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Study of the mechanism of base induced dehydrobromination of *trans*-β-bromostyrene

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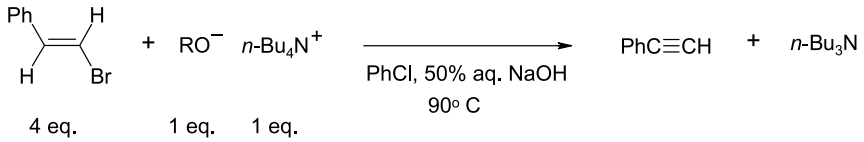
Abstract—Observation that rates of dehydrobromination of *trans*-β-bromostyrene (**1**) and the Hofmann degradation of tetrabutyl ammonium cation depend on strength of base in different ways and that treatment of **1** with base results in fast abstraction of the β-proton imply the possibility that the dehydrobromination of **1** could proceed via α-elimination and Ph migration. In order to clarify this question, β-^{13}C-labeled **1** was obtained and subjected to PTC dehydrobromination which proceeds without migration of Ph. The obtained results are consistent with an irreversible E1cB mechanism. © 2003 Published by Elsevier Science Ltd.

During our studies on co-catalysis in phase-transfer catalyzed base induced dehydrobromination of *trans*-β-bromostyrene (**1**)[1] a very interesting observation was made. The relation of the rates of two competing reactions: dehydrobromination of **1** and the Hofmann degradation of tetrabutylammonium (TBA) cation depends very much on the strength of the basic agent (Table 1). Surprisingly, the most selective was the strongest base $-OH^-$ anion which reacted practically exclusively with **1** not with TBA, whereas much weaker bases such as ArO^- reacted faster with TBA. We have shown[1] that under described conditions the degradation of the TBA cation occurs as the normal Hofmann β-elimination process, not as a nucleophilic substitution of Bu_3N in the TBA cation, so that the phenomenon cannot be explained in terms of nucleophilicity of the basic agents. The observed facts prompted us to perform some studies on the mechanism of base induced dehydrobromination of *trans*-β-bromostyrene.

1. Results and Discussion

The observations mentioned above suggest that there is a principal difference between the mechanisms of dehydrobromination of *trans*-β-bromostyrene and the Hofmann degradation of the TBA cation. Whereas the Hofmann degradation of the TBA cation most likely follows a one-step E2 mechanism,[3] in the case of *trans*-β-bromostyrene, for which an E2-type mechanism seems to be unlikely due to the geometry of the molecule, a two-step E1cB

Table 1. Dehydrobromination of *trans*-β-bromostyrene versus Hofmann degradation of TBA cation promoted by different TBA salts at 90°C



Entry	RO^-	pK_a of ROH (DMSO)[a]	Time (min)	Ratio (PhC≡CH/*n*-Bu_3N)[b]
1	HO^-	31.2	0.5	23.8
2	*n*-BuO^-	≈29.8	0.5	10.0
3	$PhCH_2O^-$	27.0	2	3.9
4	ArO^-[c]	≈18.5	60	0.6

For experimental see Ref. 1.

[a] According to Bordwell.[2]

[b] Determined by GLC and ^{1}H NMR using durene as an internal standard; the sum of PhC≡CH and *n*-Bu_3N was ≈100% in regard to the initial amount of TBA salt.

[c] Ar=2,4,6-trimethylphenyl.

Keywords: *trans*-β-bromostyrene; β-elimination; irreversible E1cB mechanism; ^{13}C-labeled compounds.

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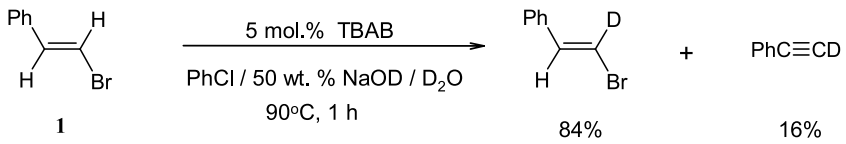
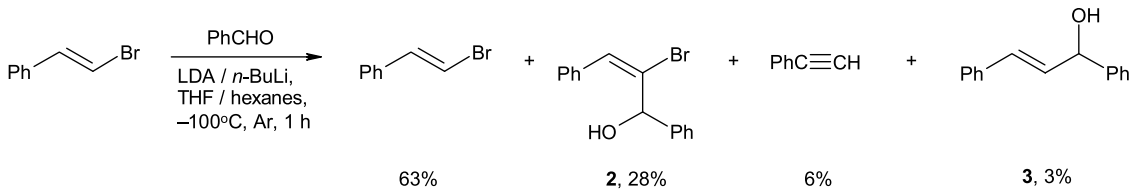
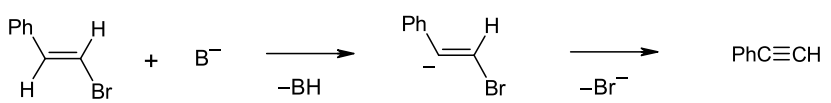


