On the Preparation of (*E*)- and (*Z*)-Stilbene from the Diastereoisomeric 1,2-Diphenyl-2-diphenylphosphinoylethan-1-ols

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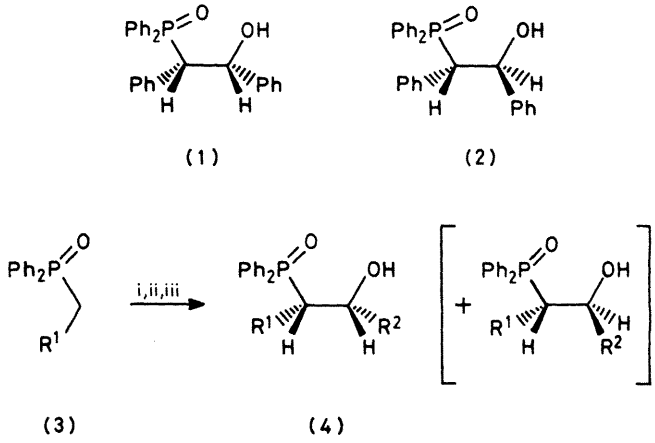
(1*RS*,2*SR*)-1,2-Diphenyl-2-diphenylphosphinoylethanol(*erythro*-isomer) (1) and its *threo*-isomer (2) have been prepared stereospecifically by opening the appropriate stilbene oxides with Ph_2PLi followed by oxidation with H_2O_2–AcOH. Compounds (1) and (2) can also be obtained stereoselectively (*erythro*-isomer predominating) *via* treatment of $Ph_2POCHLiPh$ with PhCHO.

Under all the conditions tried, treatment of the *threo*-isomer (2) with base gave (*E*)-stilbene. The *erythro*-isomer (1) under most conditions gave predominantly (*E*)-stilbene, together with variable amounts of Ph_2POCH_2Ph, though in one case mainly (*Z*)-stilbene was formed. The conversion *erythro*-(*E*)-stilbene was shown to occur *via* fragmentation to $Ph_2POCHLiPh$ and PhCHO by trapping experiments using *m*-chlorobenzaldehyde.

In 1964 Horner and Klink published a preliminary communication [1] on 'PO-activated olefination' dealing in particular with the formation of stilbene from the diastereoisomeric 1,2-diphenyl-2-diphenylphosphinoylethanols (1) and (2). This work has been reviewed in detail,[2] but full experimental details have unfortunately never been published. The key compounds (1) and (2) were only characterised by melting point, which turns out to be an unreliable criterion, no spectroscopic data being quoted. Furthermore syntheses of (1) and (2) by treatment of the epoxides of (*Z*)- and (*E*)-stilbene oxides respectively with diphenylphosphinoyl-lithium were claimed to occur by ring opening with overall retention of configuration. Arising out of recent investigations at both Cambridge [3] and Oxford [4] we have reinvestigated aspects of Horner and Klink's work to try and clarify some of the obscurities.

Authentic samples of the *erythro*- and *threo*-1,2-diphenyl-2-diphenylphosphinoylethanols (1) and (2) were prepared by treatment of (*E*)-stilbene oxide and (*Z*)-stilbene oxide respectively with lithium diphenylphosphide in tetrahydrofuran (THF) followed by protonation and oxidation using hydrogen peroxide in acetic acid.[4] Inversion of configuration in the opening of the stilbene oxides by lithium diphenylphosphide is known to occur from the related studies of Vedejs and Fuchs [5] on the phosphorus betaine method for olefin inversion. The two diastereoisomers (1) and (2) have characteristically different n.m.r. spectra. The most diagnostic features are that J_{HH} is larger for the *threo*- (9 Hz) than for the *erythro*-isomer (2 Hz), that coupling is observed to the hydroxy proton in the *threo*- but not the *erythro*-isomer, and that the *ortho*-protons of the Ph_2PO group separate from the other aromatic protons at lower field in the *erythro*-isomer. These features are shared by all simple compounds of types (1) and (2) with alkyl or aryl substituents.[6] *X*-Ray crystal structure determination [6] confirms the *erythro* stereochemistry of (4; R^1 = Me, R^2 = Ph). Unfortunately the melting points of (1) and (2) are not diagnostically different and in the absence of spectroscopic data for the compounds described by Horner and Klink [1] it is difficult to make useful comparisons.

