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Cocatalysis in phase-transfer catalyzed base induced β-elimination. Part 2: Model studies of dehydrobromination of *trans*-β-bromostyrene

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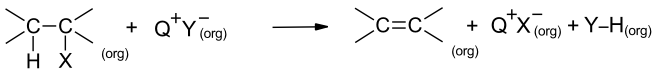
Abstract—Phase-transfer catalyzed β-elimination of HBr from *trans*-β-bromostyrene proceeds as a cocatalytic process when cocatalysts of low acidity such as *n*-butanol and highly concentrated aqueous NaOH at elevated temperatures are used. Without added cocatalyst the reaction is autocatalyzed because the produced phenylacetylene forms lipophilic acetylenide anion acting as a base in the organic phase. Competition between the β-elimination of HBr from *trans*-β-bromostyrene and the Hofmann degradation of tetrabutylammonium cation as a function of base was studied.

In our earlier paper[1] a general concept of cocatalysis in phase-transfer catalyzed (PTC) base induced β-elimination of HX from alkyl halides was formulated. It explained numerous early observations that alcohols facilitate this process.[2] Recently we reported results of our detailed studies of β-elimination of HBr from cyclohexyl bromide which proceeds efficiently under phase-transfer catalysis conditions in the presence of a proper cocatalyst Y–H according to the general mechanism presented in Eqs. (1a) and (1b).[3]

$$Y{-}H_{(org)} + Na^{+}OH^{-}_{(aq)} + Q^{+}X^{-}_{(org)} \rightleftarrows Q^{+}Y^{-}_{(org)} + Na^{+}X^{-}_{(aq)} + H_2O_{(aq)} \quad (1a)$$



(1*b*)

We have examined a series of potential cocatalysts Y–H: O–H and N–H acids such as alcohols, phenols, amides, etc. and found that their cocatalytic activity is a function of two parameters: concentration of the reacting anions Y^- in the organic phase governed by the acid–base equilibrium (Eq. (1a)) and activity of Y^- as basic reagents affording β-elimination (Eq. (1b)). The optimal cocatalytic activity was observed for Y–H of moderate acidity so there was relatively high concentration of Y^-Q^+ in the organic phase whereas Y^- anions still were sufficiently active basic agents. These results can be used as guidelines for selection of cocatalytic systems assuring efficient β-elimination from a variety of alkyl halides.

This methodology was however tested using cyclohexyl bromide as a model alkyl halide, which can be easily dehydrohalogenated to cyclohexene under relatively mild conditions. It is therefore necessary to clarify whether this concept can be expanded for haloalkanes which undergo dehydrohalogenation only under harsh conditions.

In this paper we report results of our studies on application of the cocatalysis methodology for PTC dehydrobromination of a model vinyl bromide—*trans*-β-bromostyrene **1** which is known to be rather resistant towards base induced β-elimination. For instance, an Organic Syntheses procedure for the synthesis of phenylacetylene consists in heating of **1** with KOH in ethylene glycol at 200°C to give the product in 67% yield.[4] Application of PTC for synthesis of acetylenes via base induced β-elimination was reported by Dehmlow who has shown that dehydrohalogenation of 1,2-dihalides to acetylenes proceeds satisfactorily in liquid–solid system using KOH and highly lipophilic tetraoctylammonium bromide as PT catalyst.[5] He has also shown that in some cases 50% aq. KOH in the presence of tetraoctylammonium chloride and some diols gave similar results.[2a] It was shown that use of less lipophilic TAA salts as PT catalysts in these reactions was not successful.[6,7]

It should be mentioned that dehydrobromination of **1** proceeds efficiently in the presence of concentrated aqueous NaOH and an equimolar amount of tetrabutylammonium hydrogensulfate—the so called ion-pair extraction technique.[8]

Keywords: phase-transfer catalysis; cocatalysis; β-elimination; Hofmann degradation.