Scheme 1.

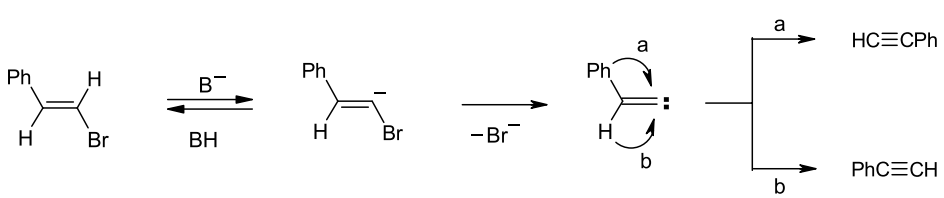


Scheme 2.

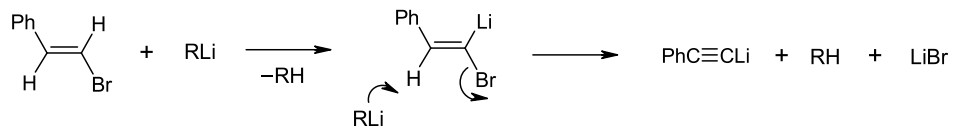
mechanism might operate. That is supported by earlier observation that in NaOH/*i*-PrOH medium *trans*-β-bromostyrene was found to be 10^5 times less reactive than the *cis*-isomer for which an E2-type mechanism is feasible.[4] Moreover, the introduction of a strongly electron withdrawing group (NO_2) into the *para* position of the aromatic ring resulted in a much more substantial acceleration of the reaction rate for the *trans*-isomer than for the *cis* one.[4] These observations suggest that carbanionic species are involved in the rate-determining step of the base induced dehydrobromination of the *trans*-isomer. Taking into account the fact that the dehydrobromination of **1** according to an E1cB mechanism would require deprotonation of a very weak C–H acid (PhCH=CHBr) the basicity of RO^- should be a more important factor in dehydrobromination of **1** than in the Hofmann degradation of the TBA cation, which, if it followed a concerted E2 mechanism, would not require the generation of a carbanion. If base induced dehydrobromination of **1** proceeds via a carbanionic intermediate (e.g. E1cB mechanism) then one might suppose that a deuterium exchange of acidic hydrogen(s) in **1** should be observed during the course of the dehydrobromination when the reaction is carried out in an OD^-/D_2O medium. We performed such an experiment under PTC conditions (Scheme 1) stopping the reaction after 16% conversion (GLC) of **1** to phenylacetylene. To our surprise a total H/D exchange in unreacted **1** took place at the β-carbon atom (β-C) whereas there was no incorporation of D at α-carbon. The observed H/D ratio=3/97 (^{1}H NMR) at β-C corresponded to the total ratio of exchangeable H and D in the studied system. Absence of any detectable H/D exchange at α-C was confirmed by ^{1}H NMR studies of the crude reaction mixture using characteristic signal from two aromatic protons of phenylacetylene (δ 7.55 ppm, m) as the internal standard. Thus, in *trans*-β-bromostyrene β-H is much more acidic than corresponding α-H, so that the former is rapidly abstracted by a base to generate the α-bromocarbanion. On the other hand, it was shown earlier that in *cis*- and *trans*- β-chlorostyrenes, β-protons exhibit higher acidity than α-protons.[5] Obviously a bromine atom as well as a chlorine atom stablizes a vinyl carbanion better than the phenyl group does. An example of successful trapping of the PhCH=C$^-$Br carbanion with TMSCl has been reported in the literature.[6] We have also succeeded in trapping the PhCH=C$^-$Br carbanion selectively by means of rapid reaction with another active electrophile – benzaldehyde. When a 1:1 molar mixture of **1** and PhCHO was treated at −100°C with a mixture of 1 equiv. LDA and 1.3 equiv. *n*-BuLi we observed the formation of the corresponding adduct **2** as a main product accompanied by a small amount of phenylacetylene as well as the adduct of metallated styrene, produced by halogen metal exchange in **1**, to benzaldehyde **3** (Scheme 2). The ratio of the products was established on the basis of the ^{1}H NMR spectrum and subsequently confirmed by isolation of **2** and unreacted **1** from the crude reaction mixture using silica column chromatography. The other products found in the crude reaction mixture were *n*-BuCH(OH)Ph (**4**, 37%), benzyl alcohol (16%) and unreacted PhCHO (16%). It is worth noting that use of LDA or *n*-BuLi as a base separately did not give access to **2**. Whereas LDA alone was proved to be too weak a base to sufficiently deprotonate **1** under the reaction conditions at −100/−70°C (the only isolated products were benzyl alcohol, unreacted **1** and excess benzaldehyde), the use of *n*-BuLi alone as a base mainly gave its adduct with benzaldehyde **4**. On the other hand,