The diastereoisomers (1) and (2) can also be obtained from reaction of the lithium derivative of benzyldiphenylphosphine oxide with benzaldehyde. We have previously shown [3] that addition of benzaldehyde to metallated (BuLi; THF; −78 °C) alkyldiphenylphosphine oxides (3) (Scheme 1) gives predominantly *erythro*-adducts (4) (*erythro* : *threo* usually >80 : 20) as does the addition of aldehydes to the less reactive metallated benzyldiphenylphosphine oxide (3; R^1 = Ph) (*erythro* : *threo* usually *ca.* 70 : 30) under the same conditions. Metallated (3; R^1 = Ph) adds to benzaldehyde in poor yield (31%) under these conditions, but the stereoselectivity is similar [(1) : (2), 65 : 35]. When an excess of lithium iodide is present during the reaction, the yield (88%) and the diastereoselectivity (83 : 17) are improved.



Scheme 1. *Reagents:* i, BuLi, 0 °C; ii, R^2CHO, −78 °C; iii, H_2O, −78 ⟶ 0 °C

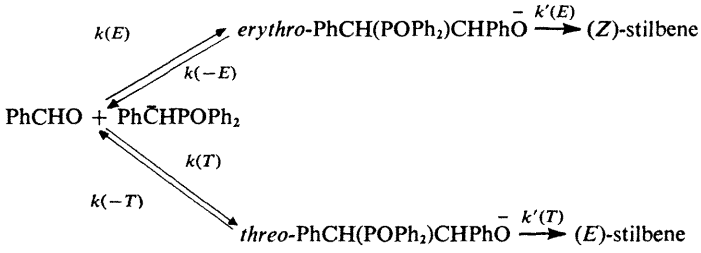
Horner and Klink [1] claimed to have isolated 90% *threo* (2) and 5% *erythro* (1) from treatment of (3; R^1 = Ph) with phenyl-lithium followed by benzaldehyde in ether at an unknown temperature. We find that changing from THF to ether reduces the *erythro*-selectivity of the reaction to *ca.* 60 : 40, but we have not observed predominance of the *threo*-adduct (2) under any conditions suggesting that, if Horner's assignment of stereochemistry is correct, the predominance of the *threo*-isomer found by him arises from reversible formation of (1) and (2).

Base-induced fragmentation of the *threo*-β-phosphinoyl alcohol (2) using a variety of base–solvent combinations gave (*E*)-stilbene in high yield and with high stereospecificity. Conditions employed include: sodium methoxide–THF (20 °C), anhydrous tetra-n-butylammonium hydroxide–THF (19 °C), 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU)–THF (reflux), and potassium hydroxide–dimethyl sulphoxide (DMSO) (50 °C). No evidence for the formation of benzyldiphenylphosphine oxide ('reverse aldol' product) was found.

Table. Base-induced fragmentations of *erythro*-1,2-diphenyl-2-diphenylphosphinoylethanol (1)

