Change of topology of the chemical interaction stage as a tool for the stereoselectivity control of PTC reactions*

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The relationship between the rate-limiting step of PTC and the site of the chemical interaction stage has been established for the cyclotriphosphazenes phenolysis reaction in liquid—liquid systems. Transfer of the site of the phenolysis of mono(aryloxy)cyclotriphosphazenes from the bulk of the organic phase to the interface results in a change in the ratio of the products of the reaction of *cis*- and *trans*- isomers of bis(aryloxy)cyclotriphosphazenes.

Key words: phase transfer catalysis, rate limiting step, interface, stereoselectivity, *cis*- and *trans*-isomers of bis(aryloxy)cyclotriphosphazenes.

The method of phase transfer catalysis (PTC) has gained recognition in organic synthesis[1,2] owing to its high selectivity. By changing the PTC conditions, first of all by acting on the "hardness—softness" of quaternary onium cations, phase transfer catalysts make it possible to significantly control also the reaction regioselectivity.[3—6] Enlargement of the stereoselectivity of phase transfer reactions remains a pressing problem.[7] It is necessary to note in this connection the works of L. A. Yanovskaya and G. V. Kryshtal concerned with the control of the stereochemistry of the Horner—Emmons reaction under PTC conditions.[8—14]

The present work deals with the use of the interface (IF) for the control of the stereoselectivity of a phase transfer process. There are known examples[15—18] of stereoselective reactions which let us suppose that it is the interface that significantly influences the interaction results. The idea itself has been formulated for a long time.[19] Evidently the IF effect could be proved only by the comparison of the data for the same reaction that occurs in one case on an IF and otherwise in the bulk. As a result at least two principal problems arise: 1) identification of the site of PTC reaction in liquid—liquid systems, and 2) alteration of this site in the same reaction without any significant change of reagent structures.

Topology of PTC processes in liquid—liquid systems

The present work uses the method applied previously by us[20—22] for the investigation of phenolysis of cyclophosphazenes (1) in liquid—liquid systems.

$$(PNCl_2)_n + ArONa \xrightarrow[-NaCl]{Q^+} P_nN_nCl_{2n-1}OAr \qquad (1)$$

This reaction of cyclophosphazenes in the two-phase system borate buffer (pH 9.18) — organic solvent (chlorobenzene, *o*-dichlorobenzene, *symm*-tetrachloroethane) was found to be satisfactorily described by the two-stage scheme that includes at first equilibrium stage the generation (2) of tetraalkyl ammonium aroxide and its consequent interaction with the substrate (3) in the organic phase. The indexes *aq*, *org*, and *if* correspond to aqueous and organic phases, and the interface, respectively).

$$ArO^-_{aq} + Q^+Cl^-_{org/if} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArO^-Q^+_{org/if} + Cl^-_{aq} \qquad (2)$$

$$ArO^-Q^+_{org/if} + (PNCl_2)_{n\,org} \xrightarrow{k_2} P_nN_nCl_{2n-1}OAr + Q^+Cl^-_{org/if} \qquad (3)$$

n = 3 and 4;

ArO^-Q^+ **1a,b** **2a,b** Ar = 2,4-$(NO_2)_2C_6H_3$ (**1**); 4-$NO_2C_6H_4$ (**2**); $Q^+ = Et_3N^+CH_2Ph$ (**a**), Bu_4N (**b**)

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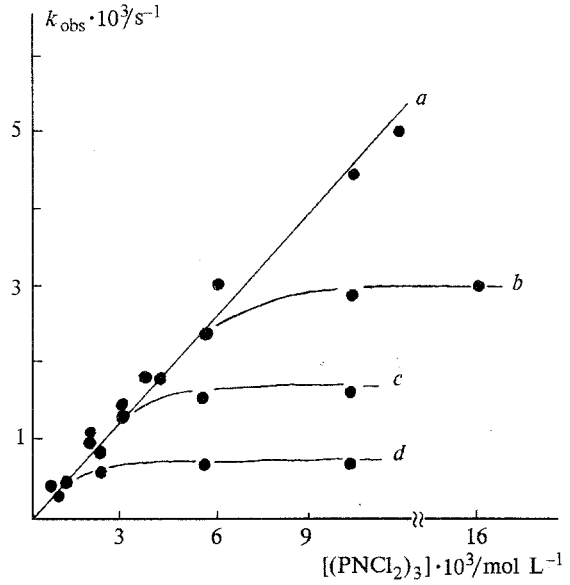


Fig. 1. Dependence of the observed rate constant (k_{obs}) for the reaction between 4-nitrophenoxide ion and hexachlorocyclotriphosphazene on the substrate concentration in two-phase borate buffer (pH 9.18) — chloroform system at different concentrations of triethylbenzylammonium chloride (25°C), mol L^{-1}: *a*, $5.00\cdot10^{-2}$; *b*, $2.92\cdot10^{-2}$; *c*, $1.99\cdot10^{-2}$; *d*, $3.65\cdot10^{-3}$.

