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Cocatalysis in Phase-Transfer Catalysed Base Induced β-Elimination. Model Studies of Dehydrobromination of Bromocyclohexane

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Abstract—Phase-transfer catalysed dehydrobromination of bromocyclohexane was studied as a model reaction. Factors determining the effectiveness of the cocatalysts were examined and guidance rules for selection of cocatalysts are formulated.

Base promoted β-elimination of hydrogen halides from haloalkanes is a general process of great practical value for synthesis and the manufacture of alkenes and alkynes.[1] Traditionally the reaction is carried out in homogeneous media via treatment of haloalkanes with basic reagents—trialkylamines, solutions of NaOH, KOH or alkoxides in lower alcohols, etc.[1,2]

Numerous base promoted reactions are most efficiently carried out in two-phase systems—a non-polar organic phase and strong bases such as NaOH, KOH and K_2CO_3 in the form of aqueous solutions or in the solid state, in the presence of tetraalkylammonium salts as phase-transfer catalysts.[3,4] In such systems reactive intermediates: carbanions, alkoxides, *N*-anions are efficiently generated via deprotonation of the appropriate precursors at the phase boundary (interface) between these two phases and subsequently transferred as ion-pairs with the liphophilic cations of the catalyst into the organic phase where they undergo the desired reactions.[5] General mechanism of this methodology named 'Phase-Transfer Catalysis' (PTC) is presented in Eq. (1) where Q^+ denotes a lipophilic tetraalkylammonium cation and subscripts 'org', 'aq' and 'int' indicate the organic phase, the aqueous phase and the interfacial region correspondingly.

$$\begin{aligned} &\rangle C{-}H_{(org)} + NaOH_{(aq)} \rightleftharpoons \rangle C^-Na^+_{(int)} + H_2O \\ &\rangle C^-Na^+_{(int)} + Q^+X^-_{(org)} \rightleftharpoons \rangle C^-Q^+_{(org)} + NaX_{(aq)} \end{aligned} \quad (1)$$

These reactions do not proceed via transfer of OH^- anions into the organic phase because for $X^-{=}Cl^-$, Br^- etc. the ion-exchange equilibrium (Eq. (2)) is strongly shifted to the left and formation of tetraalkylammonium hydroxides does not occur to any great extent.

$$Q^+X^-_{(org)} + OH^-_{(aq)} \rightleftharpoons Q^+OH^-_{(org)} + X^-_{(aq)} \quad (2)$$

In this situation application of the very efficient and economical PTC methodology for the β-elimination process, which should proceed according to Eq. (3) seems doubtful, because concentration of Q^+OH^- in the organic phase governed by the equilibrium in Eq. (2) should be negligible.

$$Q^+X^-_{(org)} + NaOH_{(aq)} \rightleftharpoons Q^+OH^-_{(org)} + NaX_{(aq)}$$

$$\underset{H\ \ X}{\overset{|}{\underset{|}{\rangle C-C\langle}}}_{(org)} + Q^+OH^-_{(org)} \longrightarrow \rangle C{=}C\langle_{(org)} + Q^+X^-_{(org)} + H_2O \quad (3)$$

Indeed, generally speaking, PTC is not a very efficient technique for base induced β-elimination, although there are numerous papers and patents reporting successful execution of such processes.[6] Efficient introduction of Q^+OH^- into the organic phase is possible when $Q^+HSO_4^-$ is used instead of Q^+Cl^- or Q^+Br^- because of the high hydrophilicity of the produced SO_4^{2-} anion which stays in the aqueous phase (Eq. (4a)). Thus when $Q^+HSO_4^-$ is used in stoichiometric amounts in relation to an alkyl halide the β-elimination proceeds rapidly since strongly basic OH^- anions are transferred into the organic phase in an amount equimolar to the alkyl halide. This methodology named ion-pair extraction is of high effectiveness,[7] however $Q^+HSO_4^-$ must be used in a stoichiometric amount because Q^+X^-, produced in the

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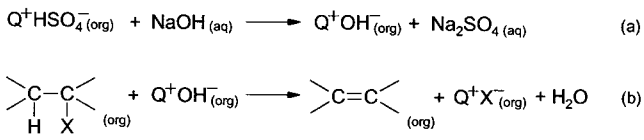
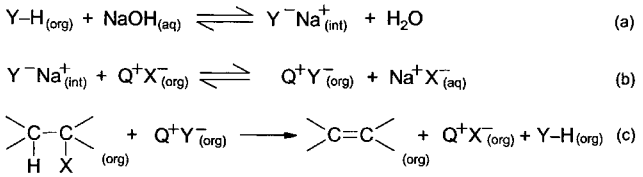
process (Eq. (4b)), can be converted into Q^+OH^- (according to Eq. (2)) only to a negligible extent, hence this methodology is impractical for large scale synthesis.