Entry	Base [a]	Solvent	Temp. (°C)	Time (h)	Yield (%) (*Z*)-Stilbene	(*E*)-Stilbene	BDPO [b]
1	PhLi (4.09)	Et_2O	20—35	3.5	1	63	11
2	BuLi (0.99)	Et_2O	19	3	Trace	58	38
3	BuLi (0.95)	THF	17	3	Trace	49	49
4	BuLi (1.0)	THF	0	*c*	58	3	39
5	BuLi (0.95)	THF–TMEDA	18	3	Trace	93	0
6	NaH (1.15)	DMSO	20	0.27	0	51	42
7	NaH (1.33)	DMSO	28	2	0	78	19
8	$(Bu^n_4N)OH$ (3.3)	THF	21	3	13	84	0
9	DBU (1.98)	THF	23	3	3	Trace	19 [d]
10	DBU (1.98)	THF	66	3	25	Trace	61
11	DBU–CaH_2 (1.95 : 3.02)	THF	66	3	29	Trace	57
12	KOH (1.0)	DMSO	50	1	8	85	7

[a] Base/phosphine oxide molar ratio given in parentheses. [b] BDPO = benzyldiphenylphosphine oxide. [c] Base added dropwise; solution allowed to warm to room temperature before water was added. [d] 65% of (1) recovered.



Scheme 2.

Attempts were made to eliminate diphenylphosphinate from the *erythro*-β-phosphinoyl alcohol (1) with the stereospecific formation of (*Z*)-stilbene using a large number of base–solvent combinations. Some of the results obtained are summarised in the Table (for a more complete list see ref. 7). In most cases where bases containing a metal counterion were used, olefin containing a high proportion of (*E*)-stilbene was obtained, frequently accompanied by benzyldiphenylphosphine oxide. The only conditions which allowed the isolation of a reasonable amount (58%) of (*Z*)-stilbene from (1) (entry 4, Table) were the use of one equivalent of base (BuLi) at a temperature low enough to minimise dissociation to benzaldehyde but high enough to allow elimination to proceed. The reaction is obviously sensitive to conditions, as at 17 °C in the same solvent very little (*Z*)-stilbene is formed, while at 0 °C in the presence of lithium iodide no elimination occurs.

Horner claimed [1] that (*Z*)-stilbene was formed from (1) on treatment with phenyl-lithium in ether, but we were unable to reproduce this result (entry 1, Table).

In general, organic bases were more successful in consistently giving high *Z*/*E* ratios of stilbene from (1) and the highest values were obtained using DBU (entries 10 and 11, Table). Unfortunately these conditions always resulted in predominant formation of benzyldiphenylphosphine oxide, the ' reverse aldol ' product. We do not recommend any route *via* (1) as a preparation of (*Z*)-stilbene.

There are two probable mechanisms to explain the formation of (*E*)-stilbene from the *erythro*-precursor (1). These involve *erythro* ⟶ *threo* interconversion by either (a) epimerisation *via* deprotonation–reprotonation at C-2, or (b) ' reverse aldol ' fragmentation to metallated phosphine oxide and benzaldehyde followed by recombination. The latter explanation was shown to be the more likely as a result of trapping experiments in which the *erythro*-β-phosphinoyl alcohol (1) was treated with base in the presence of *m*-chlorobenzaldehyde. This reactive aldehyde has previously been used in analogous experiments involving phosphonium betaines.[8] To exemplify, treatment of (1) and *m*-chlorobenzaldehyde (3 equiv.) with tetra-n-butylammonium hydroxide in THF (26 °C) gave (*E*)-*m*-chlorostilbene (59%), (*Z*)-*m*-chlorostilbene and (*Z*)-stilbene (both in trace amounts only), and benzyldiphenylphosphine oxide (31%).

The elimination reactions involving the diastereoisomers (1) and (2) thus seem to be adequately interpreted in terms of Scheme 2 which is analogous to the similar scheme used by Jones and Trippett [8] for the Wittig reaction.

Starting from *threo*-phosphine oxide, $k(-T)/k'(T)$ is small under all conditions used, presumably because there are no unfavourable Ph,Ph eclipsing interactions in the transition state for the elimination of diphenylphosphinate to give (*E*)-stilbene.

