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Halodephosphorylation of α,β-unsaturated phosphonic acid monoesters

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Abstract—Reaction of α,β-ethylenic and acetylenic phosphonic acid monoesters with (biscollidine)iodine(I) or (biscollidine)-bromine(I) hexafluorophosphate led to α,β-unsaturated halides by, without precedent, dephosphorylation reactions.
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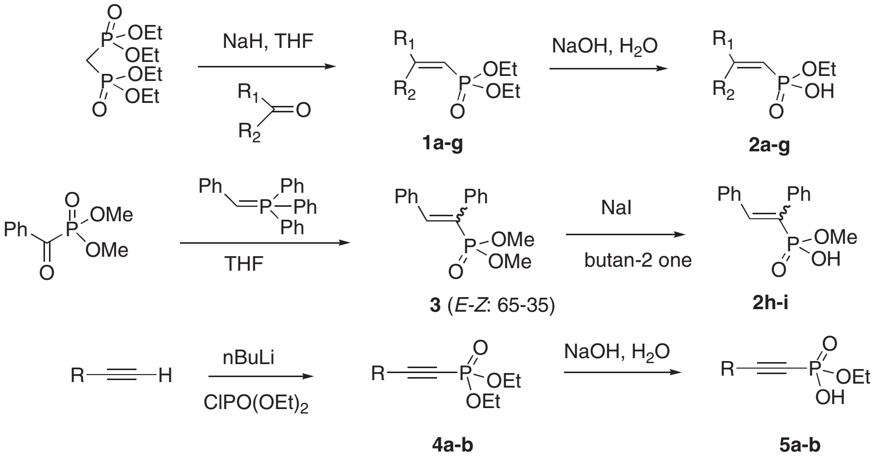
We previously reported that cinnamic acids undergo halodecarboxylations by reaction with (biscollidine)bromine(I) and iodine(I) hexafluorophosphates (respectively, HBB and HBI).[1] These decarboxylations were also observed with acetylenic acids. Until now, nothing has been reported concerning an extension of these reactions to phosphonic acids. Because of the close reactivity of these compounds, in many aspects, compared to that of carboxylic acids, we decided to examine the comportment of α,β-ethylenic and α,β-acetylenic phosphonic acid monoesters in these kind of reactions.

The desired substrates were prepared using known procedures. Ethylenic phosphonic acid monoesters **1a**–**g** were obtained in good yields in two steps by reaction of tetraethyl methylenediphosphonate with carbonyl compounds,[2] followed by a monohydrolysis of the diesters[3] leading to products **2a**–**g**. The mixture of phosphonates **3** (*E*–*Z*: 65–35) was obtained by reaction of dimethyl benzoylphosphonate with benzyltriphenyl phosphonium bromide.[4] After separation by liquid chromatography over silica gel, the two isomers were separately monohydrolyzed using NaI in 2-butanone at reflux[5] (Scheme 1). The 1-alkynyl phosphonates



Scheme 1.

Keywords: Vinyl iodide; Vinyl bromide; Phosphonate.

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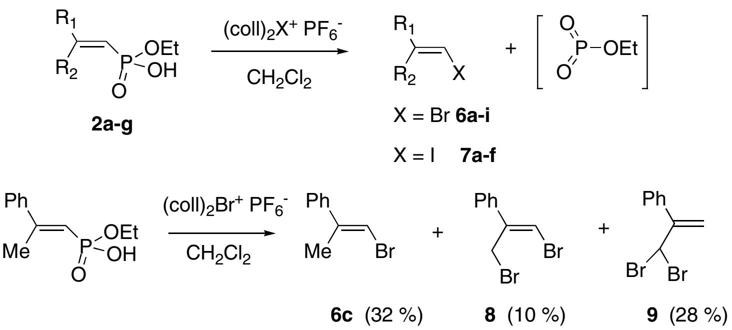
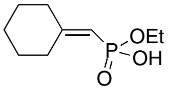
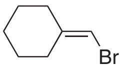
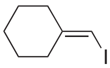
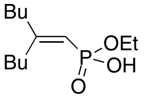
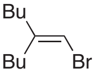
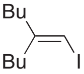
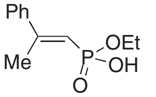
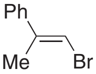
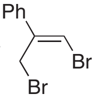
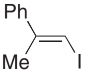
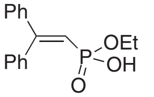
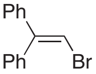
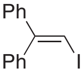
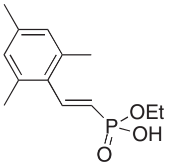
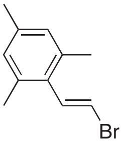
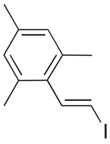
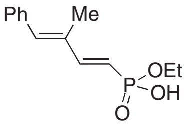
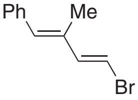
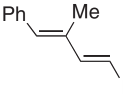
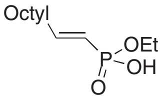
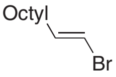
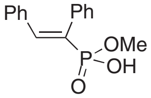
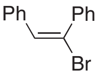
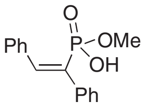
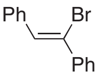


Scheme 2.