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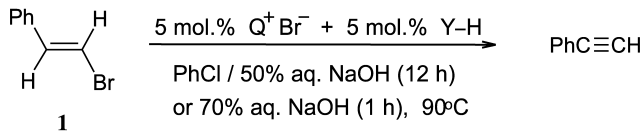
Table 1. β-Elimination of HBr from *trans*-β-bromostyrene: the cocatalytic and simple PTC systems



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Entry	Q^+Br^-	Aq. NaOH (wt%)	Y–H (pK_a)[a]	Conversion of **1** (%)[b]	Degradation of Q^+ (%)[b]
1	None	50	None	0	–
2	n-$Bu_4N^+Br^-$	50	None	64	0
3	n-$Bu_4N^+Br^-$	50	n-BuOH (≈29.8)	70	≈10
4	n-$Bu_4N^+Br^-$	50	$PhCH_2OH$ (27.0)	61	100
5	n-$Bu_4N^+Br^-$	50	Mesitol (≈18.5)	10	100
6	n-$Pr_4N^+Br^-$	50	None	60	–[c]
7	$Et_4N^+Br^-$	50	None	6	–[c]
8	$Me_4N^+Br^-$	50	None	7	–[c]
9	n-$Oct_3N^+MeBr^-$	50	None	80	–[c]
10	n-$Bu_4N^+Br^-$	70	None	40	0
11	n-$Bu_4N^+Br^-$	70	n-BuOH	75	≈10

[a] The pK_a values (in DMSO) according to Bordwell[9] are given in brackets unless noted otherwise. Sign '≈' denotes that presented pK_a value refers to a close analogue of the corresponding Y–H.
[b] Amount of tributylamine was determined by GLC using chlorobenzene as an internal standard.
[c] Not determined.

1. Results and discussion

The conditions elaborated for efficient cocatalytic β-elimination of HBr from cyclohexyl bromide (excess of 50% aq. NaOH, 5 mol% of n-$Bu_4N^+Br^-$, 5 mol% of Y–H, 40°C) were too mild for the β-elimination of HBr from **1**. The process was very slow, even after 24 h conversion did not exceed 5%. Since under the conditions employed for the cocatalytic β-elimination of HBr from cyclohexyl bromide, **1** was practically unreactive all further experiments were conducted at 90°C using chlorobenzene both as a solvent and as an internal standard for GLC measurements. Results of the experiments are given in Table 1.

Under the conditions specified in Table 1, PTC dehydrohalogenation of **1** proceeded with reasonable rate. As can be seen from these results, without PT catalyst no reaction was observed during 12 h of stirring at 90°C (Table 1, Entry 1) whereas in the presence of tetrabutylammonium bromide (TBAB) under the same conditions conversion of **1** attained 64% (Table 1, Entry 2). Addition of n-BuOH as a cocatalyst resulted in a small increase of the conversion (Table 1, Entry 3), whereas more acidic cocatalysts $PhCH_2OH$ and mesitol exert small or substantial inhibitory action (Table 1, Entries 4 and 5). It should be stressed that these compounds were efficient cocatalysts in PTC dehydrobromination of cyclohexyl bromide, more efficient than n-BuOH. Simple PTC β-elimination (without cocatalysts), in spite of the rather harsh conditions and long reaction time, was not accompanied with the Hofmann degradation of n-Bu_4N^+ cation—no n-Bu_3N was detected in the reaction mixture (Table 1, Entry 2). Such degradation proceeded to a small degree when n-BuOH was used as the cocatalyst, whereas in the presence of more acidic cocatalysts $PhCH_2OH$ and mesitol there was complete degradation of n-Bu_4N^+ as indicated by the amount of n-Bu_3N determined in the reaction mixture.

The weak cocatalytic action of n-BuOH is connected with its low acidity hence in the presence of 50% aq. NaOH only a small part of n-BuOH is converted into reactive n-BuO^-Q^+. At the high temperatures used in our experiments solubility of NaOH in water is much higher so some experiments were repeated using 70% aq. NaOH. Under such conditions basic activity of OH^- anions are much higher so deprotonation of n-BuOH is more efficient and cocatalytic reaction in the presence of n-BuOH proceeded substantially faster than simple PTC: 40 and 75%, respectively, conversion after 1 h (Table 1, Entries 10 and 11). Thus under properly selected conditions, a cocatalytic process operates also for dehydrobromination of *trans*-β-bromostyrene.

