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The Synthesis of Alkenes *via epi*-Phosphonium Species: 2. A Phosphorus Ramberg-Bäcklund Reaction

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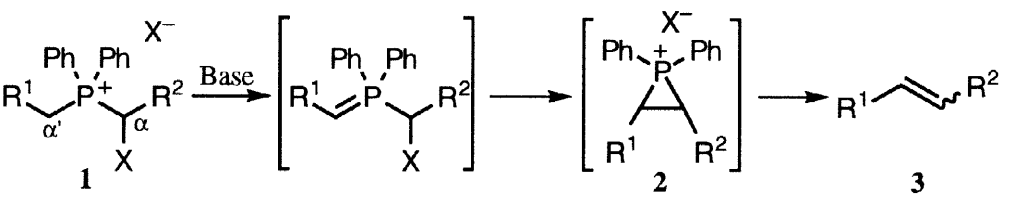
Abstract: Stilbene may be synthesised with *Z*-selectivity from (α-bromobenzyl)benzyldiphenylphosphonium bromide by the action of amine bases. A series of stilbenes was synthesised by the action of *N*-bromosuccinimide and 2,2,6,6-tetramethylpiperidine directly upon dibenzyldiphenylphosphonium salts. The reaction, essentially a phosphonium analogue of the Ramberg-Bäcklund displays *cis* selectivity. The dibenzyldiphenylphosphonium salts were prepared by the one pot polymethylhydrosiloxane/titanium(IV) isopropoxide mediated reduction/alkylation of benzyldiphenylphosphine oxides. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: alkenes; phosphonium salts; Ramberg-Bäcklund reaction; polymethylhydrosiloxane.

In the previous paper[1] we outlined the synthesis of alkenes from 1,2-phosphinyl alcohols and proposed a mechanism involving the formation of a transient *epi*-phosphonium salt. To show that the formation of these species **2** is reasonable, and that they can serve as precursors to alkenes, we developed a Ramberg–Bäcklund-type[2] reaction (**1** → **2**, scheme 1).[3] We now present the full details of that study. We chose to make the *epi*-phosphonium salt **2** by construction of the carbon-carbon bond as the ring-forming step. This was to be achieved by the intramolecular displacement of a nucleofuge present at the α-position by the ylide formed at the α'-carbon atom of a phosphonium salt **1**.



Scheme 1

The substituted bis(benzyl)diphenylphosphonium salts **1**, were prepared by the alkylation of the appropriate substituted benzyldiphenylphosphine. However, benzyldiphenylphosphine oxides are difficult to prepare by the reaction of benzyltriphenylphosphonium salts with sodium hydroxide. For example when benzyltriphenylphosphonium bromide is heated under reflux with dilute sodium hydroxide (30% w/w), triphenylphosphine oxide and toluene are obtained.[4,5] Fortunately benzyldiphenylphosphine oxide **5** can be prepared in large quantities using another known method.[6] Triphenylphosphine and dibromomethane were heated under reflux in toluene to produce (α-bromomethyl)triphenylphosphonium bromide **4**. When this phosphonium bromide **4** was treated with dilute sodium hydroxide at reflux, benzyldiphenylphosphine oxide **5** (scheme 2) was obtained along with unwanted methyldiphenylphosphine oxide **6** (**5**:**6** 60:40). The benzyldiphenylphosphine oxide **5** was separated simply by recrystallisation of the crude reaction mixture from ethyl acetate, in which **6** is soluble.

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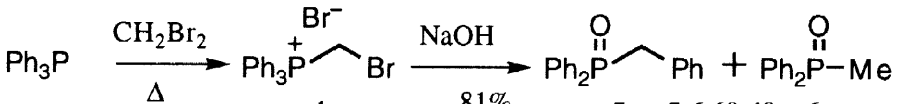
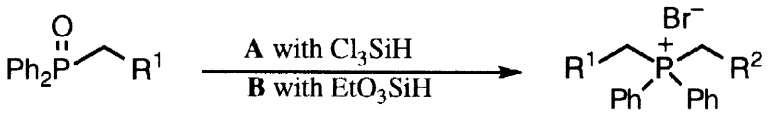


Scheme 2

To prepare the series of phosphonium salts **1** a reliable method for the reduction of benzyldiphenylphosphine oxide **5** was required. Previously we reduced phosphine oxides to phosphines by using Imamoto's reagent, lithium aluminium hydride/cerium (III) chloride.[1] This reagent was sufficient for our needs at that time. However, we were anxious to find conditions that were easier to use and most importantly avoided the need to isolate the phosphines which are sensitive to autoxidation. Reduction of **5** with trichlorosilane[7] in the presence of triethylamine followed by *in situ* quaternisation with benzyl bromide gave bis(benzyl)diphenylphosphonium bromide **7a** (46%)(scheme 3). Although this method gave the required material, the use of trichlorosilane, which is difficult and unpleasant to handle, makes the method far from ideal.



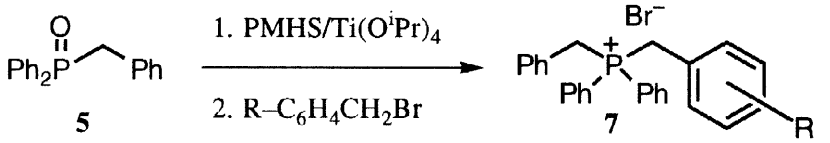
A: 1. Cl_3SiH/Et_3N, CH_3CN, 70 °C, 3 h. 2. $PhCH_2Br$, $CHCl_3$, reflux, 2 h.

B: 1. $(EtO)_3SiH$/ $Ti(O^iPr)_4$, THF, reflux, 1 h. 2. $PhCH_2Br$, THF, reflux, 1 h.