In contrast, starting from *erythro*-phosphine oxide, $k(-E)/k'(E)$ is high under many conditions, and there are indications (entries 6 and 7, Table) that the ' reverse aldol ' process $[k(-E)]$ can be fast compared to the recombination leading ultimately to (*E*)-stilbene $[k(T)]$. The lowest $k(-E)/k'(E)$ ratios were obtained either using BuLi–THF (Table, entry 4) under conditions which are difficult to reproduce (see above) or using DBU as base (Table, entries 10 and 11). Under these latter conditions virtually no recombination to the *threo*-adduct is found, presumably because benzyldiphenylphosphine oxide is a weaker acid than protonated DBU.

In summary, difficulties arise in the stereospecific fragmentation of *erythro*-β-hydroxydiphenylphosphine oxides to olefins in those cases where an aryl group is attached at the carbon bearing phosphorus. One way of minimising these

difficulties by incorporating the phosphorus atom in a five-membered ring and using β-hydroxydibenzophosphole oxides will be described in a forthcoming publication.[9]

Experimental

1,2-*Diphenyl*-2-*diphenylphosphinoylethan*-1-*ol*.—n-Butyllithium (2.3 ml; 1.5M in hexane) was added from a syringe to a stirred solution of benzyldiphenylphosphine oxide (1.0 g, 3.42 mmol) in dry THF (30 ml) at 0 °C. After 30 min the dark red coloured solution was cooled to −78 °C (acetone–solid CO_2) and benzaldehyde (363 mg, 3.42 mmol) was added dropwise from a syringe at such a rate as to maintain the internal temperature at −78 °C. The solution temperature was then allowed to reach 0 °C (during *ca.* 25 min) before water (20 ml) was added and the THF removed under reduced pressure. The aqueous residue was diluted with brine (15 ml), extracted with dichloromethane (3 × 30 ml), and the combined organic extracts dried ($MgSO_4$) before being evaporated to dryness. The product was obtained as a crystalline mixture of diastereoisomers which were separated by flash column chromatography (elution with EtOAc). The first diastereoisomer to elute from the column was the (1*RS*,2*SR*)-adduct (1) (277 mg, 20.4%), m.p. 198—199 °C (from EtOAc–light petroleum, b.p. 60—80 °C) (Found: C, 78.4; H, 6.05; P, 7.75. $C_{26}H_{23}O_2P$ requires C, 78.4; H, 5.85; P, 7.8%); $\nu_{max.}$ 3 450 (OH), 1 435 (PPh), and 1 150 cm^{-1} (P=O); δ ($CDCl_3$) 8.15—6.7 (20 H, m, 4 × Ph), 5.5 (1 H, dd, J_{HH} 2, J_{HP} 9 Hz, C*H*OH), 5.1 (1 H, s, OH), and 3.6 (1 H, dd, J_{HH} 2, J_{HP} 8 Hz, CHP) (Found: M^+, 380.1341. $C_{26}H_{23}O_2P$ requires *M*, 380.1330); *m*/*z* 380 (3%), 379 (3, *M* − 1), 292 (63, Ph_2POCH_2Ph), 291 (100, $Ph_2POCHPh^+$), and 201 (Ph_2PO^+). The second diastereoisomer to elute from the column was the (1*RS*,2*RS*)-adduct (2) (143 mg, 10.5%), m.p. 199—201 °C (from EtOAc–light petroleum, b.p. 60—80 °C) (Found: C, 78.5; H, 6.0; P, 8.05. $C_{26}H_{23}O_2P$ requires C, 78.4; H, 5.85; P, 7.8%); $\nu_{max.}$ 3 200 (OH), 1 440 (PPh), and 1 170 cm^{-1} (P=O); δ ($CDCl_3$) 7.9—6.7 (20 H, m, 4 × Ph), 5.7 (1 H, d, J_{HOH} 4 Hz, OH), 5.45 (1 H, ddd, J_{HOH} 4, $J_{HH} = J_{HP} = 9$ Hz, C*H*OH), and 3.95 (1 H, dd, $J_{HH} = J_{HP} = 9$ Hz, CHP) (Found: M^+, 380.1337. $C_{26}H_{23}O_2P$ requires *M*, 380.1330); *m*/*z* 380 (2%), 292 (93, Ph_2POCH_2Ph), 291 (100, $Ph_2POCHPh^+$), and 201 (49, Ph_2PO^+).