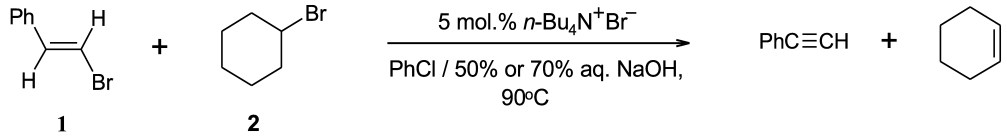
On the basis of these results, the following general picture can be proposed: in spite of the very unfavorable ion-exchange equilibrium (Eq. (2a)) classical PTC operates at high temperatures. It appears that the rate constant of the elimination reaction with very active OH^- anions (Eq. (2b)) is so high that the β-elimination proceeds with reasonable observed rate in spite of negligible concentration of Q^+OH^- in the organic phase.

$$Q^+Br^-_{(org)} + Na^+OH^-_{(aq)} \rightleftarrows Q^+OH^-_{(org)} + Na^+Br^-_{(aq)} \qquad (2a)$$

$$PhCH{=}CHBr_{(org)} + Q^+OH^-_{(org)} \rightarrow PhC{\equiv}CH_{(org)} + Q^+Br^-_{(org)} + H_2O \qquad (2b)$$

It should be stressed that the simple PTC as well as cocatalytic PTC dehydrobromination of *trans*-β-bromostyrene proceeds under very mild conditions in comparison with those recommended in Organic Syntheses.[4] It is a rather peculiar observation that 'simple' PTC β-elimination proceeds efficiently in spite of the large concentration of bromide anions in the system generated during the reaction, which practically preclude extraction of Q^+OH^- into the organic phase. Thus there is an important question in which way PTC operates in this reaction. There is no doubt that the β-elimination is PT catalyzed since in the absence of TBAB there are not even traces of phenylacetylene in the organic

Table 2. β-Elimination of HBr from *trans*-β-bromostyrene and cyclohexyl bromide under simple PTC conditions at 90°C



Entry	Educts		Aq. NaOH (wt%)	Time (h)	Conversion of **1** (%)[a]	Conversion of **2** (%)[a]
	1	**2**				
1	+	−	50	12	64	–
2	−	+	50	12	–	52
3	+	−	70	1	40	–
4	−	+	70	1	–	16
5[b]	+	+	50	3	23	25
6[b]	+	+	50	12	36	55
7[b]	+	+	70	1	28	32
8[b]	+	+	70	3	50	65
9[c]	−	+	70	1	–	27

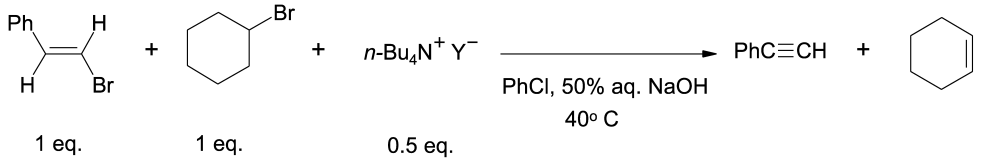
[a] Determined by GLC using chlorobenzene as an internal standard.
[b] 1:1 Molar mixture of the halides **1** and **2** was used.
[c] PhC≡CH (5 mol%) was added to the reaction mixture before the experiment.

phase whereas with this TAA salt conversion is up to 100% for a certain time of the reaction. Since in this system concentration of OH^- anions in the organic phase is really negligible the catalytic effect of TBAB could eventually be rationalized in two ways:

1. In spite of very low concentration of Q^+OH^- in the organic phase, thanks to a very high rate constant of the reaction with highly active OH^- anions, particularly at elevated temperature, the process proceeds with reasonable observed rate.
2. The reaction proceeds at the interfacial region, in which there is a gradient of concentration and concentration of OH^- in the form of Q^+OH^- in this region substantially exceeds those governed by the ion-exchange equilibrium (Eq. (2a)).