Scheme 3

Berk and Buchwald[8] had recently found that titanium(IV) isopropoxide is an efficient catalyst for the triethoxysilane reduction of esters to alcohols. We were therefore intrigued as to whether titanium(IV) isopropoxide would serve as a catalyst in the triethoxysilane reduction of phosphine oxides. First, we attempted the reduction of benzyldiphenylphosphine oxide **5** with triethoxysilane and titanium(IV) isopropoxide under the standard conditions described by Buchwald. The reaction proceeded rapidly with vigorous generation of a gas which we believe to be hydrogen, to give benzyldiphenylphosphine as judged by crude ^1H NMR and tlc (SiO_2, EtOAc), in almost quantitative yield. We were confident that the phosphine would be quaternised *in situ* by addition of an alkyl halide since Buchwald had reported that benzyl chloride is not reduced by triethoxysilane and titanium(IV) isopropoxide. Indeed, the bis(benzyl)diphenylphosphonium bromide **7a** was obtained in 98% yield by the addition of benzyl bromide in the same vessel without isolation of the phosphine (scheme 3).

The use of triethoxysilane is not ideal since it is toxic[9] (possibly causing blindness), and although it is commercially available, it is not cheap. Additionally, when no reductant is present, titanium(IV) isopropoxide is able to catalyse the disproportionation of the triethoxysilane generating silane (SiH_4), a pyrophoric gas. The use of the Buchwald system [$Ti(O^iPr)_4$/$(EtO)_3SiH$] on a large scale with a slight excess of silane has resulted in an explosion.[10] We therefore looked for an alternative silane from which to generate the titanium hydride species. Polymethylhydrosiloxane, $Me_3Si[(CH_3)HSiO]_nOSiMe_3$, (PMHS) appeared to be an attractive substitute. It is a



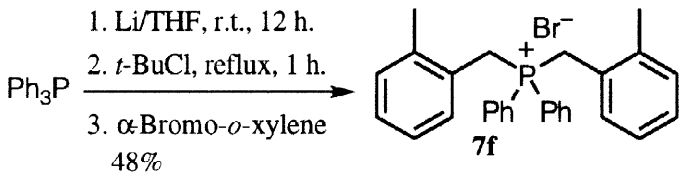
7b	R = 4–OMe	95%
7c	R = 2–Me	97%
7d	R = 4–NO_2	85%
7e	R = 4–Me	82%

Scheme 4

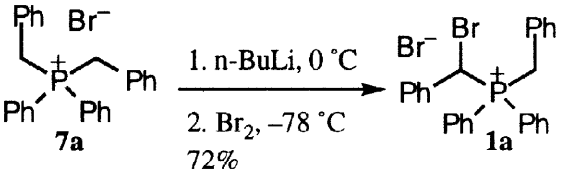
non-toxic, inexpensive, readily available polymer, that is soluble in most organic solvents. It is also generally inert in the absence of catalysts. The silane is not volatile, and as far as we know, not toxic. In addition it does not rapidly undergo disproportionation with titanium reagents. PMHS has previously been used to reduce phosphine oxides albeit at elevated temperatures. The reaction involved simply heating the benzyldiphenylphosphine oxide **5** (1 mmol) with polymethylhydrosiloxane (10 mmol) and titanium(IV)

isopropoxide (1 mmol) in tetrahydrofuran under a nitrogen atmosphere. The phosphonium salts **7b-e** were isolated in excellent yield by the addition of the appropriate benzyl bromide (2 mmol)(scheme 4).

The new reducing system [PMHS/Ti(O^iPr)$_4$] is now our favoured method for the reduction of phosphine oxides.[11] Recently, our group has extended the utility of this reagent by reducing a series of esters and carboxylic acids.[12] The symmetrical bis(2-methylbenzyl)diphenylphosphonium bromide salt **7f** was prepared by the method of Cristau and Ribeill.[13] Reaction of lithium metal with triphenylphosphine gave lithium diphenylphosphide and phenyllithium (which was destroyed by the addition of *t*-butyl chloride). Quaternisation with α-bromo-*o*-xylene finally gave the symmetrical salt in 48% yield, as shown in scheme 5a.

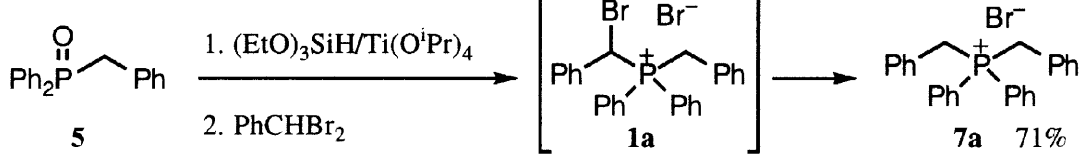


Scheme 5a



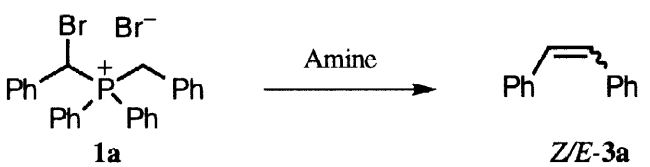
Scheme 5b

With the dibenzyldiphenylphosphonium salts **7** in hand, we next needed to functionalise the α-position to give salts of type **1**; we chose a halogen as a good leaving group. Treatment of dibenzyldiphenylphosphonium bromide **7a** with n-butyllithium (1 equivalent) at 0 °C followed by bromine (1 equivalent) at -78 °C gave the α-bromophosphonium bromide **1a**[14] (scheme 5b). We also tried to obtain the α-bromophosphonium salt **1a** by alkylation of benzyldiphenylphosphine with benzal bromide (α,α-dibromo-toluene), which if successful would represent a very attractive and flexible route to unsymmetrical bromophosphonium salts. This was attempted by reduction of benzyldiphenylphosphine oxide **5** with triethoxysilane/titanium(IV) isopropoxide in THF, followed by reaction with benzal bromide in the same pot. Unfortunately, instead of the required product we obtained the further reduced dibenzyldiphenylphosphonium bromide **7a** in good yield (71%)(scheme 6). Clearly the excess of reducing agent present in the reaction mixture is leading to further reduction.