When the above experiment was repeated with anhydrous lithium iodide (458 mg, 3.42 mmol) dissolved in the reaction solution, the (1*RS*,2*SR*)- and (1*RS*,2*RS*)-adducts were obtained as an amorphous solid (1.2 g, 88.2%) in the ratio 73 : 17 respectively as judged by n.m.r. analysis of the corresponding methine signals.

erythro-1,2-*Diphenyl*-2-*diphenylphosphinoylethanol*.—A solution of lithium diphenylphosphide,[10] prepared in THF (35 ml) from triphenylphosphine (13.1 g, 50.0 mmol), was added to a solution of *trans*-2,3-diphenyloxirane (7.35 g, 37.5 mmol) in THF (10 ml). Reaction and work-up under the usual conditions gave a solid which was recrystallized from benzene to give (1*RS*,2*SR*)-1,2-diphenyl-2-diphenylphosphinoylethanol (13.82 g, 93%), m.p. 192—194 °C after being dried *in vacuo*. The n.m.r. spectrum (in $CDCl_3$) was identical with that presented above.

threo-1,2-*Diphenyl*-2-*diphenylphosphinoylethanol*.—A solution of lithium diphenylphosphide, prepared in THF (25 ml) from triphenylphosphine (7.86 g, 30.0 mmol), was added to a 4 : 1 mixture of *cis*- and *trans*-2,3-diphenyloxirane (3.92 g, 20.0 mmol) in THF (5 ml). Reaction and work-up under the usual conditions gave a gum (9.72 g). This crystallized on addition of benzene (20 ml) and recrystallization gave (1RS,2RS)-1,2-*diphenyl*-2-*diphenylphosphinoylethanol* (4.15 g, 65%), m.p. 191—195 °C after two more recrystallizations and prolonged drying. The n.m.r. spectrum (in $CDCl_3$) was identical with that obtained above.

General Procedure for Reaction of erythro-1,2-*Diphenyl*-2-*diphenylphosphinoylethanol with Base*.—The base (relative quantity given in the Table) and the *erythro*-β-phosphinoyl alcohol in solvent (total volume 5—20 ml/mmol alcohol) were mixed (addition time *ca.* 4 min) with stirring at the temperature to be used for the subsequent reaction. The reaction period indicated in the Table was followed by work-up with water and extraction into either dichloromethane or chloroform. The acid-washed organic phase was dried (Na_2SO_4) and the solvent was then removed.

A crystalline or liquid product indicated the formation of olefinic product only, and this was confirmed by n.m.r., i.r., and t.l.c. If an amorphous solid was obtained, it was triturated with light petroleum (b.p. 30—40 °C). The insoluble phosphine oxide was filtered off, dried, and identified by n.m.r. and i.r. Benzyldiphenylphosphine oxide typically had m.p. 191—194 °C [highest recorded m.p. 195.5—196.5 °C (lit.,[11] m.p. 193—195 °C)]. Removal of solvent from the filtrate gave (*Z*)- and/or (*E*)-stilbene, identified by n.m.r., i.r., and t.l.c. The *Z*/*E* olefin ratio was estimated from the relative peak heights of the olefinic proton resonances at δ (CCl_4) 6.51 [CH=CH of (*Z*)-stilbene] and 7.01 [CH=CH of (*E*)-stilbene] and/or by g.l.c. Yields are given in the Table.

