

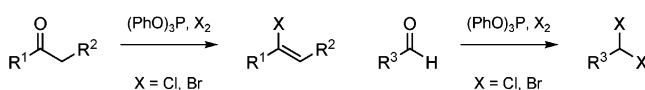
## A Mild Synthesis of Vinyl Halides and *gem*-Dihalides Using Triphenyl Phosphite–Halogen-Based Reagents

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A new application of  $(\text{PhO})_3\text{P}$ –halogen-based reagents to the synthesis of vinyl halides and *gem*-dihalides is described. Vinyl halides were prepared in good to excellent yields from enolizable ketones, whereas aldehydes afforded the corresponding *gem*-dihalides. The halogenation proceeded smoothly under mild conditions.

The role and importance of halogenated building blocks in organic synthesis is long established and undisputed, owing to the wealth of reactions they can easily undergo. Moreover, the recent development of new strategic reactions for C–C bond formation, such as the Suzuki–Miyaura, Stille, or Sonogashira coupling,<sup>1</sup> has resulted in the constant need of readily available halides as starting materials. Vinyl halides, in particular, are emerging as versatile substrates in a variety of chemical transformations,<sup>2</sup> and their importance as valuable synthons is increasing accordingly. Typically, vinyl halides are prepared from carbonyl compounds by reaction with traditional halogenating reagents such as thionyl chloride or phosphorus halides under prolonged heating in high-boiling solvents<sup>3a–f</sup> or by means of multistep procedures that require the isolation of suitable intermediates, such as vinyl phosphates<sup>3g</sup> or hydrazones<sup>4</sup> using the Barton procedure and later modifications. The quest for new synthetic methods, therefore, is still active, and the development of milder and straightforward reactions for the preparation of such halogenated derivatives represents a desirable goal.

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Recently, we described the reactivity of amides toward the halogenating reagent chlorotriphenoxyphosphonium chloride, i.e.,  $(\text{PhO})_3\text{P}^+\text{ClCl}^-$  (henceforth TPPCl<sub>2</sub>) and proposed a new and efficient protocol for the mild deacylation of *N*-monosubstituted amides.<sup>5a</sup> As part of our ongoing studies on the chemistry and applications of this versatile reagent,<sup>5</sup> we wish to describe here the reactivity of carbonyl compounds such as ketones and aldehydes toward TPPCl<sub>2</sub> and its brominated analogue TPPBr<sub>2</sub>, which resulted in a mild synthesis of vinyl halides and *gem*-dihalides.

By analogy to amides, which are known to form the corresponding iminochlorides when treated with TPPCl<sub>2</sub>,<sup>5a</sup> we reasoned that such an halogenation on a ketone or aldehyde carbonyl would also result in a halogen–oxygen exchange to yield the appropriate vinyl halide (Scheme 1). Encouraging, though scattered, literature precedents using halogenated phosphites<sup>6</sup> and phosphines<sup>3g,7</sup> hinted at the feasibility of such a transformation, whose scope and limitations, however, have never been assessed so far.

To this end, a suitable set of ketones and aldehydes was subjected to TPPCl<sub>2</sub> under standard conditions.<sup>5</sup> In a typical procedure, the carbonyl compound was treated at  $-20\text{ }^\circ\text{C}$  with a freshly prepared solution of TPPCl<sub>2</sub> in either dichloromethane or chloroform in the presence of triethylamine. After warming to rt overnight, the reaction mixture was refluxed for 2 h to achieve complete conversion, and the crude residue was purified by column chromatography. The results are reported in Table 1. Vinyl chlorides were obtained from enolizable ketones in excellent yields (Table 1, entries 1–12). If formation of *E/Z* isomers was possible, poor stereoselectivity was observed (entry 8); in the case of propiophenone (entry 2), however, nearly exclusive formation of the thermodynamically favored *Z* isomer<sup>8</sup> occurred. When nonequivalent enolizable positions were present,