Scheme 3.



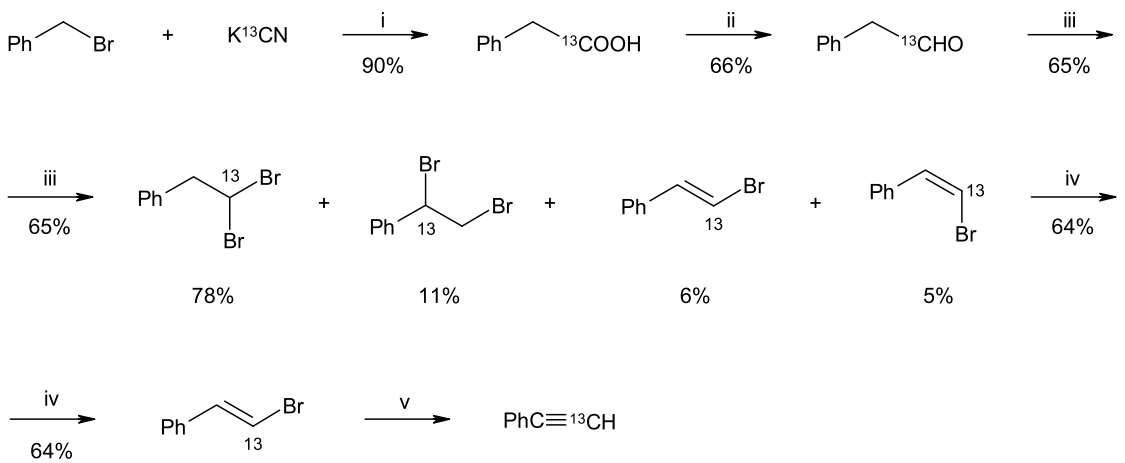
Scheme 4.



Scheme 5.

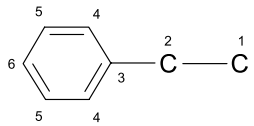
when the reaction was carried out at −78°C we observed formation of **2** and phenylacetylene in practically equal proportions.