(4)

There are also some reports that addition of alcohols[8,9] and particularly glycols,[9] promotes PTC β-elimination, but no clear cut mechanistic rationalisation was proposed for this action.[8,9]

In our preceding paper[10] we have formulated a general concept of cocatalysis in the PTC β-elimination reaction which uses compounds Y–H that upon deprotonation can form lipophilic, strongly basic and possibly non nucleophilic anions Y^-. These anions Y^- generated at the interface with concentrated aqueous NaOH are continuously transferred as ion-pairs with lipophilic tetraalkylammonium cations into the organic phase where they act as basic agents according to the process in Eq. (5).



(5)

Using CF_3CH_2OH and 2-methylindole as Y–H, we evidenced that the cocatalysis is an efficient way to execute base induced β-elimination reactions and solve the problems connected with inability of OH^- anions to be transferred into the organic phase. In this paper, results of detailed studies on the selection of cocatalysts Y–H and their effectiveness are presented using bromocyclohexane **1** as a model haloalkane.

Results and Discussion

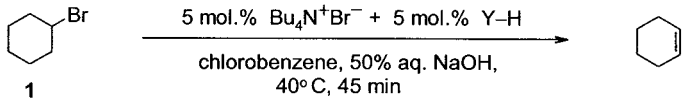
For Y–H acids (C–H, N–H, O–H, S–H) to act as cocatalysts, Y^- anions should be lipophilic, highly basic and possibly non-nucleophilic. High basicity is required for efficient proton abstraction in the E2 β-elimination process—it is however often connected with high nucleophilic activity. Whereas there is a reasonably consistent measure of basicity (value of p*K*a of the conjugated acids Y–H) no reasonably general quantitative measure of nucleophilicity is formulated. In fact, the relation of reaction rates of nucleophilic agents with electrophilic carbon centres depends on the type of such centres. Thus, only a qualitative and intuitive concept of nucleophilicity could be used here as a measure of the tendency for S_N2 substitution of a halogen at saturated carbon. On the basis of abundant literature data concerning the acidities of various Y–H compounds and rates of S_N2 reactions of Y^- one can conclude that S–H and C–H acids are not suitable candidates as cocatalysts because thiolate anions and carbanions are strong nucleophiles.

According to Eq. (5), acidities of Y–H (values of p*K*a) should have a profound effect on the effectiveness of Y–H as cocatalysts in the following way: higher acidity of Y–H (lower value of p*K*a) should facilitate its conversion into Q^+Y^- according to Eq. (5a,b), hence increasing the concentration of the acting base in the organic phase and therefore increasing the rate of the β-elimination. However less basic Y^- should exhibit lower activity in promoting the β-elimination, hence should be less efficient cocatalysts. On the other hand, from Y–H of low acidity, highly basic Y^- are generated, being very active in the β-elimination process. However, the degree of conversion of such Y–H into Q^+Y^- according to Eq. (5a,b) and consequently the concentration of Y^- in the organic phase is much lower. Thus in spite of the expected high rate constant of the β-elimination by highly basic Y^-, the observed reaction rate could be low. From this simple reasoning one could expect that Y–H of high and low acidity should be rather inefficient cocatalysts in this process. One can therefore suppose that there is an optimum of acidity of Y–H so that a sufficient concentration of Q^+Y^- in the organic phase is assured whereas Y^- exhibit reasonably high activity as basic agents in the β-elimination reaction.

To clarify this matter a series of experiments were executed in which bromocyclohexane **1**, mixed with chlorobenzene in approximately 1:1 molar ratio was subjected to the reaction with excess of 50% aqueous NaOH in the presence of $Bu_4N^+Br^-$ (5% molar) and a variety of Y–H (5% molar). These experiments were carried out under identical, arbitrarily chosen conditions (temperature, rate of stirring and time), which assure moderate conversion of **1**, usually not exceeding 50%, so differences in effectiveness of various Y–H as the PTC cocatalysts can be observed. The results are presented in Table 1.