Scheme 6

Alkali metal hydroxides have often been used as the base in Ramberg–Bäcklund reactions.[2] When potassium hydroxide was used to promote the reaction of the α-bromophosphonium salt **1a** no Ramberg–Bäcklund type reaction was observed. Benzyldiphenylphosphine oxide **5** and benzyl bromide were isolated. This result is not surprising as quaternary phosphonium salts undergo hydrolysis under these conditions. However, when the α-bromophosphonium bromide **1a** was treated with triethylamine (scheme 7, table 1), stilbene **3a** was indeed obtained, showing that the analogy with the Ramberg–Bäcklund reaction is a good one. In addition, the alkene is obtained with *cis*-selectivity (*Z*:*E* approx. 78:22 as determined by ^{1}H NMR and gas chromatography of the crude reaction mixture). The *cis*-selectivity is consistent with that commonly observed in the conventional Ramberg–Bäcklund reaction.[15]



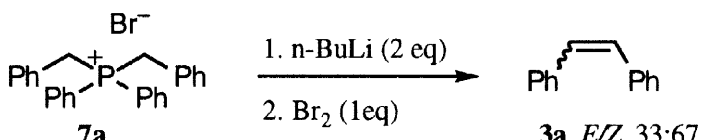
Scheme 7

Table 1. Reaction of bromobenzylphosphonium salt **1a** with amine.

Amine	Yield of stilbene **3a** (%)	*E/Z*[a]	Recovered **7a** (%)
Triethylamine	78	22:78	9
Diisopropylamine	65	25:75	31
2,2,6,6-Tetramethylpiperidine	61	20:80	~35[b]
Hexamethyldisilazane	44	22:78	~50[b]
1,8-Diazabicyclo[5.4.0]undec-7-ene	40	20:80	~10[b,c]
Diisopropylethylamine	40	20:80	48[b]

a. As measured from the ^{1}H NMR spectrum of the crude reaction mixture and/or gas chromatography of the isolated product.; b. As estimated from the ^{1}H NMR spectrum of the crude reaction mixture.; c. In addition to **7a** benzyldiphenylphosphine oxide **5** (approx. 40%) is present.

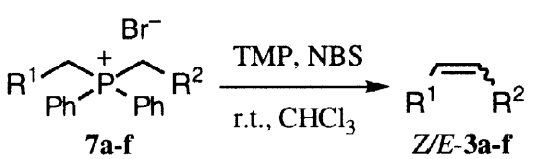
The reaction of α-bromophosphonium bromide **1a** with the amines was complicated by the formation of dibenzyldiphenylphosphonium salt **7a.** If the base only attacks the α'-hydrogen of the phosphonium salt **1a** we would expect the reaction to be high yielding. However, a side reaction must be occurring which involves the attack upon the bromine atom by the base. In the reaction of triethylamine we isolated the stilbene (78% yield) and dibenzyldiphenylphosphonium bromide **7a** (9%). We then attempted the reaction with a variety of bases to see if we could reduce the amount of the by-product **7a** (see table 1). Unfortunately we were not able to find conditions where this was the case. Indeed with some bases further by-products were obtained; with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) stilbene (40%) was obtained in poor yield together with **7a** and benzyldiphenylphosphine oxide **5**. The *Z*-selectivity (which was measured from the ^{1}H NMR spectrum of the crude mixture) is more or less independent of the base and for all the bases a small amount of phosphonium salt **7a** was formed. Since both the bromination of **7a** and the subsequent intramolecular bromide displacement occur *via* intermediate ylides we investigated whether both steps could be performed in the same pot. Such a process would be analogous to the Meyers' carbon tetrachloride/potassium hydroxide one-pot modification of the Ramberg–Bäcklund reaction.[16] We next investigated the reaction of the ylide anion of **7a**. The ylide anion of **7a** was prepared by addition of two equivalents of n-butyllithium, according to the method of Walker,[17] and treated with one equivalent of bromine. The reaction produced stilbene **3a** (*E/Z*, 33:67) but in poor yield (42%)(scheme 8).



7a **3a** *E/Z*, 33:67

Scheme 8

The direct transformation of **7a** into stilbene was achieved by reaction with 2,2,6,6-tetramethylpiperidine (TMP) and *N*-bromosuccinimide (NBS) in chloroform at room temperature (scheme 9). The other symmetrical and un-symmetrical dibenzylphosphonium salts **7b-f** were subjected to these reaction conditions. The *cis:trans* ratio of the alkenes **3a-f** was determined from the crude reaction mixture by ^{1}H NMR spectroscopy (see table 3).