Traces of 1-butyldiphenylphosphine oxide (arising from the preparation of the β-phosphinoyl alcohol) were a frequent contaminant in the olefinic product, δ (CCl_4) 1.19 (d, *J* 15 Hz, Bu^t), 7.30—7.52 (m, aromatic), 7.80—8.04 (m, aromatic) [lit.,[12] δ (CCl_4) 1.16 (d, *J* 14.0 Hz, Bu^t), 7.18—7.33 and 7.61—7.95 (Ph)], and could be removed by dissolution in light petroleum (b.p. 30—40 °C), filtration through neutral alumina, and evaporation of the filtrate.

Reaction of threo-1,2-*Diphenyl*-2-*diphenylphosphinoylethanol with Base*.—Reaction of *threo*-1,2-diphenyl-2-diphenylphosphinoylethanol with sodium methoxide in THF, tetra-n-butylammonium hydroxide in THF, or DBU in THF gave, as described below, in all cases crystalline (*E*)-stilbene, identified by n.m.r. and i.r. comparison with an authentic sample, δ (CCl_4) 7.01 (2 H, s, CH=CH), 7.10—7.52 (10 H, m, Ph); δ ($CDCl_3$) 7.08 (2 H, s, CH=CH), 7.15—7.60 (10 H, m, Ph), with no detectable impurity by t.l.c.

(*a*) *Sodium methoxide in THF*. A solution of the *threo*-alcohol (1.99 g, 5.00 mmol) in THF (30 ml) was added to sodium methoxide (6.67 mmol) in THF (5 ml). After 45 min at 20 °C the white suspension was poured into water (50 ml); extraction with diethyl ether (25 ml), followed by removal of solvent from the dried ($MgSO_4$) solution, gave (*E*)-stilbene (0.75 g, 83%).

(*b*) *Tetra-n-butylammonium hydroxide in THF*. To a solution of tetra-n-butylammonium hydroxide (1.69 mmol) in THF (6 ml) was added a solution of the *threo*-alcohol (0.20 g, 0.503 mmol) in THF (3 ml). After 3 h at 20 °C water (10 ml) was added, the mixture was extracted with diethyl ether (20 ml), and the organic phase was washed with water and dried (Na_2SO_4). Removal of solvent gave (*E*)-stilbene (85.6 mg, 95%).

(*c*) *DBU in THF*. To a refluxing solution of the *threo*-alcohol (0.20 g, 0.503 mmol) in THF (3 ml) was added a solution of DBU (96%; 0.16 g, 1.01 mmol) in THF (4 ml). After 3 h at reflux water (10 ml) was added, the mixture was allowed to cool, and diethyl ether (20 ml) was added to dissolve the suspended crystals. The organic phase was washed with water, hydrochloric acid (2M), and then more water, and dried

(Na_2SO_4). Removal of solvent gave (*E*)-stilbene (91.8 mg, 101%).

(*d*) *Potassium hydroxide in DMSO*. The *threo*-alcohol (47 mg, 0.12 mmol) was added in one portion to a stirred solution of potassium hydroxide (8 mg; 85% pure, 0.12 mmol) in dry DMSO (5 ml). The reaction solution was heated for 1 h at 50 °C and then cooled to room temperature; water (10 ml) was added and the solution extracted with diethyl ether (3 × 10 ml). The organic phases were combined, washed with water (3 × 20 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure. Bulb-to-bulb distillation (Kugelrohr) gave (*E*)-1,2-diphenylethene (20 mg, 95.2%) as needles, m.p. 120—122 °C (lit.,[13] 123—124 °C). The i.r. and n.m.r. spectra were identical with those of an authentic sample of the (*E*)-alkene. The (*Z*)-isomer was not detected by g.l.c.