The degree of the conversion of **1** into cyclohexene promoted by various Y–H, determined by GLC using chlorobenzene as the internal standard, is given in column 3. Data in column 4 show the degree of conversion of Y–H into Q^+Y^- and its extraction into the organic phase as a fraction (in %) of the total amount of Q^+ (100%). It is assumed that when the aqueous phase consists of a 50% solution of NaOH, all tetraalkylammonium cations are in the organic phase in the form of Q^+Br^- and Q^+Y^-. These values were determined in separate experiments in which Q^+Br^- and an equimolar amount of Y–H dissolved in chlorobenzene were vigorously stirred with an excess of 50% aqueous NaOH and the organic phase was thoroughly separated. The amount of Y^- and Br^- in the organic phase was determined by titration and is shown in columns 4 and 6 correspondingly. The conversion of some alcohols into tetraalkylammonium alkoxides in similar two-phase system was studied by Dehmlow.[11] Although the range of alcohols studied and the methodology are not identical, our data are essentially parallel to the reported ones. Numbers in column 5 characterise the activity of Y^- as the basic agent effecting β-elimination. These values are produced when the value in column 3 (conversion of **1** into cyclohexene) is divided by

Table 1. β-Elimination of HBr from bromocyclohexane in the phase-transfer cocatalytic system: alcohols and phenols as Y–H cocatalysts



1

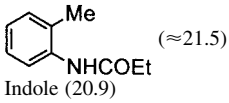
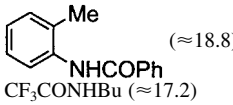
1	2	3	4	5	6	7
Entry	Y–H (p*K*a (DMSO))[a]	 (%)	$Y^-_{(org)}$ (%)	Effectiveness of Y–H	$Br^-_{(org)}$ (%)	$Y^-_{(org)}+Br^-_{(org)}$
1	None	0	−(<0.5)[c]	–	100	100 (0.5)[b]
2	*t*-BuOH (32.2)	3	1	3.00	100	101
3	*n*-BuOH (≈29.8)	15	5	3.00	96	101
4	$Me_2C(OH)C(OH)Me_2$	12	22	0.55	76	98
5	$PhCH(CH_3)OH$	22	9	2.44	87	96
6	$PhCH_2OH$ (27.0)	41	17	2.41	82	99
7	$Ph_2C(CH_3)OH$	16	6	2.67	96	102
8	Ph_2CHOH	43	23	1.87	76	99
9	Ph_3COH	27	11	2.45	90	101
10	CF_3CH_2OH (23.5)	46	34	1.35	67	101
11	$CF_3(Ph)CHOH$	58	51	1.14	52	103
12	$CF_3(Ph)_2COH$	79	77	1.03	36	113 (11)[b]
13	$(CF_3)_2(Ph)COH$	36	100	0.36	18	118 (18)[b]
14	Mesitol (≈18.5)	82 (0)[d]	92 (<0.5)[d]	0.89	25	117 (22)[b]
15	*o*-Cresol (18.2)	60	93	0.65	27	120 (20)[b]
16	*p*-Cresol (18.9)	57	91	0.63	31	122 (18)[b]
17	Phenol (18.0)	53	93	0.57	23	116 (20)[b]
18	*p*-Chlorophenol (16.7)	36	100	0.36	18	118 (25)[b]
19	2,4,6-Trichloro-phenol (≈12.7)	1	100	0.01	6	106 (6)[b]

[a] The p*K*a values according to Bordwell[12] are given in the parentheses if available. Sign ≈ denotes that presented p*K*a value refers to the close analogue of the corresponding Y–H.
[b] The results of Na^+ determination in the organic phase are given in the parentheses.
[c] The content of $Q^+OH^-_{(org)}$ is negligible (<0.5%).
[d] The results of similar experiments in which no $Q+Br^-$ was added are given in the parentheses.

value in column 4. It can be considered as information on the number of molecules of **1** converted by one anion Y^- in the given time. Assumption that all Q^+Br^- and Q^+Y^- are in the organic phase, and that no other anionic species are present in this phase, requires that the sum of columns 4 and 6 (shown in column 7) should be 100% which is usually the case. However in some instances (Entries 12–19) it exceeds this value in a notable degree because of partial coextraction of Na^+Y^-.