Taking into account the observations mentioned above we supposed that base induced dehydrobromination of **1** might follow the irreversible E1cB mechanism (Scheme 3) or might involve a migration of phenyl group or hydrogen to the electron deficient alkylidene carbene centre produced via elimination of Br^- from PhCH=C^-Br carbanion (α-elimination process, Scheme 4). Alkylidene carbenes are known species and intermediates in organic reactions, which can easily undergo 1,2-shift rearrangements to give alkynes.[7] It has already been observed that α-methyl-β-halostyrenes in the presence of strong bases gave methylphenylacetylenes.[8] For instance, treatment of diethyl ether solution of (*E*)- or (*Z*)-α-methyl-β-bromostyrene (PhC(Me)=CHBr) with equimolar amount of *n*-BuLi at −30 to 0°C gave rise to methylphenylacetylene (PhC≡CMe) in a high yield.[8c] The nature of the products and trapping experiments provided compelling evidence for the intermediacy of alkylidene carbenes in these reactions (Scheme 4).[8a] However, all our attempts to trap eventual carbene species in the studied PTC dehydrobromination of **1** have failed. When the reaction was carried out in the presence of 3 equiv. of styrene as a 'carbene trap' no corresponding cyclopropane derivatives formed from the alkylidene carbene and styrene were detected by ^{1}H NMR in the crude reaction mixture. On the other hand, the migration of phenyl or hydrogen to the carbene center (Scheme 4) should be very rapid or even simultaneous with the departure of bromide.[9,10] Thus, the life time of the carbene might be too short to make possible its trapping. The process presented in Scheme 4 is very close to the known Fritsch–Buttenberg–Wiechell rearrangement which is generally observed during the action of bases on α,α-diaryl-β-halogenoethylenes and involves α-elimination of hydrogen halide and migration of an aryl group to the neighboring carbon atom to give diarylacetylenes.[10] Experiments with labeled *cis*–*trans*-isomeric starting compounds have shown that migration of the aryl group *trans* to the vinyl halogen always predominates indicating that departure of the leaving group is assisted by the migrating group.[10,11] For direct determination of which mechanistic way, namely the normal β-elimination or α-elimination followed by 1,2-shift rearrangement of the formed carbene, operates in the case of base induced dehydrobromination of **1** it is necessary to use an isotopically labeled sample of **1**. Since the formed product (phenylacetylene) is much more acidic than the substrate, D/H isotope labeling is of no use, because the obtained phenylacetylene would always contain the equilibrium D/H isotope ratio. As was observed by Curtin et al.[11b] dehydrobromination of *cis*- and *trans*-β-bromostyrene-α-^{14}C by butyllithium in ether at −35°C — the typical conditions for the execution of the Fritsch–Buttenberg–Wiechell rearrangement of α,α-diaryl-β-bromoethylenes to diarylacetylenes, proceeds without migration of the phenyl group during the course of the reaction. However, under the conditions used by Curtin et al.[11b] (very strong base such as BuLi and low temperatures) a so-called E2cB mechanism (Scheme 5) might operate as was suggested and experimentally evidenced by Schlosser[5,10] in the case of the organolithium-induced elimination of hydrogen chloride from *cis*- and *trans*-β-chlorostyrene. It should be stressed that the particular mechanism of dehydrobromination of **1** obviously depends very much on the kind of base used and the applied conditions. For instance, Cristol et al.[12] reported that the rate of the reaction of *trans*-β-bromostyrene with phenyllithium in ether or Bu_2O at +25°C was 2–6 times faster than that of the *cis*-β-bromostyrene in contrast to their behavior toward alkali in isopropyl alcohol.[4] Taking into account the



Scheme 6. *Reagents and conditions*: (i)[13] (a) 90% aq. EtOH, 25°C, 24 h, then 50°C, 5 h; (b) 30% aq. NaOH, reflux, 24 h. (ii)[14] (a) $Me_2CHCMe_2BHCl{\cdot}Me_2S$ (2.2 equiv.), CH_2Cl_2, Ar, 0–25°C, 30 min; (b) aq. $NaHSO_3$, CH_2Cl_2/THF, 25°C, 12 h; (c) 37% aq. CH_2O (1.0 equiv.), aq. $MgSO_4$, pentane, 25°C, 1 h. (iii)[15] *o*-$C_6H_4O_2PBr_3$ (1.1 equiv.), CH_2Cl_2, Ar, 25°C, 2 h. (iv)[1,16] 50% aq. NaOH, TBAB (0.05 equiv.), mesitol (0.05 equiv.), 25°C, 24 h. (v)[1] 50% aq. NaOH, TBAB (0.05 equiv.), chlorobenzene, 90°C, 24 h (80% conversion).

