

Stereospecific synthesis of (*E*)-alkenyl(phenyl)iodonium tetrafluoroborates *via* zirconium–iodane exchange

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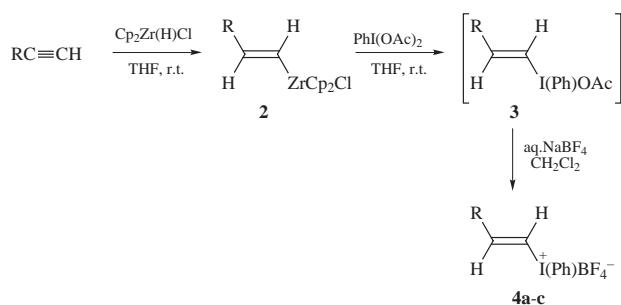
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Received (in Cambridge) 11th September 1998, Accepted 11th September 1998

Reaction of vinylzirconium with hypervalent phenyl-iodanes leads to zirconium–iodane exchange in THF at room temperature yielding alkenyl(phenyl)iodonium salts stereoselectively with retention of configuration. Vinyl-iodonium salts are highly effective as the activated species of vinyl iodides. They reacted with RMgBr in the presence of CuI to afford (*E*)-1,2-disubstituted alkenes.

Alkenyl(phenyl)iodonium salts are a novel electrophilic vinylating agent. They can undergo nucleophilic vinylic substitution under mild conditions. Thus they provide a useful route for the synthesis of various kinds of substituted alkenes.^{1–4} The general methods for the preparation of alkenyl(phenyl)iodonium salts are the reaction of vinylmetal–iodane exchange. For example, vinylsilane reacted with iodobenzene in the presence of triethyloxonium tetrafluoroborate at room temperature in CH₂Cl₂.⁵ Vinylstannanes reacted with cyano(phenyl)iodonium triflate at –40 °C in CH₂Cl₂.⁶ Vinylboronic acids or esters reacted with (diacetoxyiodo)benzene in the presence of BF₃·OEt₂ at 0 °C in CH₂Cl₂.⁷ But the reaction of vinylzirconium–iodane exchange has not been reported. We now report stereoselective synthesis of (*E*)-alkenyl(phenyl)iodonium salts *via* the reaction of vinylzirconium–iodane exchange and their application in the synthesis of (*E*)-1,2-disubstituted alkenes.

Hydrozirconation of alk-1-yne in THF at room temperature yields the (*E*)-alkenylzirconium compounds stereoselectively. We investigated the reactivity of (*E*)-alkenylzirconium compounds with (diacetoxyiodo)benzene and found that in the absence of catalyst the reaction occurs in THF at room temperature. This is due to the vinylzirconium compounds being more active than vinylsilanes and vinylboronic compounds. After ligand exchange with aqueous NaBF₄ solution, the (*E*)-alkenyl(phenyl)iodonium tetrafluoroborates **4** were obtained in high yields (Scheme 1).



Scheme 1

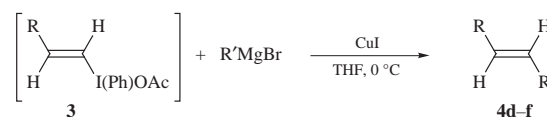
Particularly diagnostic for the stereochemistry of *E*-alkenyl(phenyl)iodonium tetrafluoroborates **4a–c** was the coupling constant between the proton H_A geminal to iodine and the vicinal proton H_B; typical values of ³J_{HH} are in the range 13.6–14 Hz which is consistent with an *E* configuration, and the melting point of **4c** is similar to the melting point of *E* type 1-phenylhex-1-ene reported.⁸

Table 1 Synthesis of (*E*)-alkenyl(phenyl)iodonium tetrafluoroborates **4a–c** and (*E*)-1,2-disubstituted alkenes **4d–f**

Product	R	R'	Yield (%) ^a
4a	CH ₃ OCH ₂		85
4b	C ₄ H ₉		80
4c	Ph		80
4d	CH ₃ OCH ₂	Ph	78
4e	C ₄ H ₉	Ph	80
4f	Ph	<i>m</i> -CH ₃ C ₆ H ₄	76

^a Isolated yield.

To our knowledge, the reaction of vinyl-iodonium salts with RMgBr has not been reported. Thus we investigated the reaction and found it affords the (*E*)-1,2-disubstituted olefins in good yield (Scheme 2) in the presence of CuI at 0 °C in THF.



Scheme 2

The stereochemistry of 1,2-disubstituted alkenes **4d–e** was easily established, since they give rise to a doublet at δ 6.20–6.38 with a coupling constant of 16 Hz typical of *E* configuration.

Since the preparation of the (*E*)-vinylzirconium compounds is very convenient by hydrozirconation of alk-1-yne and vinylzirconium–iodane exchange can occur under mild conditions, the above method provides a practical route for the stereoselective synthesis of alkenyl(phenyl)iodonium salts.