As this takes place, the observed pseudofirst order rate constant (k_{obs}) for the phase transfer process according* to the equation (4)

$$k_{obs} = \frac{k_2 K_{ArO/Cl}[Q^+Cl^-]_{org/if}[(PNCl_2)_n]_{org}}{[Cl^-_{aq}] + k_2[(PNCl_2)_n] / k_{-1}}, \quad (4)$$

$$K_{ArO/Cl} = \frac{k_1}{k_{-1}} = \frac{\alpha_{ArO}}{\alpha_{Cl}} = \frac{[ArO^-Q^+]_{org}[Cl^-]_{aq}}{[ArO^-]_{aq}[Q^+Cl^-]_{org}}, \quad (5)$$

is proportional[20] to the content of tetraalkylammonium aroxide in the organic phase. This constant is determined by the effective values of the ion-selective equilibrium constants $K_{ArO/Cl}$ or by the transfer degree α_{ArO} and in a complicated way depends on the cyclophosphazene concentration in the system.

In the range of high phase transfer catalyst concentrations ($[Cl^-]_{aq} >> k_2 [(PNCl_2)_n]_{org}/k_{-1}$) the observed phenolysis rate constant is directly proportional to the substrate concentration (Fig. 1, curve *a*)

$$k_{obs} = k_2\alpha_{ArO}[(PNCl_2)_n]_{org}. \quad (6)$$

At low concentrations of the phase transfer catalyst ($[Cl^-]_{aq} \ll k_2 [(PNCl_2)_n]_{org}/k_{-1}$) the rate constant tends to the limiting value (Fig.1, curves *b*—*d*), which depends on the reagent's phase distribution and does not depend on the substrate concentration:

$$k_{obs} = k_{-1}\alpha_{ArO}[Cl^-]_{aq}. \quad (7)$$

As this takes place, the following regularity is observed: the lower is the concentration Q^+Cl^- in the two-phase system, the lower is the limiting value of the observed phenolysis rate constant. Such relationships are not common for the reaction proceeding under homogeneous conditions[23] and were thus associated with the change of the limiting step of the PTC reaction.

The same regularities were also observed[22] for the case (reactions (8) and (9)), when tetraalkylammonium aroxide is the nucleophile, *i.e.*, $[Cl^-]_0 = 0$.

$$ArO^-_{aq} + Q^+_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArO^-Q^+_{org/if} \quad (8)$$

$$ArO^-Q^+_{org/if} + (PNCl_2)_{n\,org} \xrightarrow{k_2} \quad (9)$$

$$\longrightarrow P_nN_nCl_{2n-1}OAr + Q^+Cl^-$$

Here, too, with a low transfer degree the observed pseudofirst order phenolysis rate constant is satisfactorily described by the equation:

$$k_{obs} = \frac{k_1k_2[Q^+]_{aq}[(PNCl_2)_n]_{org}}{k_{-1} + k_2[(PNCl_2)_n]_{org}}, \quad (10)$$

derived, as well as equation (4), from the assumption of quasistationary aroxide ion concentration.

For these conditions the observed phenolysis rate constant was found to be linearly dependent on the aroxide ion content in the organic phase (Fig. 2). The data on the reactivity of different ArO^-Q^+ are given in Table 1.

The equation (10) implies the existence of two limiting cases:

1) if $k_{-1} \gg k_2 [(PNCl_2)_n]_{org}$, then the chemical interaction of an aroxide ion and substrate is the limiting step, that is exhibited as the linear dependence of the observed phenolysis rate constant on the cyclophosphazene concentration (Fig. 3, curves *1*, *1'*, *4*) in accordance to the equation

$$k_{obs} = k_2\alpha_{ArO}[(PNCl_2)_n]_{org}; \quad (11)$$

2) if $k_{-1} << k_2 [(PNCl_2)_n]_{org}$, then the nucleophile transfer is the limiting step. According to the equation

$$k_{obs} = k_1[Q^+]_{aq} \quad (12)$$

the observed rate constant is independent on the substrate content in the two-phase system (Fig.3, curves *2'*, *3*).