Table 2. ^{1}H and ^{13}C NMR data on the synthesized ^{13}C-labeled compounds



Compound	^{1}H NMR	^{13}C NMR
$PhCH_2^{13}COOH$	δ 3.7 (d, 2H, H2, $^{2}J_{H2C1}$=7.7 Hz); 7.4 (m, 5H, Ph); 10.9 (bs, 1H, COOH)	δ 41.1 (d, C2, $^{1}J_{C2C1}$=55.4 Hz); 127.3 (s, C6); 128.6 (s, C5); 129.3 (d, C4, $^{3}J_{C4C1}$=1.8 Hz); 133.2 (d, C3, $^{2}J_{C3C1}$=2.7 Hz); 178.1 (intensive s, C1)
$PhCH_2^{13}CHO$	δ 3.7 (dd, 2H, H2, $^{2}J_{H2C1}$=7.3 Hz, $^{3}J_{H2H1}$=2.4 Hz); 7.3–7.4 (m, 5H, Ph); 9.4, 10.2 (dt, 1H, H1, $^{1}J_{H1C1}$=175.6 Hz, $^{3}J_{H1H2}$=2.4 Hz)	δ 50.5 (d, C2, $^{1}J_{C2C1}$=37.5 Hz); 127.4 (s, C6); 128.9 (s, C5); 129.6 (d, C4, $^{3}J_{C4C1}$=1.8 Hz); 131.8 (d, C3, $^{2}J_{C3C1}$=2.3 Hz); 199.3 (intensive s, C1)
$PhCH_2^{13}CHBr_2$	δ 3.8 (t (unresolved dd), 2H, H2, $^{3}J_{H2H1}$=6.8 Hz, $^{2}J_{H2C1} \approx$ 6.2 Hz); 5.4, 6.3 (dt, 1H, H1, $^{1}J_{H1C1}$=178.7 Hz, $^{3}J_{H1H2}$=6.8 Hz); 7.3–7.5 (m, 5H, Ph)	δ 45.1 (intensive s, C1); 51.4 (d, C2, $^{1}J_{C2C1}$=35.7 Hz); 127.6 (s, C6); 128.6 (s, C5); 129.4 (d, C4, $^{3}J_{C4C1}$=2.2 Hz); 136.7 (d, C3, $^{2}J_{C3C1}$=2.2 Hz)
$Ph^{13}CHBrCH_2Br$	δ 4.1 (m, 2H, H1); 4.8, 5.6 (ddd, 1H, H2, $^{1}J_{H2C2}$=157.0 Hz, $^{3}J_{H2H1}$=10.1 Hz; $^{3}J_{H2H1'}$=6.0 Hz); 7.4 (m, 5H, Ph)	
trans-$PhCH{=}{}^{13}CHBr$	δ 6.3, 7.3 (dd, 1H, H1, $^{1}J_{H1C1}$=194.2 Hz, $^{3}J_{H1H2}$=14.0 Hz); 7.1–7.2 (dd, 1H, H2, $^{3}J_{H2H1}$=14.0 Hz, $^{2}J_{H2C1}$=9.2 Hz); 7.3–7.4 (m, 5H, Ph)	δ 106.5 (intensive s, C1); 126.0 (d, C4, $^{3}J_{C4C1}$=5.9 Hz); 128.2 (s, C6); 128.7 (s, C5); 135.9 (d, C3, $^{2}J_{C3C1}$=1.8 Hz); 137.1 (d, C2, $^{1}J_{C2C1}$=79.6 Hz)
cis-$PhCH{=}{}^{13}CHBr$	δ 6.0, 7.0 (dd, 1H, H1, $^{1}J_{H1C1}$=198.6 Hz, $^{3}J_{H1H2}$=8.2 Hz); 7.1 (t (unresolved dd), 1H, H2, $^{2}J_{H2C1}\approx$8.6 Hz, $^{3}J_{H2H1}$=8.2 Hz); 7.4 (m, 5H, Ph)	
$Ph^{13}CBr{=}CH_2$	δ 5.8 (dd, 1H, H1, $^{2}J_{H1C2}$=6.5 Hz, $^{2}J_{H1H1'}$=2.0 Hz); 6.2 (dd, 1H, H1′, $^{2}J_{H1'C2}$=5.3 Hz, $^{2}J_{H1'H1}$=2.0 Hz); 7.4 (m, 5H, Ph)	
$PhC{\equiv}{}^{13}CH$	δ 2.5, 3.8 (d, 1H, H1, $^{1}J_{H1C1}$=251.1 Hz); 7.4 (m, 3H, H5, H5′, H6); 7.6 (m, 2H, H4, H4′)	δ 77.2 (intensive s, C1); 84.0 (d, C2, $^{1}J_{C2C1}$=181.5 Hz); 122.0 (d, C3, $^{2}J_{C3C1}$=12.8 Hz); 128.3 (s, C5); 128.7 (s, C6); 132.1 (d, C4, $^{3}J_{C4C1}$=2.5 Hz)
$Ph^{13}C{\equiv}CH$	δ 3.1 (d, 1H, H1, $^{2}J_{H1C2}$=49.6 Hz); 7.4 (m, 3H, H5, H5′, H6); 7.6 (m, 2H, H4, H4′)	