Experimental

¹H NMR spectra were recorded on Bruker AM-300 and PMX-60 spectrometers, using CDCl₃ as the solvent with TMS as an internal standard. IR spectra were determined on a PE-683 spectrophotometer. MS spectra were obtained on an HP5989A spectrometer. Elemental analyses were conducted using a Yanaco MT-3CHN elemental analyser. Melting points were uncorrected. THF was distilled from sodium benzophenone.

General procedure for the synthesis of (*E*)-alkenyl(phenyl)iodonium acetate

A mixture of Cp₂Zr(H)Cl (1.0 mmol) and alk-1-yne (1.0 mmol) in THF (5.0 cm³) was stirred under nitrogen at room temperature for 20 min. A solution of (diacetoxyiodo)benzene (1.2 mmol) in THF (5.0 cm³) was added at room temperature and the mixture was stirred for 4.0 h.

Preparation of the (*E*)-alkenyl(phenyl)iodonium tetrafluoroborates

THF was removed from the above mixture under vacuum, CH₂Cl₂ (10 cm³) and a saturated aqueous solution of NaBF₄ (15 cm³) were then added. The mixture was stirred for 15 min at room temperature. Extraction with CH₂Cl₂, filtration and then concentration gave the crude product which was washed several times with hexane by decantation. Further purification by decantation using hexane-diethyl ether gave the (*E*)-vinyl-iodonium salts.

Compound 4a. Oil, $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3040, 1590, 1490, 1070, 826. ¹H NMR (300 MHz) 3.20 (s, 3H), 3.80 (dd, $J = 5.6, 1.2$ Hz, 2H), 6.60 (dt, $J = 13.6, 1.2$ Hz, 1H), 6.76 (dt, $J = 13.6, 5.6$ Hz, 1H), 7.40–7.55 (m, 2H), 7.60–7.65 (m, 1H), 7.98–8.03 (m, 2H). MS(EI) m/z 275 (M – BF₄)⁺ (3.6%), 204 (100), 71 (43), 45 (50), 77 (57). (Found: C, 33.43; H, 3.08. C₁₀H₁₂BF₄IO requires C, 33.18; H, 3.34%).

Compound 4b. Oil (lit.,⁷ oil), $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3075, 1560, 1465, 1440, 1050. ¹H NMR (300 MHz) 0.88 (t, $J = 7.4$ Hz, 3H), 1.05–1.5 (m, 4H), 2.30 (m, 2H), 6.70 (dt, $J = 13.6, 1.2$ Hz, 1H), 6.86 (dt, $J = 13.6, 6.8$ Hz, 1H), 7.46–7.55 (m, 2H), 7.63–7.70 (m, 1H), 7.98–8.03 (m, 2H).

Compound 4c. Mp 99–100 °C (lit.,⁸ 98–99 °C); $\nu_{\max}(\text{CHCl}_3 \text{ film})/\text{cm}^{-1}$ 3050, 1560, 1465, 1440, 1050. ¹H NMR (300 MHz) 7.30–7.40 (m, 3H), 7.41–7.46 (m, 4H), 7.48 (d, $J = 14$ Hz, 1H), 7.60 (t, $J = 2.7$ Hz, 1H), 7.79 (d, $J = 14$ Hz, 1H), 8.01–8.07 (m, 2H).

Synthesis of (*E*)-1,2-disubstituted alkenes

To the above mixture was added the solution of RMgBr (1.0 mmol) in THF (2.0 cm³) at 0 °C, then stirred under nitrogen for 1.0 h. The solvent THF was removed under vacuum and diluted with light petroleum, then stirred for 5 min. The supernatant was filtered. After evaporation of the filtrate, the residue was purified by preparative TLC on silica gel, using light petroleum as eluent.

Compound 4d. Oil (lit.,⁹ bp 107–108 °C/5 mmHg); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3040, 2940, 1610, 1500, 1460, 1260, 1100, 960, 780. ¹H NMR (60 MHz) 3.20 (s, 3H), 3.80 (d, $J = 6$ Hz, 2H), 6.20 (dt,

$J = 16, 6$ Hz, 1H), 6.37 (d, $J = 16$ Hz, 1H), 7.20–7.45 (m, 5H). MS(EI) m/z 148 (100%), 115(87), 117(87), 71(23), 105(32), 91(26), 77(25).

Compound 4e. Oil (lit.,¹⁰ bp 108.5–109 °C/10 mmHg); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3050, 1640, 1595, 1450, 960. ¹H NMR (60 MHz) 0.8–1.6 (m, 7H), 1.9–2.3 (m, 2H), 6.22 (dt, $J = 16, 7$ Hz, 1H), 6.38 (d, $J = 16$ Hz, 1H), 7.15–7.35 (m, 5H).

Compound 4f. Mp 47–48 °C (lit.,¹¹ 48.6–49.2 °C); $\nu_{\max}(\text{CHCl}_3 \text{ film})/\text{cm}^{-1}$ 3030, 1590, 950, 705, 670. ¹H NMR (60 MHz) 2.33 (s, 3H), 7.03–7.70 (m, 11H).

Acknowledgements

Project 29772007, 29672008 was supported by the National Nature Science Foundation of China and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science.

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Communication 8/07118G