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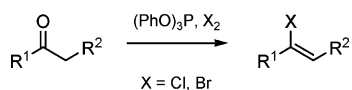
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## SCHEME 1



a regioisomeric mixture of halides was obtained, as in the case of 2-methylcyclohexanone (entry 11),<sup>9</sup> whose halogenation yielded two regioisomers in ca. 1:1 ratio. Functionalities such as ester (entry 3), boronate (entry 4), ether (entry 6), double bond (entry 7), and acetal (entry 16) were left untouched during the halogenation. When camphor (entry 12) was exposed to TPPCl<sub>2</sub>, two constitutional isomeric chloro derivatives were formed in a 2:1 ratio. In particular, the corresponding vinyl chloride was obtained as the minor product, whereas the exomethylene derivative was featured as the major halogenation product, thus confirming a behavior already described in the literature with PCl<sub>5</sub>.<sup>10</sup> When a nonenolizable ketone such as benzophenone was used as the substrate, dichlorodiphenylmethane was obtained in 93% yield (entry 13). By contrast, aldehydes always afforded exclusively *gem*-dichlorides in excellent yields (entries 14–16), regardless of the presence of enolizable protons.

By analogy to the synthesis of vinyl chlorides and *gem*-dichlorides described above, the corresponding bromo derivatives were also prepared successfully in comparable yields using (PhO)<sub>3</sub>P<sup>+</sup>BrBr<sup>-</sup> (TPPBr<sub>2</sub>) as the reagent (Table 1). Similar reaction conditions were employed, except for the temperature at which the halogenating species was generated. According to literature data,<sup>11</sup> and to our own findings as well,<sup>5a</sup> the TPPX<sub>2</sub> reagent may exist under two different species, viz. the halotriphenoxyphosphonium halide (PhO)<sub>3</sub>P<sup>+</sup>XX<sup>-</sup> and the dihalo triphenoxyphosphorane (PhO)<sub>3</sub>PX<sub>2</sub>, which bear ionic or covalent character, respectively, and the former only is active for our synthetic purposes.<sup>12</sup> While TPPCl<sub>2</sub> generated at -20 °C afforded the ionic and the covalent form in ca. 4:1 ratio, as calculated from <sup>31</sup>P NMR spectra,<sup>11,12</sup> TPPBr<sub>2</sub> at the same temperature resulted only in a poor 1:3 ratio. However, by lowering the temperature to -60 °C, the ionic/covalent ratio improved to ca. 4:1. Accordingly, carbonyl compounds were reacted at -60 °C with a freshly prepared solution of TPPBr<sub>2</sub> in dichloromethane in the presence of triethylamine and left to warm to rt overnight. After refluxing for 2 h, the reaction mixture was subjected to chromatographic purification. Enolizable ketones gave vinyl bromides in good to excellent yields (Table 1, entries 1–12), whereas *gem*-dibromides were obtained from aldehydes in good yields (entries 14–16). Comparable results were observed by using excess of TPPBr<sub>2</sub> generated at 0 °C, as reported in the literature for aldehydes.<sup>6b</sup> Surprisingly, treatment of benzophenone (entry 13) with TPPBr<sub>2</sub> did not afford the desired dibromodiphenylmethane under any of the reaction conditions employed. Formation of tetraphenylethylene<sup>13</sup> was observed instead, and traces of the expected *gem*-dibromide could be detected only by GC–MS analysis.

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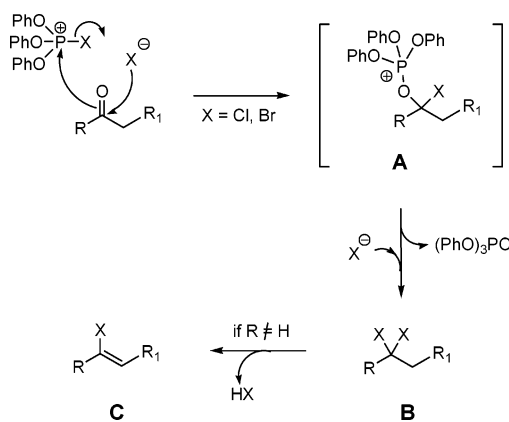
TABLE 1. Synthesis of Vinyl Halides and *gem*-Dihalides with TPPX<sub>2</sub>