considerably higher temperature under the PTC conditions applied by us (50% aq. NaOH, cat. Q^+Br^-, 90°C) we supposed that in this case the mechanism of base induced dehydrobromination of **1** might involve a migration of the phenyl group. We have synthesized a sample of β-^{13}C-labeled *trans*-β-bromostyrene in a 25% overall yield on the basis of known procedures[13–16] starting from $K^{13}CN$ (1.0 g scale) and benzyl bromide (Scheme 6, i–iv; notice a formation of considerable amounts of $Ph^{13}CHBrCH_2Br$ from $PhCH_2^{13}CHBr_2$ as a result of migration of the phenyl group to the positively charged carbon atom under acidic conditions, see Scheme 6, iii). ^{1}H and ^{13}C NMR data for the synthesized ^{13}C-labeled compounds are summarized in Table 2. Under the PTC conditions the obtained ^{13}C-labeled **1** gave phenylacetylene without any migration of the phenyl group (Scheme 6, v), i.e. path 'a' in Scheme 4 can be excluded. As was mentioned above, eventual migration of hydrogen during dehydrobromination of **1** (path 'b' in Scheme 4) cannot be determined directly by use of deuterium labeling in **1**. There is no literature data on the relative migratory aptitudes of hydrogen and phenyl for the 1,2-shift to the carbene centre. However, taking into account that both these processes are very fast[7–10] and migration of the phenyl group in **1** would be rather preferred to the migration of the α-H since Ph is in the *trans* position to the halogen,[11] the absence of any detectable migration of the phenyl group during the studied dehydrobromination of **1** suggests that α-elimination/1,2-H migration pathway 'b' is probably not operating in this case either.

On the basis of these data we could suggest that base induced dehydrobromination of *trans*-β-bromostyrene carried out under PTC conditions[17] or in alcoholic alkali medium most likely follows an irreversible E1cB mechanism (Scheme 3). Moreover, taking into account the fact that acidity of a hydrogen in the α-position to the leaving group is much higher than in the β-position, the extremely low reactivity of the *trans*-β-bromostyrene towards base induced β-elimination of HBr by the action of bases of moderate strength (OH^-, RO^-, etc.) becomes more understandable.

2. Experimental

Isomerically pure *trans*-β-bromostyrene **1** (*trans*/*cis* >99/1 by ^{1}H NMR and GLC) was obtained from commercially available β-bromostyrene (Fluka, *trans*/*cis* ≈85/15) by selective conversion of the more reactive *cis* isomer into phenylacetylene under mild cocatalytic PTC conditions, excess of 50% aq. NaOH, 1 mol% of TBAB, 1 mol% of mesitol, stirring for 24 h at room temperature,[16] followed by distillation of the crude organic product (**1**/$PhC{\equiv}CH$ ≈85/15) under reduced pressure. It was stored in a refrigerator at

0–4°C. 50 wt% NaOD/D_2O was prepared by careful treatment of Na_2O (Aldrich) with calculated amount of D_2O under Ar and external cooling with an ice/water bath. GLC analyses were performed using 'Shimadzu GC-14A' gas chromatograph; injection port temperature 120°C; injection time 1 min. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini spectrometer (200 MHz for ^1H). Chemical shifts are indirectly referenced to TMS via the solvent signal (chloroform-d_1 7.26 and 77.0 ppm).

2.1. Studies of H/D exchange during base induced dehydrobromination of *trans*-β-bromostyrene (1)

A 10 ml flask was charged with a mixture of **1** (0.366 g, 2 mmol), chlorobenzene (0.20 g), TBA bromide (0.032 g, 0.1 mmol) and 50 wt% NaOD/D_2O (1.7 g, ≈1 ml, ≈90 mmol D). The flask was tightly closed with a stopper using a metallic clip and placed on the magnetic stirrer equipped with an oil bath thermostated at 90°C. The mixture was stirred at 90°C for 1 h and cooled with cold water. Small samples of the organic phase were taken and analyzed by GLC (diluted with CH_2Cl_2) and ^1H NMR techniques.