Under the chosen standard conditions the β-elimination from **1** does not proceed in the presence of phase transfer catalyst (tetrabutylammonium bromide) without addition of a cocatalyst Y–H because transfer of OH^- anions into the organic phase measured as its basicity is negligible. Also, Y–H in the absence of the phase transfer catalyst Q^+Br^- does not promote β-elimination and no Y^- (in the form of a Na^+ salt) can be detected in the organic phase. Introduction of O–H acids (alcohols or phenols) as cocatalysts promote the β-elimination, often to a substantial degree (Entries 3–18). Unfortunately for a great majority of alcohols which were studied as Y–H, no p*K*a values are available, nevertheless in Table 1 they are presented in order of expected growing acidity. The least acidic *t*-butanol and *n*-butanol (Entries 2 and 3) under the standard conditions are converted into the corresponding alkoxides BuO^-Q^+ to a low extent (1% and 5%). Highly basic butoxide anions are active species in promoting the β-elimination, however due to their low concentration, the overall effectiveness of these alcohols as cocatalysts is not satisfactory. The interesting behaviour of pinacol (Entry 4) should be noted. This aliphatic ditertiary alcohol (glycol) is converted into the corresponding monoanion to a substantial degree (22%), as was earlier observed by Dehmlow,[11] however this anion exhibits low activity as a basic agent inducing β-elimination. Obviously it is due to strong intramolecular hydrogen bonding between the alkoxide anion and the vicinal OH-group. Much higher cocatalytic activity was exhibited by the more acidic benzylic alcohols $Ph_nCH_{(3-n)}OH$ n=1,2,3 (Entries 6,8,9). Interestingly, consecutive replacement of hydrogen in CH_3OH with phenyl groups has no linear additive effect. Thus benzyl and benzhydryl alcohols (Entries 6,8) have similar cocatalytic effect on the conversion of **1**, although the latter forms RO^-Q^+ to a somewhat higher degree. The triphenyl carbinol (Entry 9) is the least efficient because of a low degree of conversion into RO^-Q^+. Replacement of a hydrogen in benzyl and benzhydryl alcohols with methyl groups (Entries 5 and 7) results in a decrease of the conversion into Q^+Y^- and the catalytic effectiveness. Acidity and also lipophilicity of alcohols is substantially increased by trifluoromethyl substituents, thus trifluoromethyl carbinols should be efficient cocatalysts. Indeed 2,2,2-trifluoroethanol, 1-phenyl-2,2,2-trifluoroethanol and 1,1-diphenyl-2,2,2-trifluoroethanol (Entries 10–12) are converted into the corresponding alkoxides RO^-Q^+ to a substantial degree, whereas these alkoxides are sufficiently active to promote the β-elimination. The acidity of an alcohol containing two trifluoromethyl groups (Entry 13) is much higher so it is converted into RO^-Q^+ quantitatively, however due to low basic activity of the corresponding alkoxide anion the overall degree of β-elimination in the presence of this cocatalyst is not very high. It could be considered as a moderately efficient cocatalyst.

Table 2. β-Elimination of HBr from bromocyclohexane in the phase-transfer cocatalytic system: amides and nitrogen heterocycles as Y–H cocatalysts

1	2	3	4	5	6	7
Entry	Y–H (p*K*a (DMSO))[a]	 (%)	$Y^-_{(org)}$ (%)	Effectiveness of Y–H	$Br^-_{(org)}$ (%)	$Y^-_{(org)}+Br^-_{(org)}$
1	MeCONHBu (≈25.9)	3	2	1.50	94	96
2	PhCONHBu (≈23.5)	7	6	1.17	96	102
3	 (≈21.5)	46	48	0.96	53	101
4	Indole (20.9)	36	62	0.58	40	102
5	Carbazole (19.9)	40	78	0.51	24	102
6	 (≈18.8)	13	96	0.14	5	101
7	$CF_3CONHBu$ (≈17.2)	14	97	0.14	6	103

[a] The p*K*a values according to Bordwell[12] are given in the parentheses if available. Sign ≈ denotes that presented p*K*a value refers to the close analogue of the corresponding Y–H.