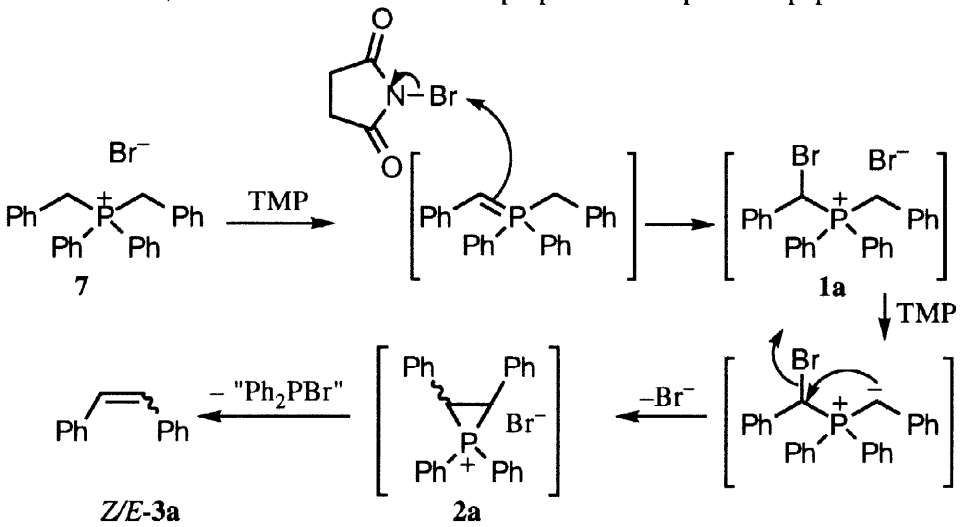
7a-f *Z/E*-**3a-f**

Scheme 9

Table 2. Synthesis of stilbenes from phosphonium salts **7**

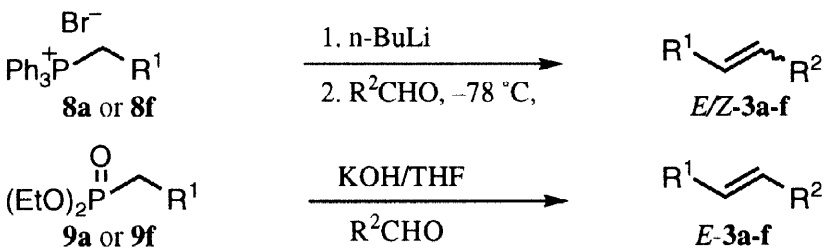
7	R^1	R^2	Yield (%)	*E:Z*
a	Ph	Ph	70	20:80
b	Ph	4-$MeOC_6H_4$	56	40:60
c	Ph	2-MeC_6H_4	79	20:80
d	Ph	4-$NO_2C_6H_4$	85	50:50
e	Ph	4-MeC_6H_4	94	30:70
f	2-MeC_6H_4	2-MeC_6H_4	77	26:74

The tetramethylpiperidine is sufficiently basic to remove the α-proton of **7a** [p*K*a approx. (25 °C; DMSO) = 12][18] to give an ylide that reacts with *N*-bromosuccinimide. The Ramberg-Bäcklund-type reaction can then occur by deprotonation at the α'-position of **107** to generate the intermediate *epi*-phosphonium species **2a**, as outlined in scheme 10; a mechanism similar to that proposed in the previous paper.



Scheme 10

Authentic samples of the alkenes were prepared to aid our NMR assignments by the Wittig reaction[19,20,21] (giving a mixture of the *E/Z*-alkene) and the Horner–Wadsworth–Emmons (HWE) reaction[22] (giving only the *E*-alkene). The benzyltriphenylphosphonium salts **8a** and **8f** were sequentially treated with n–butyllithium and the appropriate substituted benzaldehyde to produce a mixture of *E*- and *Z*-alkenes (table 3, scheme 11). The selectivity, or lack of it, is typical of semi-stabilised ylids generated under these conditions. The *trans* isomers *E*-**3a-f** were prepared by the potassium hydroxide promoted HWE reaction of the diethyl benzylphosphonates **9a** and **9f**. The Ramberg–Bäcklund reaction exhibited better *cis* selectivity than the conventional Wittig reaction, where comparisions could be made.



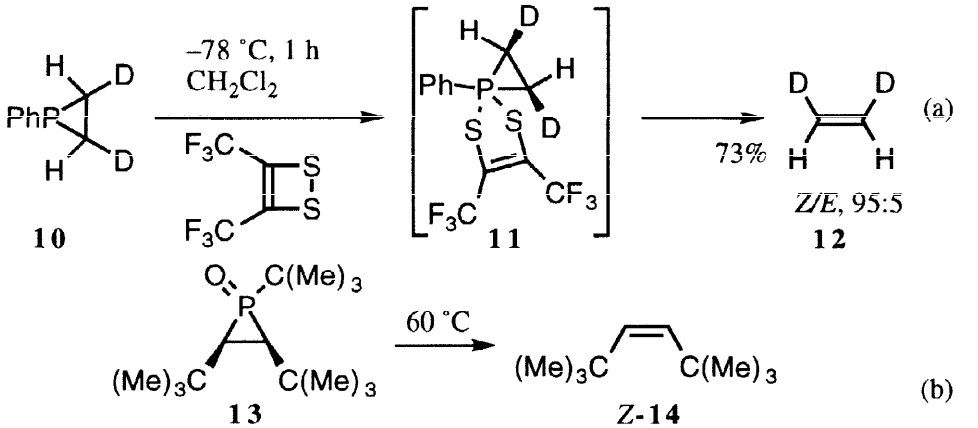
Scheme 11

Table 3. Synthesis of stilbenes **3a-f** by standard Wittig methods

			(**8** → **3**)		(**9** → **3**)	
	R^1	R^2	yield (%)	*E:Z*[a]	yield (%)	*E:Z*[a]
3a	Ph	Ph	81	70:30	75	>98:2
3b	Ph	2-MeC_6H_4	76	46:54	97	96:4
3c	Ph	4-MeC_6H_4	98	35:65	71	>98:2
3d	Ph	4-$NO_2C_6H_4$	75	76:24	76	>98:2
3e	Ph	4-$MeOC_6H_4$	65	50:50	92	>98:2
3f	2-MeC_6H_4	2-MeC_6H_4	72	36:64	78	>98:2

a. As measured from the ^1H nmr spectrum of the crude reaction mixture.

We believe that the reaction **1** → **3** and **7** → **3** proceed *via* a mechanism similar to that of the Ramberg–Bäcklund transformation. Clearly this requires the formation of an *epi*-phosphonium species **2**. It is known that the parent phosphines (phosphiranes) are highly strained and hence highly reactive.[23] Very little is known about the reactivity of *epi*-phosphonium salts.[14] However a recent paper has described the synthesis, isolation and X-ray crystal structure of 1-methyl-1-phenylphosphiranium triflate.[24]



Scheme 12

There is precedent for the decomposition of three membered-ring phosphorus containing compounds to alkenes. Denney[25] has shown that a phosphirane **11** (prepared from **10**) containing a pentacoordinate phosphorus atom decomposes by a stereospecific concerted process to give the alkene *Z*-**12** (scheme 12a). In our reaction the decomposition of **2** may therefore require attack by a nucleophile (triethylamine or chloride ion) to produce a similar transient pentacoordinate phosphorus species. Another example relevant to our study has been described by Heuschmann and co-workers (scheme 12b).[26] They found that the extrusion of the phosphorus group from **13** is clearly stereospecific, giving the thermodynamically less stable *cis* alkene *Z*-**14**. The stereospecificity of such reverse cheletropic reactions is well known, including examples of the elimination of stereochemically defined *epi*-sulfones.[2] A similar process for a phosphinate has also been described.[27]

The *cis* selectivity of our new reaction is intriguing and follows the same preference of the Ramberg-Bäcklund reaction for which no definitive explanation has been given.[2] Our method joins several other Ramberg-Bäcklund like reactions in which the sulfone group is replaced by sulfide,[28] sulfoxide,[29] sulfoximine,[30] and more pertinently, phosphine oxide and phosphinate groups.[26]

Acknowledgements : We thank the Pakistan Ministry of Education for a scholarship (F.M.) and the Nuffield Foundation for financial support.