In order to verify the latter hypothesis less lipophilic TAA salts were used as the catalysts in supposition that the interfacial processes should be less sensitive to the lipophilicity of TAA cations. The experiments in which *n*-$Pr_4N^+Br^-$, $Et_4N^+Br^-$ and $Me_4N^+Br^-$ were used as PT catalysts indicated, that the first salt was almost as efficient as TBAB whereas the two latter salts did not show marked activity (Table 1, Entries 6–8). Perhaps low effectiveness of the latter is due to their insufficient solubility in the organic phase. On the other hand use of the much more lipophilic salt *n*-$Oct_3N^+MeBr^-$ gave substantial improvement over TBAB (Table 1, Entry 9). It shall be therefore accepted for PT catalyzed β-elimination of HBr from *trans*-β-bromostyrene in the presence of concentrated aqueous NaOH and TAA salts at elevated temperatures that the reaction proceeds via transfer of Q^+OH^- into the organic phase, albeit to a very low extent. It should be noted that in the vigorously stirred system the concentration of Q^+OH^- in the organic phase can exceed those measured in the equilibrated static systems.[10] In spite of very low concentration, high activity of these anions at elevated temperatures assures a reasonable reaction rate. This conclusion is supported by control experiments with cyclohexyl bromide, which is known to be much more susceptible to β-elimination than **1**. When cyclohexyl bromide **2** was subjected to PTC β-elimination under analogous conditions as **1** the elimination took place to a similar extent (Table 2, Entries 1 and 2). Surprisingly under these conditions the reaction with **2** proceeded somewhat slower than with **1**. Comparison of the conversion degree of **1** and **2** when 70% aq. NaOH was used revealed that under such conditions **1** reacted much faster than **2**—conversion 40 and 16% correspondingly (Table 2, Entries 3 and 4). These surprising and peculiar results, namely faster reaction of otherwise much less active compound should be rationalized, because one can expect that explanation of this phenomenon should help understanding how the PTC reaction operates in these situations. For direct comparison of rates of PTC β-elimination of **1** and **2** we performed competitive experiments in which mixtures of equimolar quantities of these halides were subjected to the PTC β-elimination in the presence of 50 and 70% aq. NaOH (Table 2, Entries 5, 6 and 7, 8). In all these experiments cyclohexyl bromide **2** reacted somewhat faster than **1**. The apparent discrepancy between the results shown in Table 2 (Entries 1, 2 and 3, 4) in which the single halides were subjected to the reaction, with those competitive in which equimolar mixtures of **1** and **2** were used, can be reasonably rationalized taking into account that the product of the β-elimination from **1**—phenylacetylene is a moderately acidic C–H acid, pK_a=28.7 (DMSO).[9] When produced in the system it undergoes deprotonation at the interface and the generated carbanion of phenylacetylene forms, with the TAA cation, a lipophilic ion pair entering the organic phase. The carbanion derived from weak C–H acid exhibits high basicity and affect fast β-elimination of HBr from **1** and **2**. So in fact the reactions with **1** proceed as cocatalytic PTC processes. On the other hand, during PTC β-elimination of HBr from **2** there is no cocatalyst to increase the rate of the elimination, thus it proceeds slower than analogous process with **1** for which the cocatalysis, being actually autocatalysis, operates. This reasoning is supported by the observation that this cocatalytic effect is much stronger when more concentrated NaOH is used, thus weak C–H acids such as phenylacetylene can be

Table 3. Competitive β-elimination of HBr from **1** and **2** promoted by different TBA salts



Entry	Y^-	Time	Conversion of **1** (%)[a]	Conversion of **2** (%)[a]
(a) *Two-phase system (chlorobenzene/50% aq. NaOH)*				
1	OH^-	1 min[b]	24	27
2	Br^-	48 h	27	29
3	ArO^-[c]	0.5 h	0	86
(b) *Homogeneous system (chlorobenzene solution)*				
4	OH^-	0.5 min[b]	5	8
5	OH^-	2 min[b]	5	14
6	OH^-	10 min[b]	6	19
7	OH^-	3 h[b]	7	32
8	OH^-	>12 h[b]	7	42