The results obtained, among them the change in the reaction order on the substrate concentration, could be

* Henceforward the satisfactory correlation between the equations given here and the experimental data was deduced from the equality of the rate constants k_2 calculated and obtained in separate organic phase.[21,22]

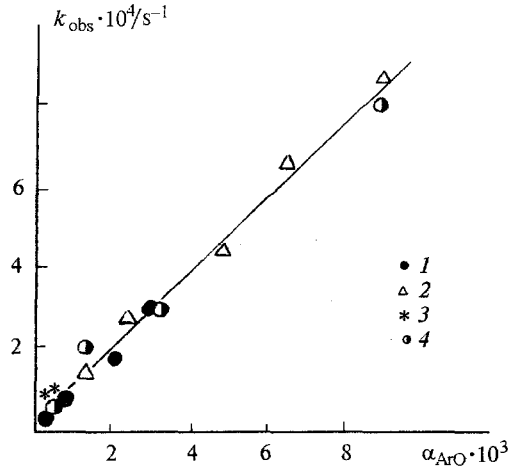


Fig. 2. Dependence of the observed phase transfer rate constant (k_{obs}) on the value α_{ArO} for the reaction of tetraalkylammonium aroxide with hexachlorocyclotriphosphazene in the two-phase borate buffer (pH 9.18) — chloroform system: *1*, **1a**; *2*, **2b**; *3*, **2a**; *4*, **2a**, chloroform.

Table 1. Reactivity of tetraalkylammonium aroxides in phenolysis reactions of hexachlorocyclotriphosphazene in the organic solvents saturated with water, 25 °C[a]

Solvent	ArO^-Q^+	$k_{2(relat.)}$[b]
PhCl	**1a**	1.0
PhCl	**2b**	500.0
PhCl	**2a**	430.0
$CHCl_3$	**2a**	9.3

[a] Initial reagents concentration $[ArO^-Q^+]_0 = 1\cdot10^{-4}$ mol L^{-1}; $[(PNCl_2)_3]_0$: $[ArO^-Q^+]_0$ = (10–30) : 1. [b] The values of constants are given relative to k_2 for **1a**, which was assumed to be 1. k_2^{1a} = (2.32 ± 0.10) L mol^{-1} s^{-1}.

explained from the another point of view. The zero order on the substrate concentration is known to be the feature of the IF occurrence of the reaction.[2,24,25]

All the above allowed us to suppose, that contrary to the commonly[1,2,24] accepted distinction between the extractive and phase transfer mechanisms, PTC reactions are really characterized by a single mechanism, which could be presented as Scheme 1.

Thus, topology of the chemical interaction depends on the same factors, as does the limiting step. Therefore, varying the lipophilicity-nucleophilicity ratio of the phase transfer reagent it is possible to change purposefully the site of its interaction with substrate. Topology of such a model reaction should be sensitive to these changes, that would require the high rate of the corresponding homogeneous reaction and the high hydrophilicity of the ionic reagent.

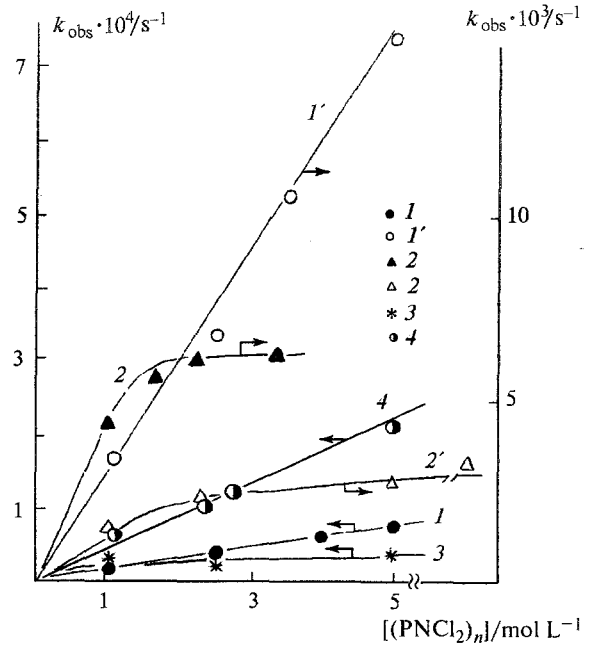
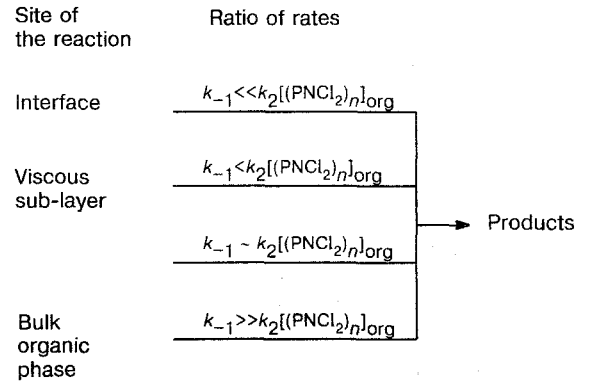