Experimental

General experimental details are outlined in the previous paper.

Bromomethyltriphenylphosphonium bromide **4**.—To triphenylphosphine (100 g, 0.38 mol) in toluene (300 cm^3) was added dibromomethane (60 cm^3, 0.85 mol) at room temperature. The mixture was heated at reflux for 24 h under nitrogen. The resulting suspension was filtered and the solid dried *in vacuo*. The crude solid was dissolved in methanol, precipitated with EtOAc and washed with Et_2O, to give phosphonium salt **4** (83.03 g, 50%) as white needles, m.p. 239-240 °C (lit.,[31] m.p. 240-241 °C).

Benzyldiphenylphosphine oxide **5**—To phosphonium salt **4** (129.33 g, 0.363 mol) in methanol (120 cm^3) was added sodium hydroxide (105 g, 2.62 mol) in water (300 cm^3). The mixture was heated for 1.5 h at 100 °C (oil-bath temp.). The mixture was allowed to cool to room temperature and water was added (200 cm^3). The mixture was extracted with chloroform (3 × 100 cm^3). The organic extracts were dried ($MgSO_4$) and evaporated

in vacuo. The crude solid was recrystallised from ethanol to give phosphine oxide **5** (36.5 g, 34.5%) as long white needles; m.p. 192-194 °C (lit.[32] m.p. 192-193 °C).

Dibenzyldiphenylphosphonium bromide **7a**.—To phosphine oxide **5** (5 g, 17 mmol) in dry THF (34 cm^3) was added triethoxysilane (9.4 cm^3, 51 mmol) followed by titanium(IV) isopropoxide (0.5 ml) at room temperature. The reaction mixture was heated under reflux for 1 h and cooled to room temperature. Benzyl bromide (4 cm^3, 34 mmol) was added and the reaction mixture refluxed for 1 h. The mixture was cooled to room temperature, filtered and washed with ethyl acetate to give the phosphonium salt **7a** (7.52 g, 98%) as cubes, m.p. 260-264 °C (lit.[13] m.p. 260 °C).

General method for the preparation of phosphonium bromides 7 from benzyldiphenylphosphine oxide 5 and PMHS.—To phosphine oxide **5** (3 g, 10.27 mmol) in dry THF (25 cm^3) was added PMHS (9 cm^3, 154 mmol) and titanium(IV) isopropoxide (4.5 cm^3, 15.4 mmol) at room temperature under nitrogen. The reaction mixture was heated under reflux for 6 h and cooled to room temperature. The substituted benzyl bromide (20 mmol) was added to the reaction mixture and heated under reflux for a further 1 h. The mixture was allowed to cool to room temperature, giving a crude solid. The solid was filtered and washed with dry THF (20 cm^3).

(4-Methoxybenzyl)benzyldiphenylphosphonium bromide **7b**.—(4.64 g, 95%) as an amorphous solid, m.p. 140-141 °C, R_f 0.61 (EtOAc/MeOH, 7:3); Found: C, 67.6; H, 5.3; Br, 16.3. $C_{27}H_{26}BrOP$ requires C, 67.9; H, 5.5; Br, 16.7%; $\nu_{max.}$ (KBr)cm^{-1} 2840 (OMe), 1440 (P–Ph); δ^1H (200 MHz, $CDCl_3$) 3.62 (3 H, s, CH_3), 4.83 (2 H, d, *J* 14.0 Hz, CH_2Ar), 4.85 (2 H, d, *J* 14.6 Hz, CH_2Ar), 6.52 (2 H, d, *J* 8.5 Hz, H-3 and H-5), 6.85–7.67 (17 H, m, 3 × Ph, H-2 and H-6); $\delta^{13}C$ (75 MHz, $CDCl_3$) 28.9 (d, $J_{P\text{-}C}$ 45.0 Hz), 29.3 (d, $J_{P\text{-}C}$ 45.0 Hz), 55.2, 114.1, 116.0, 117.1, 118.8, 119.0, 127.6, 127.7, 128.1, 128.7, 129.6, 129.7, 130.7, 130.8, 131.9, 134.3, 134.4, 134.7, 159.3; *m/z* (FAB), 398 (100%, M + H – Br), 121 (98, Ph_2PCH_2Ph).

(2-Methylbenzyl)benzyldiphenylphosphonium bromide **7c**.—(2.29 g, 97%) as a crystalline solid, m.p. 240-241 °C, R_f 0.46 (EtOAc/MeOH, 7:3, v/v); Found: C, 70.5; H, 5.3; Br, 17.8; P, 6.5. $C_{27}H_{26}BrP$ requires C, 70.3; H, 5.7; Br, 17.3; P, 6.7%; $\nu_{max.}$ (KBr)cm^{-1} 1440 (P–Ph); δ^1H (200 MHz, $CDCl_3$) 1.59 (3 H, s, CH_3), 4.95 (2 H, d, *J* 14.9 Hz, CH_2Ar), 5.13 (2 H, d, *J* 14.6 Hz, CH_2Ar), 6.91–7.72 (19 H, m, 3 × Ph, C_6H_4); $\delta^{13}C$ (75 MHz, $CDCl_3$) 19.6, 27.5 (d, $J_{P\text{-}C}$ 45.0 Hz), 29.6 (d, $J_{P\text{-}C}$ 45.0 Hz), 116.3 (d, $J_{P\text{-}C}$ 81.7 Hz), 126.0, 126.2, 126.5, 127.7, 128.1, 128.1, 128.5, 128.8, 129.6, 129.7, 130.9, 131.0, 131.2, 134.3, 134.4, 134.9, 138.7; *m/z* (FAB), 381 (100%, M^+ – Br).