[a] Determined by GLC using durene as an internal standard; no significant degradation of TBA cation was observed in all these experiments.
[b] At 25°C.
[c] Ar=2,4,6-trimethylphenyl.

deprotonated efficiently. Moreover, in separate experiments using 70% aq. NaOH we were able to observe a considerable cocatalytic action of Ph≡CH in the β-elimination of HBr from cyclohexyl bromide (Table 2, Entries 4 and 9).

An almost identical degree of β-elimination of HBr from **1** and **2** under simple PTC conditions in spite of much higher sensitivity of **2** to the action of base (see e.g. Table 2, Entry 5) indicates that in both these cases the reaction is promoted by the highly active reagent being in very low concentration, apparently Q^+OH^- and $PhC{\equiv}C^-Q^+$ and the conversion is limited not by the rate constant of the chemical reaction but by availability of OH^- or other strongly basic anions in the organic phase, thus in fact diffusion controlled. This supposition is supported by the results of competitive experiments in which equimolar quantities of **1** and **2** were subjected to β-elimination under various conditions (Table 3). These results indicate that the reaction progress is limited by availability of the highly active basic agent in the organic phase because there is no discrimination between **1** and **2** (Table 3, Entries 1 and 2), although the reaction progress in the presence of TBAB is relatively slow due to the very low concentration of OH^- in the organic phase. On the other hand rates of β-elimination of these halides with a mild basic agent (e.g. ArO^-) differ tremendously, the reaction of **2** is much faster. The experiments (Table 3, Entries 1–3) were carried out in the presence of an excess of 50% aq. NaOH in order to remove water or ArOH generated during the reaction. The same competitive experiments carried out with Q^+OH^- in a chlorobenzene solution in the absence of 50% aq. NaOH (Table 3, Entries 4–8) revealed that the competition depends on the degree of conversion. Obviously OH^- anions hydrated by water generated in the reaction are much weaker bases[11] so the reaction with **2** is preferred.

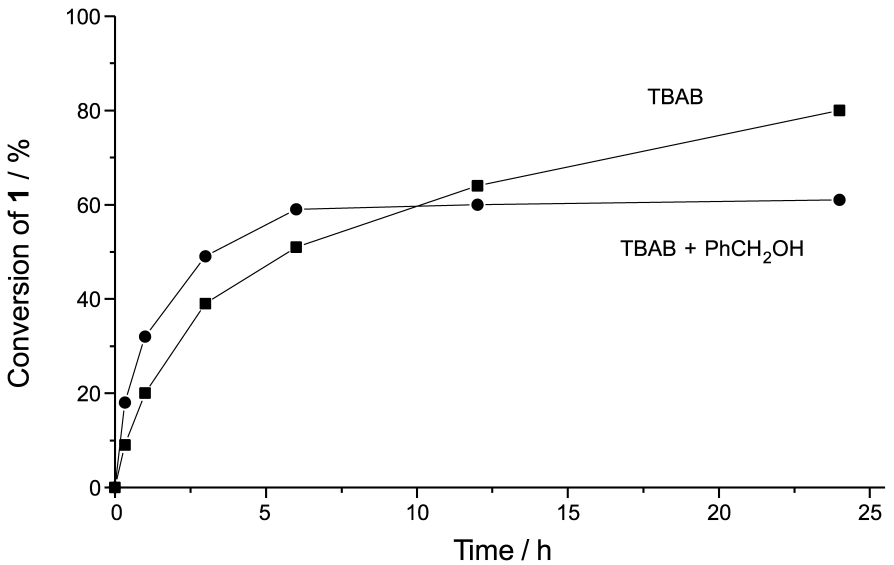
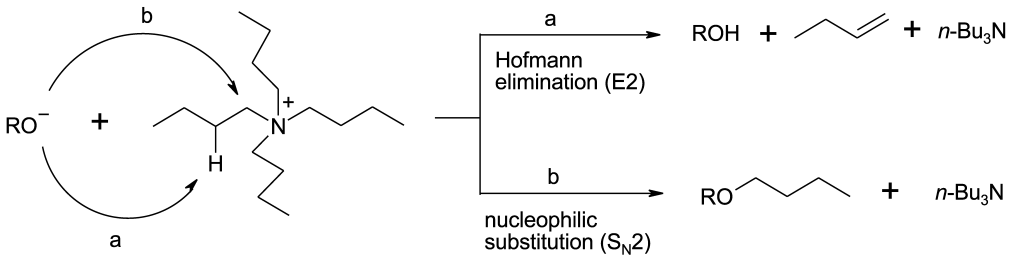


