

# Hydrozirconation of alkynyl(phenyl)iodonium salts and stereoselective synthesis of (*E*)-trisubstituted olefins

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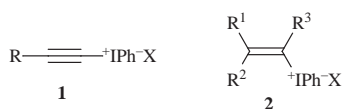
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Hydrozirconation of alkynyl(phenyl)iodonium salts affords alkenylchlorozirconocenes with the Zr–C bond geminal to the iodonium moiety, and two subsequent substitution reactions proceed with retention of the configuration of the carbon–carbon double bond.

## Introduction

In recent years, alkynyl- **1** and alkenyl(phenyl)iodonium salts **2** have received much attention and become very useful in organic synthesis.<sup>1</sup> The powerful inductive electron-withdrawing ability and the excellent leaving ability of the phenyliodonium moiety impart unique reactivity to alkynyliodonium salts. Up to now, however, the studies on the chemistry of alkynyliodonium salts have been mainly limited to nucleophilic substitution as well as Diels–Alder and 1,3-dipolar cycloaddition processes.<sup>1c</sup>

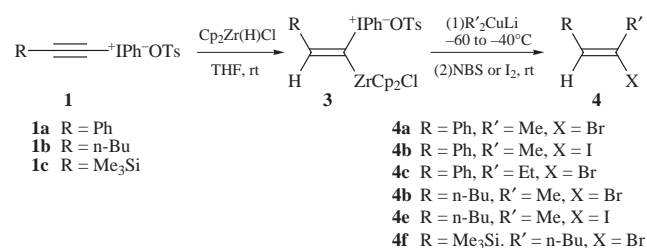


On the other hand, hydrozirconation of alkynes or alkenes has provided an easy preparation of alkenyl- and alkylchlorozirconocenes, which have emerged as one of the most useful transition metal derivatives in organic synthesis.<sup>2</sup> Herein we report the first example of hydrometallation of alkynyliodonium salts, and as one of its many potential applications, stereoselective synthesis of (*E*)-halo trisubstituted olefins.

## Results and discussion

We found that hydrozirconation of alkynyliodonium salts proceeds readily. Addition of alkynyliodonium salts into a suspension of Cp<sub>2</sub>Zr(H)Cl in THF or CH<sub>2</sub>Cl<sub>2</sub> gives a yellow–orange solution rapidly, which is in accord with the usual formation of hydrozirconation products Cp<sub>2</sub>ZrR(Cl).<sup>2b</sup> Various alkynyliodonium salts were employed and all reacted smoothly.

*syn*-Addition of Cp<sub>2</sub>Zr(H)Cl onto the carbon–carbon triple bond has been well established, however, the regioselectivity of hydrozirconation of internal alkynes is not so well established.<sup>2c</sup> According to the <sup>1</sup>H-NMR spectra of the products in Scheme



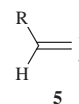
Scheme 1

1, we have established that hydrozirconation of alkynyliodonium salts affords alkenylchlorozirconocenes with the Zr–C bond geminal to the iodonium moiety. Ochiai *et al.*<sup>3</sup> have studied the substitution reaction of alkenyliodonium salts with

R<sub>2</sub>CuLi and found that the reaction proceeds with retention of the stereochemistry of the C=C bond. To explain this outcome a mechanism involving ligand coupling has been proposed. On the other hand, it is well established that halogenation of alkenylzirconocenes proceeds with retention of the configuration at the carbon.<sup>4,5</sup> Indeed, (*E*)-halo olefins were obtained as shown in Scheme 1, the <sup>1</sup>H-NMR and IR spectra of which were in accordance with those reported by others.

We attempted to obtain (*Z*)-disubstituted alkenyl(phenyl)iodonium salts by hydrolysis of the intermediates **3**, but failed. Ochiai *et al.*<sup>3</sup> also failed to obtain (*Z*)-disubstituted alkenyl(phenyl)iodonium salts through the reaction of vinylsilane and iodosylbenzene, although they consider these compounds to be labile as a result of *anti*-β-elimination of the β-hydrogen and the organoiodine substituent.