(4-Nitrobenzyl)benzyldiphenylphosphonium bromide **7d**.—(2.13 g, 85%) as an amorphous solid, m.p. 229-230 °C, R_f 0.51 (EtOAc/MeOH, 7:3, v/v); Found: C, 63.1; H, 4.3; Br, 16.5; P, 6.1. $C_{26}H_{23}BrPNO_2$ requires C, 63.4; H, 4.7; Br, 16.2; P, 6.3%; $\nu_{max.}$ (KBr)cm^{-1} 1440 (P–Ph), 1520 and 1345 (ArylNO_2); δ^1H (200 MHz, $CDCl_3$) 5.01 (2 H, d, *J* 14.8 Hz, CH_2Ph), 5.53 (2 H, d, *J* 15.7 Hz, C$H_2C_6H_4NO_2$), 6.81–7.80 (19 H, m, 3 × Ph, C_6H_4); $\delta^{13}C$ (75 MHz, $CDCl_3$) 29.4 (d, $J_{P\text{-}C}$ 44.3 Hz), 30.0 (d, $J_{P\text{-}C}$ 44.3 Hz) 114.7, 115.8, 123.3, 127.0, 127.1, 128.0, 128.5, 129.6, 129.7, 130.4, 131.5, 131.6, 134.3, 134.4, 134.9, 136.1, 136.2, 147.0; *m/z* (FAB), 411 (100%, M – H – Br), 395 (26, M – OH – Br), 365 (20, M – HNO_2 – Br), 91 (22, $PhCH_2$).

(4-Methylbenzyl)benzyldiphenylphosphonium bromide **7e**.—(1.94 g, 82%) as a crystalline solid, m.p. 145-147 °C, R_f 0.42 (EtOAc/MeOH, 7:3, v/v); Found: C, 70.5; H, 5.8; Br, 17.2. $C_{27}H_{26}BrP$ requires C, 70.3; H, 5.7; Br, 17.3%; $\nu_{max.}$ (KBr)cm^{-1} 1440 (P–Ph); δ^1H (200 MHz, $CDCl_3$) 2.21 (3 H, d, *J* 2.46 Hz, CH_3), 4.90 (2 H, d, *J* 14.4 Hz, CH_2Ar), 4.95 (2 H, d, *J* 14.7 Hz, CH_2Ar), 6.88 (4 H, s, H-2,3,5,6), 7.04–7.71 (15 H, m, 3 × Ph); $\delta^{13}C$ (75 MHz, $CDCl_3$) 21.0, 29.2 (d, $J_{P\text{-}C}$ 44.9 Hz), 29.4 (d, $J_{P\text{-}C}$ 44.9 Hz), 116.5 (d, $J_{P\text{-}C}$ 82.5 Hz), 124.0, 124.1, 127.6, 128.1, 128.7, 129.4, 129.4, 129.5, 130.6, 130.7, 130.8, 134.3, 134.4, 134.7, 138.0; *m/z* (FAB), 381 (100%. M^+ – Br).

Bis(o-methylbenzyl)diphenylphosphonium bromide **7f**.—To triphenylphosphine (5 g, 19.1 mmol) in dry THF (30 cm^3) was added lithium metal (0.27 g, 38.2 mmol) under nitrogen. The solution was stirred overnight at room temperature to give a red solution of lithium diphenylphosphide. Dry distilled *t*–butyl chloride (2.25 cm^3,

19.1 mmol) was added and the mixture heated under reflux for 1 h. The reaction mixture was cooled to room temperature and α-bromo-*o*-xylene (5 cm^3, 38.2 mmol) was added. The mixture was heated under reflux for 2 h. The solid was filtered and recrystallised from EtOAc/MeOH (9:1, v/v) to give phosphonium salt **7f** (4.22 g, 48%) as needles, m.p. 253-254 °C, R_f 0.63 (EtOAc/MeOH, 7:3); Found: C, 70.4; H, 6.2; P, 6.1. $C_{28}H_{28}BrP$ requires C, 70.7; H, 5.9; P, 6.5%; $\nu_{max.}$ (KBr)cm^{-1} 1440 (P–Ph); δ^1H (200 MHz, $CDCl_3$) 1.59 (6 H, s, 2 × CH_3), 5.04 (4 H, d, *J* 14.9 Hz, 2 × CH_2Ar), 6.93–7.77 (18 H, m, 2 × Ph, 2 × C_6H_4); $\delta^{13}C$ (75 MHz, $CDCl_3$) 19.6, 27.0 (d, $J_{P\text{-}C}$ 44.7 Hz), 116.1 (d, $J_{P\text{-}C}$ 80.2 Hz), 125.9, 125.0, 126.3, 126.4, 128.5, 128.5, 129.4, 129.6, 130.9, 131.1, 134.0, 134.2, 134.9, 134.9, 139.0, 139.0; *m/z* (FAB), 395 (100%, M^+ – Br).