Figure 1. Conversion of *trans*-β-bromostyrene **1** as a function of time for simple PT system (5 mol% TBAB) and cocatalytic PT system (5 mol% TBAB+5 mol% $PhCH_2OH$).



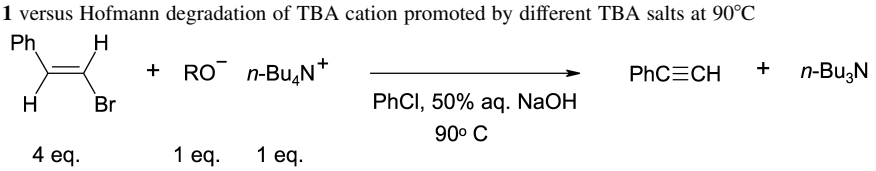
Scheme 1.

Another interesting issue is that during PTC dehydrohalogenation of **1** at high temperature, which proceeds apparently via transfer of OH^- and $PhC{\equiv}C^-$ into the organic phase, the Hofmann degradation of the TBA cation is not observed. On the other hand in the presence of cocatalysts *n*-BuOH, $PhCH_2OH$ and mesitol the degradation proceeded to a small extent (*n*-BuOH) or completely ($PhCH_2OH$ and mesitol). In fact, the absence of a cocatalytic effect of $PhCH_2OH$ (Table 1, Entry 4) in the β-elimination is an artifact. This alcohol acts as an efficient cocatalyst for the β-elimination which indicates high conversion after a short time whereas after 5 h the PTC process is arrested due to total degradation of TBAB. This can be seen in Fig. 1, where conversion of **1** is shown as a function of time. Formation of phenylacetylene is accelerated in the presence of $PhCH_2OH$ at the beginning of the process, so there is an efficient cocatalytic β-elimination however accompanied by Hofmann degradation, after that it stops because all the TBA cation is degraded, whereas without this cocatalyst the PTC reaction, although slower at the beginning, is not arrested even after a long reaction time. Deceleration of the process with time is due to consumption of the educts and accumulation of Br^- in the aqueous phase so concentration of OH^- and $PhC{\equiv}C^-$ anions in the organic phase decreases continuously.

Since the degradation of the tetrabutylammonium cation was monitored via the determination of tributylamine, it should be clarified whether it is indeed produced due to Hofmann elimination or eventually S_N2 substitution which also could produce tributylamine (Scheme 1).[12] Taking into account the observed preference for degradation by anions of low basicity such as $PhCH_2O^-$ and ArO^-, the S_N2 type reaction appeared feasible. When a solution of *n*-Bu_4N^{+-} $PhCH_2O^-$ in chlorobenzene was heated at 90°C for 5 h in a tightly closed flask ^1H NMR analysis of the crude reaction mixture indicated that it contained *n*-Bu_3N ($(PrCH_2)_3N$ δ 2.48, t), $PhCH_2OH$ (δ 4.76, s) and $-CH_2-CH{=}CH_2$ (δ 2.15, 2H, m; 5.95, 1H, m; 5.05, 2H, m) in an approximate ratio of 1:1:0.5 and traces of unreacted *n*-Bu_4N^+, whereas characteristic signals for benzyl *n*-butyl ether $PhCH_2OCH_2$-Pr (δ 4.6, s; δ 3.5, t) were absent. On the other hand an equimolar mixture of benzyl butyl ether and tributylamine under the same conditions did not give rise to benzyl alcohol and butene. Furthermore, no traces of the corresponding $ArOCH_2Pr$ ethers were found in the reaction mixtures of the competitive experiments with TBA ArO^- (Table 4, Entries 4 and 5). These observations allowed us to exclude the S_N2 reaction pathway for the degradation of TBA cation in the cocatalytic PTC system and confirmed that classic Hofmann elimination operates in this case.