entry <sup>a</sup>	substrate	product(s)	yield (%)	
			X = Cl	X = Br
1			87	86
2			78 Z/E 95:5	76 Z>98%
3			86	61
4			76	65
5			91	96
6			83	76
7			96 <sup>b</sup>	99 <sup>b</sup>
8			94 <sup>b</sup> Z/E 60:40	85 <sup>b</sup> Z/E 55:45
9			96 <sup>b</sup>	91 <sup>b</sup>
10			80	86
11			81 (55:45)	67 (66:34)
12			82 (65:35)	50 (81:19)
13			93	- <sup>c</sup>
14			80	70
15			75	60
16			93	65

<sup>a</sup> Reaction conditions: ketone or aldehyde (1.0 mmol), (PhO)<sub>3</sub>P (1.1 mmol), X<sub>2</sub> (1.1 mmol), triethylamine (1.2 mmol), dichloromethane or chloroform (20 mL). <sup>b</sup> Determined by GC. <sup>c</sup> GC–MS analysis revealed formation of *gem*-dibromide only in traces, while tetraphenylethylene represented the major reaction product.

The formation of vinyl halides from enolizable ketones is most likely to proceed through a TPPX<sub>2</sub>-promoted dihalode-oxobisubstitution<sup>14</sup> and can be rationalized as follows (Scheme 2). The well-known strong oxophilicity of the phosphorus atom must trigger off the rapid formation of a putative oxyphosphonium halide species **A**, which evolves to *gem*-dihalide **B** by

## SCHEME 2. Reaction Mechanism



loss of triphenyl phosphate. The geminal derivative **B**, in turn, undergoes base-promoted dehydrohalogenation to afford vinyl halide **C** (Scheme 2). Formation of a transient *gem*-dihalide **B** was indeed detected when the reaction was monitored by GC–MS and was confirmed unambiguously when 4-eptanone (entry 8) was treated with TPPCl<sub>2</sub> in the absence of triethylamine. In fact, analysis of the crude reaction mixture by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy revealed the presence of a conspicuous amount of an additional compound, along with the expected reaction product 4-chlorohept-3-ene (as a mixture of *E/Z* stereoisomers). By means of HSQC and HMBC experiments, δ<sub>H</sub> and δ<sub>C</sub> values for the additional product were assigned unambiguously and were found to match perfectly with those of 4,4-dichloroheptane prepared independently from 4-heptanone oxime by treatment with chlorine.<sup>15</sup> In particular, the signal at 95 ppm was diagnostic for the presence of a quaternary carbon bearing two chlorine atoms. In the case of TPPBr<sub>2</sub>, the quaternary carbon atom of the *gem*-dibromo intermediate (4,4-dibromoheptane) was found to resonate at 77 ppm, as reported in the literature.<sup>16</sup>

It is noteworthy that when enolizable aldehydes were used as the substrate (entries 14–15), the reaction with TPPX<sub>2</sub> stopped inevitably to *gem*-dihalide **B**, and no vinyl derivative was isolated, even in the presence of a stronger base such as DBU under prolonged heating. A similar behavior has been recently experienced by Furrow and Myers, who were able to prepare vinyl bromides from ketones in the presence of either triethylamine or a stronger and more hindered tetramethylguanidine base, whereas no vinyl halides were obtained from aldehydes, which gave exclusively the corresponding geminal derivative.<sup>4f</sup> This observation is in line with the fact that primary *gem*-dihalides exhibit indeed a remarkable reluctance toward dehydrohalogenation, and the literature offers only a few methods to achieve directly this transformation, such as use of molten salts<sup>17</sup> or via flash vacuum pyrolysis over magnesium.<sup>18</sup> Surprisingly, however, treatment of 2,2-dibromoethylbenzene

(entry 14) with DBU in refluxing chloroform did yield quantitatively the corresponding *trans*-(2-bromovinyl)benzene, most likely favored by the formation of a more extended conjugated system.