(*Z*)-1,2-*Diphenylethene*.—n-Butyl-lithium (0.12 ml; 1.5M in hexane) was added dropwise from a syringe to a stirred solution of the *erythro*-alcohol (1) (73 mg, 0.18 mmol) in dry THF (10 ml) at 0 °C. As each drop of n-butyl-lithium was added a yellow colour formed which at first rapidly disappeared, but then persisted when all the base had been added. The reaction solution was allowed to warm to room temperature, after which time a white solid had precipitated out. The precipitate was dissolved by adding water (10 ml) and then the THF was removed under reduced pressure. The aqueous residues were extracted with dichloromethane and the combined organic extracts dried ($MgSO_4$) before removing the solvent under reduced pressure. Bulb-to-bulb distillation (Kugelrohr apparatus) gave the alkene (20 mg, 60.6%) as a colourless liquid, b.p. 148—151 °C at 20 mmHg (lit.,[14] b.p. 133—136 °C at 10 mmHg). The i.r. and n.m.r. spectra were identical with those of an authentic sample of the (*Z*)-alkene. G.l.c. analysis showed that the product contained *ca.* 5% of the *E*-isomer. The distillation residue (20 mg) gave an n.m.r. spectrum similar to that of benzyldiphenylphosphine oxide.

Reaction of erythro-1,2-*Diphenyl-2-diphenylphosphinoylethanol with Tetra-n-butylammonium Hydroxide in the Presence of* m-*Chlorobenzaldehyde*.—A solution of tetra-n-butylammonium hydroxide (4.16 mmol) in THF (15 ml) was added during 15 min to a stirred suspension of *erythro*-1,2-diphenyl-2-diphenylphosphinoylethanol (1.67 g, 4.20 mmol) and *m*-chlorobenzaldehyde (1.80 g, 12.81 mmol, 3.05 equiv.) in THF (15 ml). All the suspended β-phosphinoyl alcohol dissolved during the addition, and the yellow solution was stirred at 26 °C for 3 h. Water (50 ml) was added during 2 min, followed by diethyl ether (25 ml). The ethereal solution was washed with water and the solvent removed to give a damp solid which was triturated with light petroleum (b.p. 40—60 °C) (20 ml). The insoluble benzyldiphenylphosphine oxide was filtered off, washed with light petroleum and dried (0.38 g, 31%), m.p. 192—194 °C, identified by n.m.r. and i.r. The filtrate and washings were concentrated to 20 ml, and the solution was shaken with aqueous sodium hydrogen sulphite (52% w/v; 25 ml) to remove aldehydes and allowed to stand for several hours, during which time a considerable amount of crystalline precipitate appeared. The organic layer was then washed with water and dried (Na_2SO_4–$Na_2S_2O_5$). Removal of the solvent gave solid (*E*)-*m*-chlorostilbene (0.53 g, 59%), δ (CCl_4) 6.95 and 7.02 (2 H, AB quartet with low field outer line obscured by aromatic region, J = 17 Hz, CH=CH) and 7.12—7.50 (9 H, m, aromatic). Recrystallization from aqueous ethanol gave (*E*)-*m*-chlorostilbene (0.34 g, 38%), m.p. 71.0—72.5 °C (lit.,[15] m.p. 73—74 °C), $\lambda_{max.}$ (EtOH) 221 (ε 1.68 × 10^4), 228 (1.85 × 10^4), 233 (1.82 × 10^4), 297 (3.19 × 10^4), and 307 nm (2.99 × 10^4) [lit.,[16] $\lambda_{max.}$ (cyclohexane) 300 nm (ε 2.68 × 10^4)]. Chloroform extraction of the mother-liquor gave a yellow liquid–solid mixture (70 mg); t.l.c. and n.m.r. indicated that it contained (*E*)-*m*-chlorostilbene, (*Z*)-stilbene, and (*Z*)-*m*-chlorostilbene, δ (CCl_4) 6.51 [s, CH=CH of (*Z*)-stilbene], 6.47 and 6.61 [AB quartet, J 12 Hz, CH=CH of (*Z*)-*m*-chlorostilbene].

Similar results were obtained using sodium hydride–THF and sodium methoxide–THF as bases.

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