Additionally a very interesting observation was made that relation of rates of the competing reactions: β-elimination of HBr from **1** and *n*-Bu_3N from the TBA cation (the Hofmann degradation) depends very much on the strength of the basic agent (Table 4). 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. Such a behavior suggests a principal difference between the mechanisms of dehydrobromination of *trans*-β-bromostyrene and the Hofmann degradation of tetrabutylammonium cation. Whereas the Hofmann degradation of the TBA cation most likely follows a one-step E2 mechanism,[12] in the case of *trans*-β-bromostyrene, for which the E2-type mechanism seems to be unlikely due to the geometry of the molecule, two-step E1cB mechanism might operate. That is

Table 4. β-Elimination of **1** versus Hofmann degradation of TBA cation promoted by different TBA salts at 90°C



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

[a] According to Bordwell.[9]
[b] Determined by GLC and ^1H NMR using durene as an internal standard; the sum of $PhC{\equiv}CH$ and *n*-Bu_3N was ≈100% in regard to the initial amount of TBA salt.
[c] Ar=2,4,6-trimethylphenyl.

supported by the 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.[13] Moreover, 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.[13] This suggests that carbanionic species are involved in the rate determining step of the base induced dehydrobromination of the *trans*-isomer. Taking into account that 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 crucial for dehydrobromination of **1** rather than for the Hofmann degradation of TBA cation, which, if follows concerted E2 mechanism, does not require generation of carbanion. This phenomenon is a subject of further investigation.

We can conclude that the cocatalytic process operates also for the PTC β-elimination requiring harsh conditions, although at elevated temperature simple PTC β-elimination proceeds satisfactorily. The Hofmann degradation of tetrabutylammonium cation takes place much slower than β-elimination of HBr from **1** under the simple PTC conditions, whereas use of cocatalysts of moderate acidity promotes the degradation.

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 RT) followed by distillation of the crude reaction mixture (**1**/PhC≡CH≈85/15) under reduced pressure. It was stored in a refrigerator at 0–4°C. The analyses of the reaction mixtures were performed using 'Shimadzu GC-14A' gas chromatograph; injection port temperature 120°C; injection time 1 min. ^{1}H NMR spectra were recorded on Varian Gemini (200 MHz) spectrometer. All the experiments were carried out using a magnetic stirrer equipped with a temperature-controlled oil bath.

2.1. General procedure for β-elimination of HBr from *trans*-β-bromostyrene (1) or cyclohexyl bromide (2) under phase-transfer catalysis conditions at 90°C (Tables 1 and 2)

A mixture of the bromide(s) (20 mmol; 3.66 g of **1** and/or 3.26 g of **2**), chlorobenzene (2.00 g), and the corresponding Y–H (1 mmol) (when indicated) was added to a 25 mL flask charged with concentrated aqueous solution of NaOH (≈200 mmol; 10 mL of 50% aq. NaOH or 70% aq. NaOH prepared from 5 mL of 50% aq. NaOH and 5.1 g of solid NaOH) thermostated at 90°C. Then powdered Q^+Br^- (1 mmol) was added, the flask was tightly closed with a stopper using a metallic clip. The reaction mixture was stirred for a given time at 90±1°C. The flask was cooled, CH_2Cl_2 (25 mL) was added to the reaction mixture and the separated organic layer was washed with water (3×5 mL), dried over $MgSO_4$ and analyzed by GLC using chlorobenzene, present in the mixture, as an internal standard. When the time profile of the reaction had to be established (see Fig. 1), small samples of the corresponding reaction mixtures (Entries 2 and 4) were periodically taken and analyzed by GLC after dilution with CH_2Cl_2 and washing with water.