The peculiar attitude of aldehydes to afford exclusively *gem*-dihalides when treated with TPPX<sub>2</sub> offers a valuable synthetic opportunity. *gem*-Dihalides, in fact, represent important intermediates in many processes used for the preparation of pharmaceutical, agricultural and fine chemicals,<sup>14</sup> and much synthetic effort has been devoted to their synthesis.<sup>14,19</sup> In particular, *gem*-dihalides feature as the substrates of choice for the synthesis of useful alkylidene precursors,<sup>20</sup> including metathesis catalysts.<sup>21</sup>

Halogenation of ketones and aldehydes using halogenated species of organophosphorus compounds to yield vinyl halides and *gem*-dihalides, respectively, is not unprecedented. Examples include (PhO)<sub>3</sub>PX<sub>2</sub>,<sup>6,22</sup> Ph<sub>3</sub>P•X<sub>2</sub>,<sup>3g,7</sup> and related alkyl-, aryl- or alkylarylphosphite–halogen-based compounds.<sup>23</sup> In most cases, however, aldehydes were used as substrates to afford *gem*-dibromides,<sup>6b,22,23</sup> whereas ketones have featured only sporadically.<sup>3g,6a,7</sup> Most recently, PPh<sub>3</sub>•X<sub>2</sub> has been used as the halogenating species for the synthesis of vinyl halides from ketones.<sup>3g</sup> However, such a protocol always required a preliminary conversion step of the starting ketone into an activated phosphoenol ester intermediate. By contrast, the TPPX<sub>2</sub> protocol described here allows a direct halogenation of the carbonyl compound and results in higher yields. For instance, tetralone (entry 5) was converted into the corresponding vinyl chloride and bromide in 91% and 96% yield, whereas Kamei and co-workers reported a 73% and 48% overall yield,<sup>3g,24</sup> respectively.

In summary, vinyl halides and *gem*-dihalides can be prepared in good to excellent yields from ketones and aldehydes, respectively, using a straightforward TPPX<sub>2</sub>-based halogenation. The method has been applied successfully to a range of structurally diverse carbonyl compounds and has showed a good functional group compatibility that further expands the literature data available from other synthetic applications of this reagent.<sup>5,6,25</sup> The experimental protocol is mild, simple and high-yielding, and should be of value for synthetic chemists as an

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expeditious access to vinyl halides and *gem*-dihalides from ketones and aldehydes, respectively.

### Experimental Section

**Typical Procedure for the Synthesis of Vinyl Chlorides with TPPCl<sub>2</sub>.** Triphenyl phosphite (1.85 mL, 7.0 mmol) was dissolved in anhydrous dichloromethane (20 mL) and cooled to -20 °C under Ar flow. Chlorine was bubbled into the clear colorless solution until it became bright yellow. The color was discharged by addition of a few drops of triphenyl phosphite until the solution faded to almost colorless. Anhydrous triethylamine (1.15 mL, 7.7 mmol) and tetralone (934 mg, 6.4 mmol) were added. The reaction mixture was stirred for 18 h while warming to rt. After the mixture was refluxed for an additional 2 h, the crude material was purified by column chromatography on silica gel to afford 1-chloro-3,4-dihydronaphthalene as a yellowish oil (955 mg, 91%).

**Typical Procedure for the Synthesis of Vinyl Bromides with TPPBr<sub>2</sub>.** To a cold solution of triphenyl phosphite (1.85 mL, 7.0 mmol) in anhydrous dichloromethane (20 mL) maintained at -60 °C under Ar flow, bromine (400 μL, 7.7 mmol) was dropped in. Anhydrous triethylamine (1.2 mL, 8.4 mmol) and tetralone (936

mg, 6.4 mmol) were added to the faint orange solution. The reaction mixture was stirred for 18 h, while warming to rt, and heated to reflux for a further 2 h. Purification by column chromatography yielded 1-bromo-3,4-dihydronaphthalene as a dark orange oil (1.28 g, 96%).

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**Supporting Information Available:** General considerations, detailed experimental procedures, and characterization data for all products, including references to known compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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