

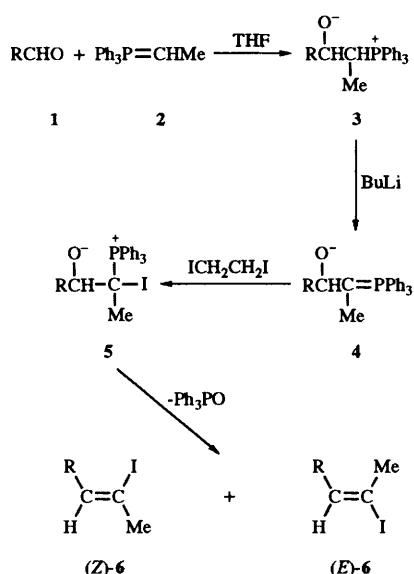
A direct and stereoselective route to (*Z*)-2-iodoalk-2-enes via β -oxido phosphonium ylides

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(*Z*)-2-Iodoalk-2-enes have been synthesized with high stereoselectivity by direct reaction of β -oxido phosphonium ylides with 1,2-diiodoethane.

Vinyl iodides of defined stereochemistry are useful building blocks in organic synthesis, particularly for the synthesis of biologically active compounds.¹ Although a variety of methods have been reported for the stereocontrolled preparation of alkenyl iodides from acetylenic precursors they are multi-step procedures.² Furthermore, the preparation of 2-iodoalk-2-enes from acetylenic precursors has limited application because of difficulties in controlling the regioselective hydrometallation of the internal triple bond.³ Not only does the reaction of aldehydes with Wittig reagents ($\text{Ph}_3\text{P}=\text{CHX}$) usually give a mixture of *Z*- and *E*-isomers but the preparation of the ylide is quite complicated.⁴ β -Oxido ylides, first reported by Schlosser, have the potential to react with a variety of halogenating reagents to afford vinyl halides,⁵ although Corey *et al.* found that their reaction with iodine failed to do so.^{5a} An indirect method using mercuric acetate and THF-HMPA, followed by a reaction with anhydrous lithium iodide-iodine, was claimed.^{5d} Because of the importance of vinyl iodides we have studied their synthesis and have found a direct and stereoselective method for the preparation of (*Z*)-2-iodoalk-2-enes in moderate yields (32–51%, 4 steps) from 1,2-diiodoethane and β -oxido ylides. The reaction sequence is shown as follows:



The β -oxido ylides **4**, generated from ethylene(triphenyl)phosphorane **2**, aldehydes and butyllithium reacted with diiodoethane to give 2-iodoalk-2-enes **6** with the *Z*-isomer as major product. The results are listed in Table 1.

The reaction is of wide scope and, since R may be aromatic or aliphatic, should be useful in the synthesis of biologically active compounds.

Table 1 2-Iodoalk-2-enes **6**

Compd.	R	Yield ^a (%)	Ratio ^b Z:E
6a	<i>n</i> -C ₅ H ₁₁	34	94:6
6b	<i>n</i> -C ₆ H ₁₃	35	92:8
6c	<i>n</i> -C ₈ H ₁₇	48	95:5
6d	<i>n</i> -C ₉ H ₁₉	36	90:10
6e	Ph	32	93:7
6f	4-MeC ₆ H ₄	41	98:2
6g	4-MeOC ₆ H ₄	51	97:3
6h	4-FC ₆ H ₄	39	97:3

^a Isolated yields. The products were characterized on the basis of spectroscopic evidence. ^b The ratios of *Z*- and *E*-isomers were estimated on the basis of their NMR spectra.

Experimental

IR spectra were obtained as films on a Shimadzu IR-440 spectrometer. NMR spectra (chemical shifts in ppm from internal TMS for ¹H NMR and from external TFA for ¹⁹F NMR) were measured on a Bruker AM-300 spectrometer at 300 MHz or a Varian EM-360 spectrometer at 60 MHz with CDCl₃ as solvent. Mass spectra were recorded on Finnigan GC-MS 4021 or MHT8430 mass spectrometers.

General procedures for the preparation of 2-iodoalk-2-enes

To a suspension of ethyl(triphenyl)phosphonium bromide (4 mmol) in THF (20 cm³) at -20 °C under nitrogen was added butyllithium (4 mmol) in hexane. After being stirred at 0 to 25 °C for 30 min, the clear solution was cooled to -78 °C and treated with the aldehyde (4 mmol). After 10 min butyllithium (4 mmol) in hexane was added to the yellow solution which turned deep red and was then stirred first at -78 °C for 5 min, then at 0 °C for 2 min and finally at -78 °C. After 1,2-diiodoethane (5 mmol) had been added to the mixture it was warmed to 25 °C, stirred for 30 min and then evaporated to give a residue. This was purified by column chromatography on silica gel eluting with light petroleum (bp 60–90 °C) to afford the product **6**.

2-Iodoct-2-ene 6a.⁶—Oil, $\nu_{\text{max}}/\text{cm}^{-1}$ 1650, 1460, 1375 and 660; m/z 238 (M^+ , 56), 181 (15) and 111 (5); δ_{H} 6.15 (m, 0.06 H, *E*-3-H), 5.40 (tq, 0.94 H, *J* 7.0, 1.4, *Z*-3-H), 2.49 (d, 0.94 \times 3 H, *J* 1.4, *Z*-1-H), 2.36 (m, 0.06 \times 3 H, *E*-1-H), 2.14–1.97 (m, 2 H), 1.54–1.17 (m, 6 H) and 0.90 (t, 3 H, *J* 6.9).