2.2. Preparation of chlorobenzene solution of TBA salts (Tables 3 and 4)

Chlorobenzene solutions of *n*-$Bu_4N^+RO^-$ salts (R=H; *n*-Bu; $PhCH_2$; Ph and 2,4,6-trimethylphenyl) were prepared according to the ion-pair extraction procedure[14] from an equimolar mixture of TBA hydrogensulfate, ROH (R≠H) and excess of 50% aq. NaOH. Thus to obtain 2.5 mL of a solution which contains ≈0.5 mmol of the *n*-$Bu_4N^+RO^-$ (R≠H) a mixture of TBA hydrogensulphate (0.34 g, 1 mmol), corresponding ROH (1 mmol), chlorobenzene (5 mL) and 50% aq. NaOH (5 mL) was stirred in a small flask for 5 min at room temperature. After short separation of the phases (2–3 min) 2.5 mL of the clear upper organic layer was taken by a pipette. A solution of TBA hydroxide (10 mL; ≈2.5 mmol) was obtained in a similar way: a mixture of TBA hydrogensulphate (1.50 g, 4.4 mmol), chlorobenzene (15 mL) and 50% aq. NaOH (10 mL) was stirred for 5 min at room temperature and treated as above. Concentrations of RO^- in the prepared chlorobenzene solutions were determined by titration with 0.5 M HCl (bromophenol blue). Under these conditions the content of RO^- anions in the organic phase was ≈100% (R≠H) and ≈90% for OH^- anion in regard to the total amount of Q^+ in the system. The solutions of TBA hydroxide and alkoxides in chlorobenzene are unstable and can be stored only for a short time at low temperature.

2.3. Competitive β-elimination of HBr from 1 and 2 promoted by different TBA salts in the two-phase system (Table 3(a))

10 mL of a freshly prepared solution of the corresponding TBA salt (2.5 mmol) in chlorobenzene was added under vigorous stirring to the thermostated at given temperature mixture of the bromides **1** and **2** (0.915 and 0.815 g, 5 mmol each), durene (≈0.3 g) and 50% aq. NaOH (10 mL). The mixture was stirred for a given time. A sample of the organic phase was washed with equal volume of saturated aqueous NaI in order to remove any residual basic species, dried with Na_2SO_4 and analyzed by GLC using durene as an internal standard.

2.4. Competitive β-elimination of HBr from 1 and 2 promoted by TBA hydroxide in a homogeneous system (Table 3(b))

Ten milliliters of a freshly prepared solution of TBA hydroxide (2.5 mmol) in chlorobenzene was rapidly added under vigorous stirring to the thermostated at 25°C mixture of the bromides **1** and **2** (0.915 and 0.815 g, 5 mmol each) and durene (≈0.3 g). After certain time intervals small samples of the organic phase were taken, rapidly mixed with saturated aqueous NaI (≈1:1 v/v) and vigorously shaken.

After separation from the aqueous phase the samples were dried with Na_2SO_4 and analyzed by GLC using durene as an internal standard.

2.5. Competitive β-elimination of HBr from 1 and Hofmann degradation of TBA cation promoted by different TBA salts at 90°C (Table 4)

Freshly prepared chlorobenzene solution of the corresponding TBA salt (2.5 mL, 0.5 mmol) was rapidly added with vigorous stirring to the thermostated at 90°C 10 mL flask charged with **1** (0.366 g, 2 mmol), durene (≈0.1 g) and 50% aq. NaOH (3 mL). The flask was tightly closed with a stopper using a metallic clip and the mixture was stirred for a given time at 90±1°C. Samples of the organic phases were rapidly mixed with saturated aqueous NaI (≈1:1 v/v) and vigorously shaken. After separation from the aqueous phase the samples were dried with Na_2SO_4 and analyzed by GLC and ^1H NMR using durene as an internal standard.

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