$ 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 coworkers 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).

## 2. Results and discussion

### 2.1. Attempted synthesis of 3-bromopyrylium tetrafluoroborate **2**

Initially, we attempted the synthesis of 3-bromopyrylium

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https://doi.org/10.1016/j.tet.2018.02.053
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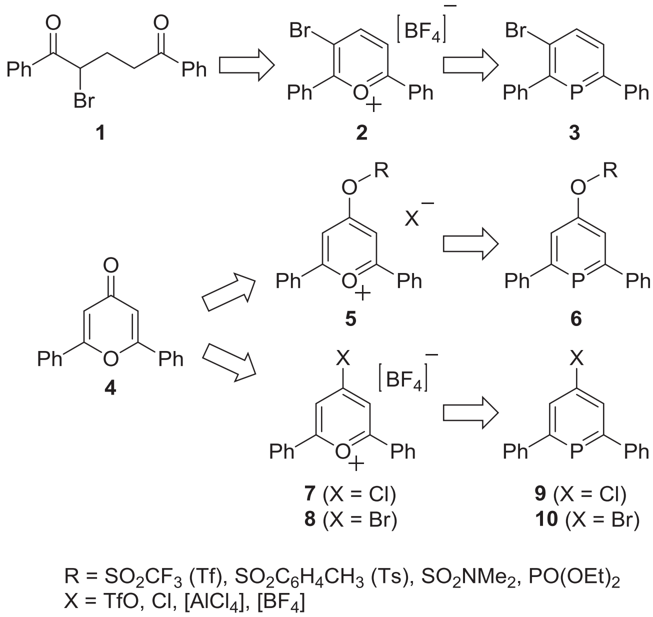


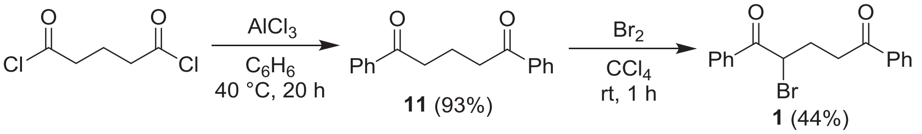
R = $SO_2CF_3$ (Tf), $SO_2C_6H_4CH_3$ (Ts), $SO_2NMe_2$, $PO(OEt)_2$
X = TfO, Cl, $[AlCl_4]$, $[BF_4]$

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

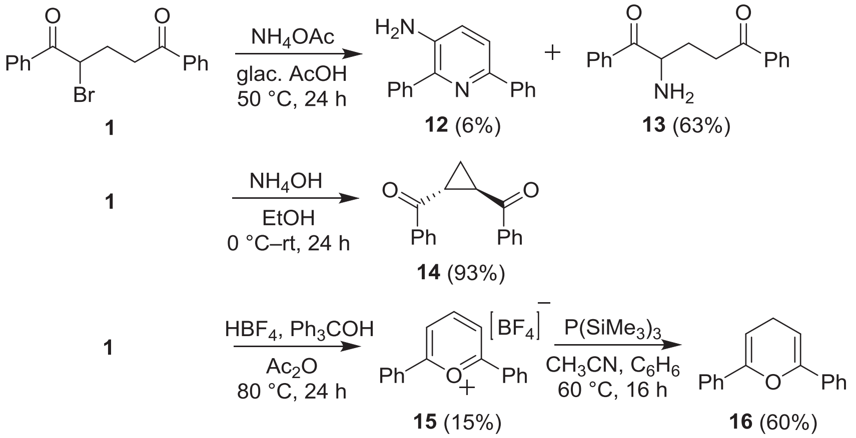
tetrafluoroborate **2** via 2-bromo-1,5-diphenylpentane-1,5-dione (**1**) (Scheme 2). A Friedel-Crafts reaction of glutaryl chloride with benzene in the presence of aluminum chloride afforded 1,5-diphenylpentane-1,5-dione (**11**) in 93% yield. A subsequent bromination of **11** in tetrachloromethane 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).

### *2.2. Reactions of 2,6-diphenyl-4H-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



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



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