Surprisingly some substituted phenols show high cocatalytic effectiveness in the PTC β-elimination. Due to relatively high acidities, under the applied conditions they are converted almost quantitatively into the corresponding phenolates which are in most cases sufficiently basic to afford β-elimination. The most efficient is mesitol (Entry 14), *o*- and *p*-cresoles and even phenol (Entries 15–17) are also highly efficient cocatalysts. On the other hand, the highly acidic *p*-chlorophenol (Entry 18) and particularly 2,4,6-trichlorophenol (Entry 19) form much less basic phenolates so they exhibit low activity as the cocatalysts (Entry 18) or are totally inactive (Entry 19).

Thus in the large range of O–H acids studied as the potential cocatalysts according to Eq. (5), it was possible to observe that there are two extreme cases: low acidic aliphatic alcohols such as *t*- and *n*-butanol and highly acidic chlorophenols are not suitable as the cocatalysts for the PTC β-elimination of **1**. In the former cases highly basic alkoxides are continuously produced in concentrations too low to be efficient cocatalyst, whereas in the latter case chlorophenolates, although produced in high concentration are insufficiently basic to afford the β-elimination. There is however a large set of alcohols and phenols that exhibit high cocatalytic effectiveness, from which a proper cocatalyst can be selected.

In cases of highly acidic Y–H (O–H acids) total amounts of anions Br^- and Y^- in the organic phase exceeded 100%, often to a significant extent (Entries 12–19). It was apparently due to coextraction of Na^+Y^- with Q^+Y^- (and Q^+Br^-), and the relevant quantities of Na^+ were determined in the organic phase via flame atomic absorption spectrometry (FAAS) (numbers in parentheses in column 7). The supposition that Na^+Y^- enter the organic phase together with Q^+Br^- and Q^+Y^- in a kind of coextraction process was supported by experiments in which mesitol or phenyltrifluoromethylcarbinol dissolved in chlorobenzene were treated with aqueous NaOH, without Q^+Br^-. No Y^-Na^+ was detected in the organic phase by titration method and no elimination of HBr was observed when **1** was added to such systems.

The latter experiments also indicate that cocatalysts Y–H, although being very efficient when applied together with phase-transfer catalyst $Bu_4N^+Br^-$, are totally inactive by themselves and both catalysts should be present for the β-elimination to proceed.

Similar regularities were observed in experiments in which the use of N–H acids as the cocatalysts was tested. Results of these experiments carried out under identical conditions as in Table 1 are shown in Table 2. Although the range of the compounds studied was much smaller, here also one can observe the same patterns as in the case of O–H acids. N–H acids of low acidities (*N*-butylacetamide and *N*-butylbenzamide) (Entries 1,2) were converted into the corresponding anions $BuN^-COR\ Q^+$ to a low extent and are inefficient cocatalysts in spite of the rather high basicity of the corresponding anions. On the other hand, highly acidic *N*-benzoyl-*o*-toluidine or *N*-butyltrifluoroacetamide are converted into the corresponding anions practically completely, however being weakly basic these anions do not promote the β-elimination to a reasonable extent. The most efficient are N–H acids of moderate acidity such as *N*-propionyl-*o*-toluidine, indole or carbazole (Entries 3,4,5) which can be considered as suitable cocatalysts.

It should be also stressed that in general O–H acids (alcohols and phenols) are more active cocatalysts that N–H acids (amides or heterocycles) of similar acidity.

As we have already mentioned efficient cocatalytic action of Y–H in PTC β-elimination requires that in the reaction with an alkyl halide Y^- abstracts a proton but does not substitute halogen. In the studied model **1** this requirement is apparently met by all the Y–H listed in Tables 1 and 2. Nevertheless somewhat less efficient cocatalytic behaviour of *o*- and *p*-cresols and phenol than mesitol in spite of almost the same basicity of their anions could be explained by partial alkylation of the phenolates, thus part of the cocatalyst is destroyed. Indeed some amounts of the corresponding cyclohexylaryl ethers (10–50% in respect to the initial ArOH) were detected in the reaction mixtures. Due to steric hindrance alkylation of mesitolate with **1** takes place to a lower extent than with the other phenolates as can be seen from the data given in Table 3 where the degree of alkylation and ratio of elimination to alkylation as determined by GLC analysis of the reaction mixture is given.