2-Iodonon-2-ene 6b.⁷—Oil, $\nu_{\text{max}}/\text{cm}^{-1}$ 1650, 1460, 1335 and 665; m/z 252 (M^+ , 21), 238 (6), 83 (46) and 69 (100); δ_{H} 6.15 (tq, 0.08 H, *J* 1.4, *E*-3-H), 5.40 (tq, 0.92 H, *J* 6.7, 1.5, *Z*-3-H), 2.48 (d, 0.92 \times 3 H, *J* 1.5, *Z*-1-H), 2.36 (d, 0.08 \times 3 H, *J* 1.4, *E*-1-H), 2.12–2.01 (m, 2 H), 1.41–1.26 (m, 8 H) and 0.89 (t, 3 H, *J* 6.8).

2-Iodoundec-2-ene 6c.⁸—Oil, $\nu_{\text{max}}/\text{cm}^{-1}$ 1645, 1460, 1375 and 660; m/z 280 (M^+ , 37), 181 (18), 97 (74) and 55 (100); δ_{H} 6.14

(m, 0.05 H, *E*-3-H), 5.40 (tq, 0.95 H, *J* 6.8, 1.3, *Z*-3-H), 2.49 (d, 0.95 × 3 H, *J* 1.5, *Z*-1-H), 2.35 (d, 0.05 × 3 H, *J* 1.4, *E*-1-H), 2.12–2.00 (m, 2 H), 1.43–1.17 (m, 12 H) and 0.88 (t, 3 H, *J* 7.0).

2-Iodododec-2-ene 6d.—Oil, $\nu_{\max}/\text{cm}^{-1}$ 1640, 1460, 1380 and 660; m/z 294 (M^+ , 57), 181 (23), 168 (35) and 55 (100); HRMS m/z 294.0813 (*M*, requires 294.0845); δ_{H} 6.15 (tq, 0.10 H, *J* 6.8, 1.4, *E*-3-H), 5.40 (tq, 0.90 H, *J* 6.7, 1.4, *Z*-3-H), 2.49 (d, 0.9 × 3 H, *J* 1.4, *Z*-1-H), 2.34 (d, 0.1 × 3 H, *J* 1.4, *E*-1-H), 2.10–2.00 (m, 2 H), 1.42–1.20 (m, 14 H) and 0.88 (t, 3 H, *J* 6.4).

2-Iodo-3-phenylprop-2-ene 6e.⁹—Oil, $\nu_{\max}/\text{cm}^{-1}$ 1600, 1490, 1270 and 695; m/z 244 (M^+ , 40), 117 (73), 115 (100) and 91 (46); δ_{H} 7.45–7.25 (m, 5.07 H, ArH and *E*-3-H), 6.66 (m, 0.93 H, *Z*-3-H), 2.73 (d, 0.93 × 3 H, *J* 1.5, *Z*-1-H) and 2.64 (d, 0.07 × 3 H, *J* 1.6, *E*-1-H).

2-Iodo-3(p-tolyl)prop-2-ene 6f.—Oil, $\nu_{\max}/\text{cm}^{-1}$ 1640, 1510, 1480 and 660; m/z 258 (M^+ , 100), 131 (59) and 116 (37); HRMS m/z 257.9930 (*M*, requires 257.9906); δ_{H} 7.38–7.15 (m, 4.02 H, ArH and *E*-3-H), 6.62 (m, 0.98 H, *Z*-3-H), 2.70 (d, 0.98 × 3 H, *J* 1.5, *Z*-1-H), 2.62 (d, 0.02 × 3 H, *J* 1.5, *E*-1-H) and 2.35 (s, 3 H).

2-Iodo-3(p-methoxyphenyl)prop-2-ene 6g.—Oil, $\nu_{\max}/\text{cm}^{-1}$ 1610, 1510, 1175 and 530; m/z 274 (M^+ , 100), 147 (36) and 132 (11); HRMS m/z 273.9833 (*M*, requires 273.9855); δ_{H} 7.47–6.85 (m, 4.03 H, ArH and *E*-3-H), 6.59 (m, 0.97 H, *Z*-3-H), 3.80 (s, 3 H), 2.69 (d, 0.97 × 3 H, *J* 1.4, *Z*-1-H) and 2.61 (d, 0.03 × 3 H, *J* 1.4, *E*-1-H).

2-Iodo-3(p-fluorophenyl)prop-2-ene 6h.—Oil, $\nu_{\max}/\text{cm}^{-1}$ 1600, 1500, 1235 and 570; m/z 262 (M^+ , 100), 135 (79) and 115 (48); HRMS m/z 261.9669 (*M*, requires 261.9655); δ_{H} 7.45–6.93 (m, 4.03 H, ArH and *E*-3-H), 6.60 (m, 0.97 H, *Z*-3-H), 2.70 (d, 0.97 × 3 H, *J* 1.6, *Z*-1-H) and 2.58 (d, 0.03 × 3 H, *J* 1.6, *E*-1-H); δ_{F} 35.7 (s, 1 F).

Acknowledgements

The authors thank the National Natural Science Foundation of China, Laboratory of Organometallic Chemistry and Academia Sinica for financial support.

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Paper 5/01341K

Received 6th March 1995

Accepted 30th March 1995