(α-Bromobenzyl)benzyldiphenylphosphonium bromide **1a**.—n-Butyllithium (6.5 cm^3 of a 2.5 M solution in hexane, 16 mmol) was added to phosphonium bromide **7a** (7.3 g, 16.3 mmol) in dry THF (20 cm^3) at 0 °C and stirred for 30 min. at 0 °C. The red solution was cooled to –78 °C. In another flask, bromine (0.95 cm^3, 18.5 mmol) in dry THF (20 cm^3) was cooled to –78 °C under nitrogen. The red solution was added to the bromine solution dropwise *via* a cannula at –78 °C. The reaction mixture was stirred for 30 min. –78 °C and then for 2.5 h at room temperature. Water (100 cm^3) was added and the mixture extracted with chloroform (3 × 50 cm^3). The extracts were washed with water (2 × 100 cm^3), dried ($MgSO_4$) and evaporated *in vacuo*. The residue was recrystallised from methanol to give phosphonium bromide **1a** (6.18 g, 72%) as cubes, m.p. 246-247 °C, R_f 0.56 (EtOAc/MeOH, 7:3, v/v); Found: C, 59.0; H, 4.3; Br, 30.2: P, 5.8. $C_{26}H_{23}Br_2P$ requires C, 59.3; H, 4.4; Br, 30.4; P, 5.9%; $\nu_{max.}$ (KBr)cm^{-1} 1440 (P–Ph); δ^1H (200 MHz, $CDCl_3$) 3.92 (1 H, dd, *J* 1 and 13.6 Hz, PCH_aH_bPh), 5.74 (1 H, t, *J* 15.4 Hz, PCH_aH_bPh), 6.8–7.94 (20 H, m, 4 × Ph), 8.50 (1 H, d, *J* 6.9 Hz, BrC*H*Ph); $\delta^{13}C$ (75 MHz, $CDCl_3$) 28.4 (d, $J_{P\text{-}C}$ 44.1 Hz), 38.2 (d, $J_{P\text{-}C}$ 45.0 Hz), 112.8 (d, $J_{P\text{-}C}$ 81.0 Hz), 114.5 (d, $J_{P\text{-}C}$ 87.0 Hz), 128.2, 128.9, 129.5, 129.5, 129.7, 130.0, 130.5, 130.5, 131.0, 135.1, 135.3, 135.9, 136.0, 136.0; *m/z* (FAB), 448 (100%, M + H – Br), 368 (39, M – HBr_2).

Standard procedure for the preparation of stilbene by the Ramberg–Bäcklund–Type reaction.—To phosphonium salt **1a** (1 mmol) in chloroform (5 cm^3) was added the amine (2 mmol) at room temperature. After 2–3 h water (50 cm^3) was added and the mixture extracted with chloroform (3 × 25 cm^3). The organic extracts were washed with dilute hydrochloric acid (50 cm^3), saturated sodium bicarbonate solution (50 cm^3) and dried (Na_2SO_4) and evaporated *in vacuo*. The residue was purified by chromatography (SiO_2, hexane) to afford *E/Z* stilbenes. The ratio of *E/Z* stilbenes measured from the ^1H NMR spectrum of the crude reaction mixture.

General Method for the one-pot Ramberg–Bäcklund–Type reaction.—To a stirred mixture of phosphonium salt **7a** (1 mmol) and 2,2,6,6-tetramethylpiperidine (6 mmol) in dry dichloromethane (10 cm^3) was added *N*-bromosuccinimide (3 mmol) under nitrogen. The mixture was stirred at room temperature for 2.5 h. Water (50 cm^3) was added and the mixture extracted with dichloromethane (3 × 25 cm^3). The organic extracts were washed with dilute hydrochloric acid (50 cm^3), saturated sodium bicarbonate solution (50 cm^3) and dried (Na_2SO_4) and evaporated *in vacuo*. The residue was purified by chromatography (SiO_2, hexane) to give the alkene. The *E/Z* ratio was measured from the ^1H NMR spectrum of the crude reaction mixture.

(2-Methylbenzyl)triphenylphosphonium bromide **8f**.—α-Bromo-*o*-xylene (1.06 cm^3, 7.9 mmol) was added to triphenylphosphine (2.07 g, 7.9 mmol) in dry THF (10 cm^3). The reaction mixture was heated under reflux for 1 h. After addition of water (50 cm^3), the mixture was extracted with chloroform (3 × 25 cm^3). The organic extracts were dried ($MgSO_4$) and evaporated *in vacuo*. The product was recrystallised from isopropanol to give phosphonium bromide **8f** (2.21 g, 63%) as white needles, m.p. 252–254 °C (lit.,[33] m.p. 253–255 °C).

General Method for the Wittig Reaction.—To a stirred solution of triphenylbenzylphosphonium bromide **8a** or **8f** (1 mmol) in dry THF (10 cm^3) was added n-butyllithium (2.5 M solution in hexane, 1 mmol) at 0 °C. After 1 h the mixture was allowed to cool to –78 °C. Substituted benzaldehyde (1 mmol) was added at this temperature and the mixture was allowed to warm to room temperature. After 3 h stirring water (25 cm^3) was added. The mixture was extracted with chloroform (3 × 25 cm^3), dried ($MgSO_4$) and evaporated *in vacuo*. The residue was purified by chromatography (SiO_2, hexane) to give the alkene. The following alkenes were prepared:

E/Z-1,2-Diphenylethene **3a**.—(*E/Z*, 20:80)(63 mg, 70%), R_f 0.43 (hexane); $\nu_{max.}$ (KBr)cm^{-1} 960 (*trans* PhC=CPh); δ^1H (200 MHz, $CDCl_3$) 6.64 (2 H, s, CH=CH for *Z*), 7.16 (2 H, s, CH=CH for *E*), 7.27–7.58 (20 H, m, 4 × Ph for *E/Z*); *m/z*, (FAB), 180 (100%, M^+).

E/Z-1-Phenyl-2-(4'-methoxyphenyl)ethene **3b**.[20]—(*E/Z*, 40:60)(123 mg, 56%); δ^1H (200 MHz, $CDCl_3$) 3.80 (3 H, s, OCH_3, *Z*), 3.86 (3 H, s, OCH_3, *E*), 6.53 (2 H, s, CH=CH, *Z*), 6.76 (2 H, d, *J* 8.7 Hz, Ar H, *Z*), 6.95 (2 H, d, *J* 8.8 Hz, Ar H, *E*), 6.98 (1 H, d, *J* 16.4 Hz, C=CH, *E*), 7.09 (1 H, d, *J* 16.4 Hz, C=CH, *E*), 7.47 (2 H, d, *J* 8.8 Hz, Ar H, *E*), 7.72 (2 H, d, *J* 8.7 Hz, Ar Hs, *Z*), 6.89–7.68 (10 H, m, Ar H, *E/Z*).