2.1.1. *trans*-β-Bromostyrene (1). ^1H NMR (see also Table 2) δ 6.8 (d, 1H, H1, $^3J_{H1H2}$=14.0 Hz); 7.1 (d, 1H, H2, $^3J_{H2H1}$=14.0 Hz); 7.3–7.4 (m, 5H, Ph). ^{13}C NMR (see also Table 2): δ 106.5 (C1); 126.0 (C4); 128.2 (C6); 128.7 (C5); 135.9 (C3); 137.1 (C2).

2.1.2. *trans*-β-Bromostyrene-β-*d* (1-*d*). ^1H NMR δ 7.15 (t, 1H, H2, $^3J_{H2D1}$=2.0 Hz); 7.3–7.4 (m, 5H, Ph).

2.2. Base induced condensation of *trans*-β-bromostyrene with benzaldehyde

A 25 ml oven-dried three-neck round-bottom flask equipped with a septum, an inlet of dry Ar and an oil pump was degassed in vacuum and filled with Ar (3 times). The flask was cooled to about −80°C (an ether–liquid nitrogen bath) and charged with dry THF (3 ml, distilled from Na/benzophenone prior to use) and dry diisopropyl amine (0.28 ml, 2 mmol). A 1.6 M solution of *n*-BuLi in hexanes (2.8 ml, 4.5 mmol) was added to the flask with vigorous stirring. The flask was then cooled to −100°C and a solution of **1** (0.366 g, 2 mmol) and benzaldehyde (0.212 g, 2 mmol) in dry THF (2 ml) was added dropwise during 10 min period time to give a yellow homogeneous mixture. The mixture was stirred for 1 h at −100°C and quenched with an excess of acetic acid (1 ml). After warming to 0–20°C, ether (10 ml) and water (5 ml) were added. The organic layer was separated, washed with saturated $NaHCO_3$ (2×5 ml) and dried with Na_2SO_4. After evaporation of the solvents under reduced pressure, the residue was subjected to flash chromatography (SiO_2, hexane→hexane/acetone (10/1)) to give the following compounds:

(*E*)-2-Bromo-1,3-diphenylallyl alcohol (2): An analytically pure sample was obtained by recrystallization from *n*-pentane of the crude material after SiO_2 column. Mp 79–80°C (uncorrected). ^1H NMR δ 2.7 (broad s, 1H, OH), 5.9 (s, 1H, H1), 7.3–7.5 (m, 11H, H3+2Ph). ^{13}C NMR: δ 71.2, 125.8, 127.7, 128.0, 128.3, 128.6, 131.6, 134.9, 135.3, 140.3. MS (EI, 70 eV) *m/z* (%): 290 (36), 288 (37), 209 (86), 191 (74), 131 (72), 103 (67), 77 (100). $C_{15}H_{13}BrO$ calculated: C 62.30, H 4.53, Br 27.63; found: C 62.06, H 4.34, Br 27.52.

***trans*-1,3-Diphenylallyl alcohol (3):** ^1H NMR δ 2.5 (broad s, 1H, OH), 5.4 (d, 1H, H1, *J*=6.4 Hz), 6.4 (dd, 1H, H2, J_1=6.4 Hz, J_2=15.9 Hz), 6.7 (d, 1H, H3, *J*=15.9 Hz), 7.3–7.5 (m, 11H, 2Ph) (consistent with the literature data[18]).

1-Phenyl-1-pentanol (4): ^1H NMR δ 0.9 (t (unresolved dd), 3H, H5, *J*≈6.9 Hz), 1.4 (m, 4H, H4+H3), 1.8 (m, 2H, H2), 2.3 (broad s, 1H, OH), 4.7 (dd, 1H, H1, J_1=6.0 Hz, J_2=7.2 Hz), 7.3–7.4 (m, 5H, Ph). ^{13}C NMR: δ 14.0, 22.6, 28.0, 38.8, 74.5, 125.8, 127.2, 128.2, 144.8 (consistent with the literature data[19]).

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