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One-Pot Conversion of Terminal Alkynes into *gem*-Disubstituted-Alkenes

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Abstract: A one-pot reaction of terminal alkynes with in situ generated hydrogen iodide and organozinc compounds in the presence of $Pd(PPh_3)_4$ provided a simple and useful method for the preparation of *gem*-disubstituted-alkenes.

gem-Disubstituted-alkenes are an important class of compounds extensively used as the monomers for the polymerization process.[1] Carbozincation of terminal alkynes followed by protonation can afford *gem*-disubstituted-alkenes.[2] However, only allylzinc compound gave good yield in the carbozincation, other organozinc compounds seemed to be less reactive toward the acetylenic group. Carbocupration of 1-alkynes with heterocuprates also affords *gem*-disubstituted-alkenes.[3] However, only alkyl or branched alkyl groups worked well in this kind of transformation. Carboalumination of 1-alkynes faced the same limitations as described in the carbocupration of terminal alkynes.[4] Recently, Ishii has reported a highly stereoselective synthesis of 2-iodo-1-alkenes from terminal alkynes by using hydrogen iodide, generated in situ from chlorotrimethylsilane/sodium iodide/water in CH_3CN.[5] In addition, palladium-catalyzed cross-coupling reactions of vinyl iodide with aryl, heteroaryl, alkenyl, or alkynylzinc compound are well documented in the literature.[6] Based on these works, herein, we reported a new, simple, and one-pot method for the conversion of terminal alkynes into *gem*-disubstituted-alkenes containing various substituents attached on the double bond. As representative terminal alkynes phenyl acetylene and 1-octyne were chosen. The results as well as the feasibility of this kind of conversion are shown in Table I.

It is noted that various organozinc compounds, including methyl and *n*-hexylzinc chloride, worked well in this conversion process. Although we have found (*E*)- and (*Z*)-2-phenyl-2-octene in 8% and 3% yields, respectively, in the reaction shown in entry 9.[7] We did not observe any detectable amount of rearranged or isomeric products in other cases as judged from GLC and ^1H NMR spectrum analysis.

In a typical procedure, CH_3CN (5 mL), $(CH_3)_3SiCl$ (0.55 g, 5 mmol), water (0.09 g, 5 mmol), and phenylacetylene (0.51 g, 5 mmol) were sequentially added to a dry flask containing sodium iodide (0.75 g, 5 mmol) under a nitrogen atmosphere. After 5 - 10 min, the reaction mixture was allowed to react with 1.1 equiv amount of pertinent organozinc chloride, prepared from the corresponding organolithium or Grignard reagent and zinc chloride in THF, in the presence of $Pd(PPh_3)_4$ (5 mol %) at room temperature for another 6 h. The reaction mixture was quenched with water, extracted with ether, concentrated, and purified.

Thus, we have developed a one-pot reaction of terminal alkynes with in situ generated hydrogen iodide and various organozinc compounds. It would provide a simple and useful method for the preparation of *gem*-disubstituted-alkenes.

Acknowledgment We thank the National Science Council and Academia Sinica of the Republic of China for financial support.

References and Notes:

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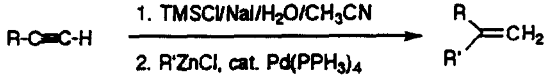
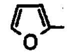
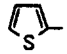
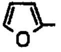
Table I. One-Pot Conversion of Terminal Alkynes into *gem*-Disubstituted-Alkenes.



$$R\text{-}C\equiv C\text{-}H \xrightarrow[\text{2. R'ZnCl, cat. Pd(PPH}_3)_4]{\text{1. TMSCl/NaI/H}_2\text{O/CH}_3\text{CN}} RR'C{=}CH_2$$

Entry	R =	R' =	Product yield (%)
1	Ph	Me	57
2	"	n-Bu	54
3	"	Ph	60
4	"	 Ph	63
5	"	n-C_6H_{13}-C≡C-	57
6	"		63
7	"		61
8	n-C_6H_{13}	n-C_6H_{13}	71
9	"	Ph	67[a]
10	"	 Ph	74
11	"		60
12	"		64
13	"	n-C_4H_9C≡C-	70

[a] In addition to the expected product, we also isolated (E)- and (Z)-2-phenyl-2-octene in 8% and 3% yields, respectively.

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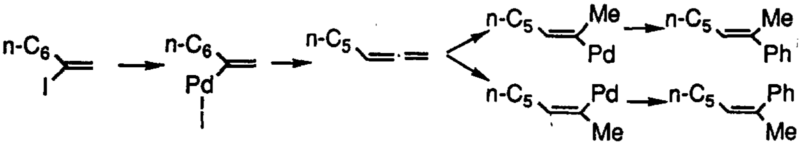
7. The two products were plausible obtained via oxidative addition of Pd to the vinyl iodide, followed by β-elimination, re-hydropalladation, and cross-coupling reaction as shown below.



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