Since alkenylzirconocenes and alkenyliodonium salts can be easily substituted by many electrophiles or nucleophiles, respectively,<sup>1c,2c</sup> the unique species **3** may be considered as an equivalent of synthon **5**, which can be expected to serve as a precursor of various olefins. Moreover various alkynyliodonium salts have been prepared easily in recent years.<sup>6</sup> As a result, hydrozirconation of alkynyliodonium salts has provided a valuable 1,1-difunctional reagent for stereoselective synthesis of various olefins.



## Experimental

<sup>1</sup>H-NMR spectra were recorded in CCl<sub>4</sub> on a JEOL PMX60Si spectrometer (hexamethyldisilane as the internal standard), IR spectra were recorded on Perkin-Elmer 683 spectrometer. THF and Et<sub>2</sub>O were freshly distilled from Na and benzophenone. Light petroleum refers to the fraction with bp 30–60 °C. Cp<sub>2</sub>Zr(H)Cl<sup>7</sup> and alkynyliodonium salts<sup>8</sup> were prepared according to literature procedures. R<sub>2</sub>CuLi was prepared by adding dropwise RLi into a suspension of CuI in THF.<sup>9</sup> All reactants were dried before used. All reactions were carried out under N<sub>2</sub> atmosphere.

### (*E*)-(2-Bromoprop-1-enyl)benzene<sup>10</sup> (**4a**)

To a stirred suspension of Cp<sub>2</sub>Zr(H)Cl (0.360 g, 1.4 mmol) in THF (6 cm<sup>3</sup>) was added phenyl(phenylethynyl)iodonium tosylate (0.476 g, 1 mmol), and gradually the mixture turned into a clear solution at room temp. Using a syringe, the solution was added dropwise into Me<sub>2</sub>CuLi (2 mmol) in THF (4 cm<sup>3</sup>) while stirring at –60 °C, and the reaction mixture was kept at –40 °C for 8 h. NBS (1.068 g, 6 mmol) was added portionwise and the temperature was allowed to rise to room temp. The mixture was stirred for 2 h, and then was quenched with water, extracted with diethyl ether (4 × 15 cm<sup>3</sup>), filtered, concentrated and purified by preparative TLC (light petroleum as the eluent), giving **4a** (0.107 g, 54%) as a yellowish oil. δ<sub>H</sub> 7.40–6.90 (5H, m), 6.80 (1H, br s), 2.60 (3H, d, *J* 1.5). ν<sub>max</sub>(film)/cm<sup>–1</sup> 3085, 2987, 2945, 2872, 1500, 1455, 1380, 1150, 750, 690, 600.

**(E)-(2-Iodoprop-1-enyl)benzene**<sup>11</sup> (**4b**)

A yellow oil, yield 57%.  $\delta_{\text{H}}$  7.40–7.0 (6H, m), 2.60 (3H, br s).  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3082, 2992, 2940, 2888, 1500, 1454, 1380, 1070, 1030, 750, 690, 570.

**(E)-(2-Bromobut-1-enyl)benzene**<sup>12</sup> (**4c**)

A yellowish oil, yield 42%.  $\delta_{\text{H}}$  7.60–7.10 (5H, m), 6.72 (1H, br s), 2.64 (2H, q, *J* 7.5), 1.20 (3H, t, *J* 7.5).  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3060, 2998, 2980, 2800, 1612, 1505, 1464, 750, 690.

**(E)-2-Bromohept-2-ene**<sup>13</sup> (**4d**)

A colorless oil, yield 45%.  $\delta_{\text{H}}$  5.60 (1H, m), 2.40 (3H, s), 2.20 (2H, m), 1.50 (4H, m), 0.90 (3H, t).  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  2986, 2942, 2884, 1480, 1410, 1386, 730.

**(E)-2-Iodohept-2-ene**<sup>14</sup> (**4e**)

A pale yellow oil, yield 51%.  $\delta_{\text{H}}$  6.0 (1H, m), 2.30 (3H, s), 2.0 (2H, m), 1.40 (4H, m), 0.90 (3H, t).  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  2982, 2940, 2880, 1660, 1470, 1410, 610.

**(E)-(2-Bromo-1-hexenyl)trimethylsilane**<sup>15</sup> (**4f**)

A colorless oil, yield 38%.  $\delta_{\text{H}}$  5.85 (1H, br s), 2.19 (2H, t), 1.40 (4H, m), 1.0 (3H, t), 0.20 (9H, s).  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  2984, 2952, 2880, 1668, 1475, 1410, 1390, 1255, 835, 750, 685.

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