E/Z-1-Phenyl-2-(2'-methylphenyl)ethene **3c**.[20]—(*E/Z*, 20:80) (100 mg, 79%); δ^1H (200 MHz, $CDCl_3$) 2.29 (3 H, s, CH_3 for *Z*), 2.45 (3 H, s, CH_3 for *E*), 6.65 (1 H, s, CH=CH, *Z*), 7.09 (1 H, d, *J* 16.1 Hz, CH=CH, *E*), 7.35 (1 H, d, *J* 16.1 Hz, CH=CH, *E*), 7.16–7.70 (18 H, m, 2 × Ph, 2 × Ar, *E/Z*); *m/z*, (FAB), 194 (100%, M^+), 189 (25), 178 (44), 165 (28), 115 (21), 91 (18).

E/Z-1-Phenyl-2-(4'-nitrophenyl)ethene **3d**.[21]—(*E/Z*, 50:50) (108 mg, 85%); δ^1H (200 MHz, $CDCl_3$) 6.61 (1 H, d, *J* 12.2 Hz, CH=CH for *Z*), 6.82 (1 H, d, *J* 12.2 Hz, CH=CH for *Z*), 7.13 (1 H, d, *J* 16.3 Hz, CH=CH, *E*), 7.63 (2 H, d, *J* 8.8 Hz, Ar Hs, *E*), 8.06 (2 H, d, *J* 8.9 Hz, Ar Hs, *Z*), 8.21 (2 H, d, *J* 8.8 Hz, Ar Hs, *E*), 7.20–7.58 (15 H, m, CH=CH, Ar Hs, 2 × Ph, *E/Z*).

E/Z-1-Phenyl-2-(4'-methylphenyl)ethene **3e**.[21]—(*E/Z*, 30:70)(110 mg, 94%); δ^1H (200 MHz, $CDCl_3$) 2.34 (3 H, s, CH_3Ar, for *Z*), 2.40 (3 H, s, CH_3Ar for *E*), 6.58 (2 H, s, CH=CH for *Z*), 7.07 (2 H, s, CH=CH, *E*), 7.11–7.42 (14 H, m, 2 × Ar H, *E/Z*), 7.48 (2 H, d, *J* 8.1 Hz, Ar Hs, *Z*), 7.57 (2 H, d, *J* 8.1 Hz, Ar Hs, *E*).

E/Z-1,2-Bis(o-methylphenyl)ethene **3f**.[34] —(160 mg, 77%); δ^1H (200 MHz, $CDCl_3$) 2.32 (3 H, s, CH_3 for *Z*), 2.47 (3 H, s, CH_3 for *E*), 6.75 (2 H, s, CH=CH for *Z*), 7.22 (2 H, s, CH=CH, *E*), 6.94–7.65 (16 H, m, 4 × Ar, *E/Z*); *m/z*, (FAB), 208 (100%, M^+), 91 (10, $C_6H_4CH_3$).

General Method for the Preparation of E-Alkenes by the Horner-Wadsworth-Emmons Method.—To phosphonate **9a**[35] or **9f** (1 mmol) and benzaldehyde (1 mmol) in THF (10 cm^3) was added KOH powder (2 mmol) at room temperature. After 1 h the mixture was heated under reflux for 3 h. Water (30 cm^3) was added and the mixture extracted with diethyl ether (3 × 25 cm^3). The organic extracts were washed with water (2 × 50 cm^3), dried ($MgSO_4$), and evaporated *in vacuo*. Recrystallisation (ethanol) gave the following alkenes (table 4).

Table 4. Selected data for *trans* stilbenes *E*-**3a-f**

	Yield (%)	m.p.	CHN Found (%)	CHN Expected (%)
3a	75	121-122 °C, lit.[36] 122-123 °C	C, 93.0; H, 6.6	C, 93.3; H, 6.6
3b	92	135-136 °C lit.[37] 134-135 °C	C, 85.4; H, 7.0	C, 85.7; H, 6.7
3c	97	isolated[a] as an oil.[38]	—	—
3d	76	157-158 °C lit.[39] 158-160 °C	C, 74.4; H, 5.2; N, 5.9	C, 74.6; H, 4.9; N, 6.2
3e	71	120-121 °C lit.[40] 119-120 °C	C, 92.5; H, 7.5	C, 92.8; H, 7.2
3f	78	79–80 °C lit.[41] 78.5–80 °C	C, 92.0; H, 7.9	C, 92.3; H, 7.7

a: purified by chromatography (silica/hexane)

Diethyl (2-methylbenzyl)phosphonate **9f**.—α-Bromo-*o*-xylene (2 cm^3, 15 mmol) and triethylphosphite (10 cm^3, 57.5 mmol) were heated under reflux for 2 h. Distillation of triethylphosphite left the phosphonate **9f** (2.98 g, 83) as an oil, R_f 0.58 (EtOAc); Found: C, 59.2; H, 8.2; P, 12.5. $C_{12}H_{19}O_3P$ requires C, 59.5; H, 7.9; P, 12.8; $\nu_{max.}$ (neat)cm^{-1} 1150 (P=O); δ^1H (200 MHz, $CDCl_3$) 1.22 (6 H, t, *J* 7.1 Hz, 2 × CH_3CH_2), 2.38 (3 H, d, *J* 1.7 Hz, $CH_3C_6H_4$), 3.16 (2 H, d, *J* 21.9 Hz, $CH_2C_6H_4$), 3.97 (4 H, quint, *J* 7.1 Hz, CH_2CH_3), 7.1–7.26 (4 H, m, C_6H_4); $\delta^{13}C$ (75 MHz, $CDCl_3$) 16.4 (d, J_{P-C} 6.0 Hz), 20.0, 30.2, 32.0, 62.1 (d, J_{P-C} 5.2 Hz), 126.1 (d, J_{P-C} 3.7 Hz), 127.1 (d, J_{P-C} 3.7 Hz), 130.1 (d, J_{P-C} 9 Hz), 130.5 (d, J_{P-C} 3.7 Hz), 130.6 (d, J_{P-C} 5.2 Hz), 137.0 (d, J_{P-C} 6.7 Hz); *m/z*, (FAB), 243 (100, M + H), 105 (32, $CH_2C_6H_4CH_3$).

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