

The Preparation of α -Phosponovinylzirconocenes and their Application in the Stereospecific Synthesis of α -Halo-1-alkenylphosphonates

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Abstract: Hydrozirconation of 1-alkynylphosphonates gives the organozirconium(IV) complexes **2** in *syn*-addition way. Complexes **2** was trapped with NCS, NBS or I₂ to afford stereodifined α -halo-1-alkenylphosphonates in moderate to high yields.

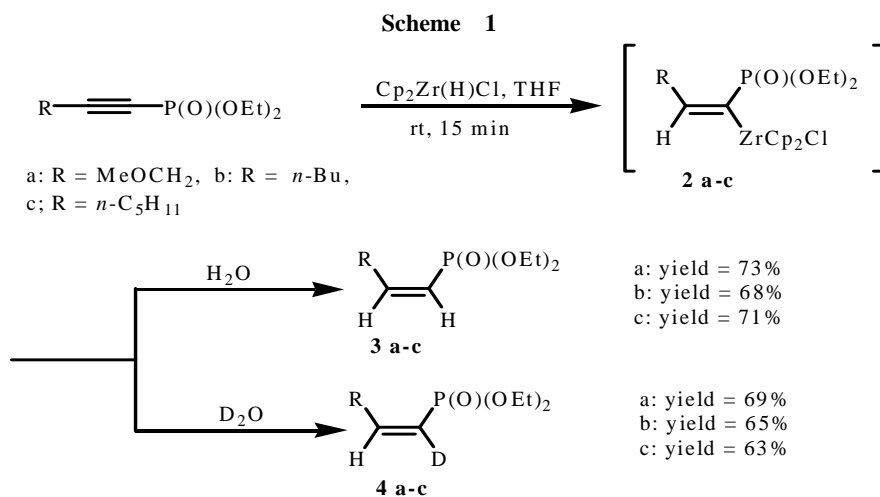
Keywords: 1-Alkynylphosphonates, hydrozirconation, α -halo-1-alkenylphosphonates.

The use of 1-alkynylphosphonates in organic synthesis has attracted increasing interest in recent years¹. On the other hand, it has become popular to transform alkenylzirconium (IV) complexes to other functional groups with a high level of stereochemical purity². However, no efforts have been focused on the bifunctional ethenyl reagents containing phosphor and zirconium, these compounds are important intermediates in organic synthesis, they can be converted to a variety of α -substituted-1-alkenylphosphonates. Herein, we wish to report the synthesis of α -phosponovinyl zirconocene and their reaction with electrophiles *via* the hydrozirconation of 1-alkynylphosphonates.

The hydrozirconation of the 1-alkenylphosphonates with 1.0 equiv of Cp₂Zr (H)Cl in THF for 15 min at room temperature gave a clear solution of **2**. The hydrolysis or deuterolysis of **2** afforded *Z*-vinylphosphonate **3** or *Z*- α -deuterovinylphosphonate **4**, respectively (**Scheme 1**). For example, the hydrozirconation-hydrolysis of 1-hexenylphosphonate afforded *Z*-vinylphosphonate **3b**. The ¹H NMR spectrum of 1-hexenylphosphonate exhibits a ddt peak at δ 6.56 (³J_{HP} = 53 Hz, ³J_{CH₂CH=C} = 7.6 Hz, ³J_{CH=CH} = 13.0 Hz) and dd peak at δ 5.58. The *Z*-olefinic geometry of **3b** was verified by the coupling constant of the vicinal olefinic protons and the coupling constant of β -vinylhydron and phosphor atom (³J_{HH} = 13.0 Hz, ³J_{HP} = 53 Hz). In addition, the ¹H NMR spectrum of the product is also identical to the previous reported³. After the parallel experiment of hydrozirconation-deuterolysis, the disappearance of the dd peak at

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§ 6.26 shows that the deuterium must be attached to the α -position of the phosphonate group. The hydrozirconation of other 1-alkenylphosphonates gives the similar results.



Complexes **2** can react with various electrophiles such as NCS, NBS, I₂ to give stereodefined α -halo-vinylphosphonates (**Scheme 2**, **Table 1**), which are a class of important synthetic intermediates and useful reagents for the synthesis of biologically active compounds or as investigative reagents⁴.

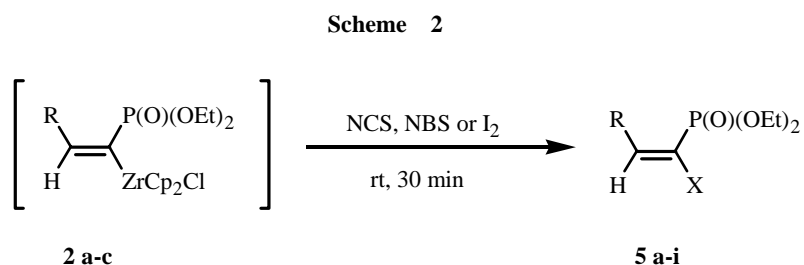


Table 1 Reaction of **2** with electrophiles

Entry	R	E-X ^a	Product	Yield (%) ^b
1	MeOCH ₂	NCS	5a	73
2	MeOCH ₂	NBS	5b	68
3	MeOCH ₂	I ₂	5c	70
4	<i>n</i> -C ₄ H ₉	NCS	5d	57
5	<i>n</i> -C ₄ H ₉	NBS	5e	61
6	<i>n</i> -C ₄ H ₉	I ₂	5f	67
7	<i>n</i> -C ₅ H ₁₁	NCS	5g	64
8	<i>n</i> -C ₅ H ₁₁	NBS	5h	70
9	<i>n</i> -C ₅ H ₁₁	I ₂	5i	63

^a Reaction conditions: E-X (1.0 equiv.), THF, rt, 30 min.

^b Isolated yields based on 1-alkynylphosphonates.

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In summary, we have studied the hydrozirconation of 1-alkynylphosphonates and the reaction of organozirconium (IV) complexes **2** with electrophiles such as NCS, NBS, and I₂. This procedure provides a facile route to the synthesis of stereodefined α -halo-vinylphosphonates

Acknowledgments

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