Table 3. β-Elimination of HBr from bromocyclohexane in the phase-transfer cocatalytic system: ratio of β-elimination to substitution (E/S_N) for the phenols (ArOH) as Y–H

Entry	ArOH	β-Elimination  (%)	Substitution  (%)[a]	E/S_N
1	Phenol	53	2.0 (40)	27
2	Mesitol	82	0.5 (10)	164
3	*p*-Cresol	57	2.5 (50)	23
4	*o*-Cresol	60	1.5 (30)	40
5	*p*-Chlorophenol	36	1.0 (20)	36

[a] The yields of cyclohexylaryl ethers calculated on the initial amount of the ArOH used (i.e. consumption of the cocatalyst Y–H) are given in the parentheses.

Relations of rates of the β-elimination to nucleophilic substitution for phenol and cresols are between 23–40, whereas for mesitole 164. This is undoubtedly due to steric hindrance in the mesitolate anion approaching the electrophilic carbon centre. Thus, data concerning catalytic activity of cresols and phenol (Entries 15–17) are artefacts because part of the cocatalysts is destroyed during the process, and mesitole could be recommended as an appropriate cocatalyst for PTC β-elimination being efficient and inexpensive.

The results presented in this paper indicate that phase transfer catalysis can be an efficient methodology for base induced β-elimination provided a proper cocatalyst is chosen. Taking into account large varieties of potential cocatalysts we suggest, that it will be possible to select an appropriate one for a desired β-elimination process.

Experimental

All the reagents used were either commercially available in sufficiently pure form or synthesised in one step from the readily available starting materials by known procedures. Sodium hydroxide was analytical-reagent grade, its concentrated aqueous solution was prepared using distilled water and kept as a stock solution. The analysis of the reaction mixtures was performed using 'Shimadzu GC-14A' gas chromatograph. All the experiments were carried out using magnetic stirrer equipped with a temperature-controlled oil bath.

Comparative experiments on β-elimination of HBr in the phase-transfer cocatalytic system. A homogeneous mixture of bromocyclohexane (3.26 g, 20 mmol), chlorobenzene (2.00 g), tetrabutylammonium bromide (0.322 g, 1 mmol) and the corresponding cocatalyst Y–H (see Tables 1 and 2) (1 mmol) was rapidly added to 50% aqueous solution of NaOH (10 ml, ≈190 mmol) thermostated at 40°C and the stirring was turned on. The reaction mixture was stirred for 45 min at 40±1°C and then removed from the heating bath. 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 analysed by GC using chlorobenzene present in the mixture as the internal standard. The yields of cyclohexene are presented in Tables 1 and 2.

Determination of the degree of extraction of Y^- into organic phase in the phase-transfer cocatalytic system. A solution of tetrabutylammonium bromide (0.967 g, 3.00 mmol) and corresponding compound Y–H (3.00 mmol) in chlorobenzene (total volume of the solution 25.0 ml, concentration of each component 0.12 M) was added to 50% aqueous solution of NaOH (15 ml, ≈285 mmol) thermostated at 40°C. The mixture was stirred for 15 min at 40±1°C and the stirring was turned off. The mixture was allowed to separate into two layers for several min and ca 20 ml sample of the organic phase was taken off and additionally subjected to a centrifugal separation. Two aliquots 5.0 ml each were taken from the well separated organic phase, mixed with ca 5 ml of methanol and titrated with 0.05 M HCl using bromophenol blue as the indicator. The basicity of the organic phase was assigned to Y^- anion extracted with quaternary ammonium cation. Another 10.0 ml sample of the analysed organic phase was taken and chlorobenzene was evaporated under reduced pressure. The residue was dissolved in methanol to obtain the same total volume (10.0 ml) as the initial sample. The methanol solution was then potentiometrically titrated with 0.01 M $AgNO_3$ in order to determine the content of Br^-. In some cases (marked in Table 1) the obtained methanol solutions were additionally analysed by flame atomic absorption spectrometry (FAAS) (λ=330.2/330.3 nm) to estimate the content of Na^+. The results obtained are summarised in Tables 1 and 2. It was found that extension of the stirring time up to 60 min does not affect the degree of extraction of Y^- observed after 15 min of stirring. No traces of Bu_3N (the product of possible Hofmann's elimination in Q^+Y^-) were detected in the separated organic phases by GLC.

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