4a–b were obtained by phosphorylation of 1-alkynes. The monohydrolyses were then carried out with sodium hydroxide. The subsequent reactions of all these phosphonic acid monoesters with (biscollidine)bromine(I)

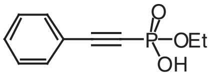
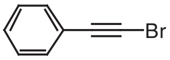
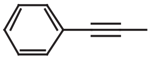
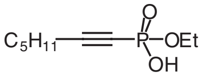
Table 1. Reaction of α,β-ethylenic phosphonic acid monoesters with biscollidine bromo(I) and iodo(I) hexafluorophosphate

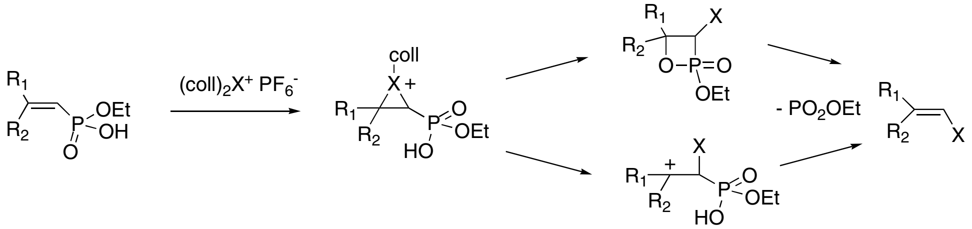
Entry	α,β-Unsaturated phosphonate **2**	Products **6** and **7**	
		Reaction with HBB (yield, %)	Reaction with HBI (yield, %)
a		 (41)	 (57)
b		 (54)	 (48)
c		 (58)[a]+  (11)	 (65)
d		 (72)	 (73)
e		 (81)	 (45)
f		 (31)	 (10)
g		 (14)	[b]
h		 (31)	NR
i		 (55)	NR

[a] Reaction in the presence of 5% of 3,5-di*tert*-butylphenol.

[b] Degradation.

Table 2. Reaction of α,β-acetylenic phosphonic acid monoesters with (biscollidine)bromine(I) and iodine(I) hexafluorophosphate

Entry	α,β-Acetylenic phosphonate **5**	Products **10**, **11**	
		Reaction with HBB (yield, %)	Reaction with HBI (yield, %)
a		 (44)	 (23)
b	 $C_5H_{11}C\equiv CP(O)(OEt)OH$	$C_5H_{11}C\equiv CBr$ (17)	NR



Scheme 3.

and iodine(I) hexafluorophosphate were carried out in methylene chloride at room temperature.[6] After reaction, the unsaturated halides were isolated by liquid chromatography over silica gel (Scheme 2) and characterized from their spectral data and by comparison with those reported in the literature. The instable ethyl meta phosphonate could not be isolated. Our results are collected in Table 1.

With 2,2-disubstituted α,β-ethylenic phosphonates **2a**–**d** we observed the formation of vinyl halides in satisfactory yields (entries a–d). In the particular case of phosphonate **2c**, the reaction with (biscollidine)bromine(I) hexafluorophosphate led to the formation of three products (Scheme 2), two of them corresponding to a double reaction of the bromonium reagent. These side products were partially avoided when the reaction was carried out in the presence of 3,5-di*tert*-butylphenol (5 mol %). Reaction of vinyl bromide **6c** with the bromonium reagent did not lead to the formation of compounds **8** or **9**. This result suggests that compound **8** is probably formed first by allylic bromination of the phosphonate **2c**, followed by a dephosphorylation, the dibromo compound **9** being probably formed by a radical induced allylic rearrangement of the dibromo compound **8**. In the case of 1-monosubstituted α,β-ethylenic phosphonates **2e**–**g** low yields were observed if the substituents were alkyl or alkenyl groups (entries f and g). However, yield was satisfactory if the substituent was an aryl group (entry e). These dephosphorylations were found to be diastereoselective (entries c and h–i). We checked also the reactivity of 1-alkynyl phosphonates. Our results are reported in Table 2. Low yields were obtained in our conditions. These results are very different to those that we published in the case of carboxylic acids.[1]

We found that the mechanism of the halodecarboxylation of carboxylic acids depends on the nature of the substituents. In particular, formation of β-lactones was observed when the substituents were alkyl groups and spontaneous elimination of carbon dioxide occurred in the case of aryl groups.[7] With phosphonates we were never able to detect the oxaphosphetane intermediate formation. However, we cannot completely exclude their formations due to their probably low stability at room temperature. The intervention of carbocations as intermediates is also possible (Scheme 3). Further experiments are necessary to choose between these two mechanisms.

In conclusion we report for the first time the halodephosphorylation of α,β-unsaturated phosphonate monoesters. These reactions led to the formation of α,β-unsaturated bromides or iodides and can probably be useful in synthesis.

References and notes

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6. *Representative procedure*: To a solution of phosphonate monoester **2** (1 mmol) in methylene chloride (10 mL) was added over 2 h a methylene chloride solution (10 mL) of bis(collidine)bromine(I) hexafluorophosphate (1.3 mmol). After complexion of the addition, the solvent was removed under vacuum and the residue purified by liquid chromatography over silica gel (petroleum ether–ether).
7. Homsi, F.; Rousseau, G. *J. Org. Chem.* **1999**, *64*, 81–85.