Fig. 3. The influence of substrate concentration on the phenolysis rate constant (k_{obs}) in two-phase borate buffer (pH 9.18) — organic solvent system, 25°C: *1*) **1b**, chlorobenzene; *1′*) **1a**, chlorobenzene; *2*) **2b**, octachlorocyclotetraphosphazene, chlorobenzene; *2′*) **2b**, chlorobenzene; *3*) **2a**, chlorobenzene; *4*) **2a**, chloroform.

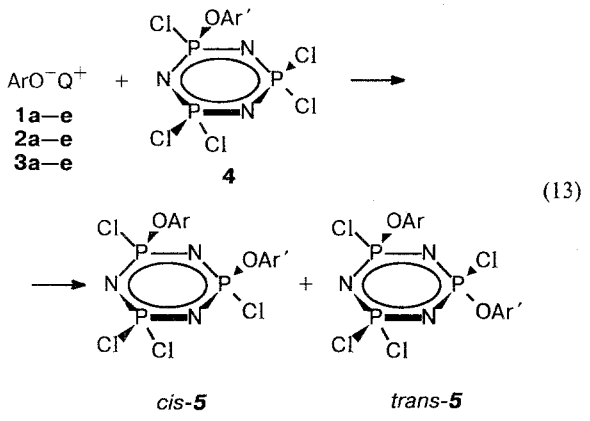
Scheme 1



Influence of IF on the stereoselectivity of phase transfer phenolysis of cyclophosphazenes

These requirements are met by the model reaction of the formation of *cis*- and *trans*-isomers of bisaryloxycyclophosphazenes that are the products of phase transfer phenolysis of trimer phosphazene monoaryloxy derivatives (reaction 13).

In all cases at twofold excess of the substrate **4** the reaction (13) gives a mixture of 1,3-substituted *cis*- and



(13)

Ar = 2,4-$(NO_2)_2C_6H_3$ (**1**), 4-$NO_2C_6H_4$ (**2**), Ph (**3**);
Ar′ = Ph, 4-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$;
Q = Et_3NCH_2Ph (**a**), Bu_4N (**b**), Me_4N (**c**), $Me_3NCH_2CH_2Cl$ (**d**), Na (**e**)

trans-isomers **5** and ~3% of an admixture of 1,1-substituted products in 95% yield. At homogeneous conditions the *cis*- and *trans*-isomers ratio is independent of the reagents structure, the organic solvent nature and is equal to 57:43. Small excess of the *cis*-isomer was usually associated[26] with the "interspatial" interaction between 2p-orbital of the oxygen of aryloxy group and 3d-orbital of the phosphorus in the initial product.

Reactivity of monoaryloxy-substituted cyclophosphazenes in the reaction (13) is 2—3 times lower than that of hexachlorocyclotriphosphazene (in the reaction with $1 \cdot 10^{-4}$ mol L^{-1} **2a** in chlorobenzene saturated with water[27] its rate constant is k_2 ~1000 L mol^{-1} s^{-1}), and the effective transfer degree of tetraalkylammonium aroxides from water into chlorobenzene is <1.0 for **1b**, which is the most lipophilic salt among the used ones (in other cases this degree is 10^2—10^4 times lower[22]). This suggests that in the phenolysis reactions (13) the limiting step and, consequently, the site of the phase transfer interaction, can be changed easily. From the above data on the phase transfer interaction between the unsubstituted hexachlorocyclophosphazene and the salt **2a** it follows that with chloroform as the solvent the reaction occurs in the bulk of the organic phase, but in the case of chlorobenzene, which poorly solvate the tetraalkylammonium aroxide, it occurs at the interface. These regularities were examined for the reaction (13) between the substrate **4** (Ar′ = 4-$NO_2C_6H_4$) and the reagent **2a**. The extraction of triethylbenzylammonium 4-nitrophenoxide in the two-phase system borate buffer (pH 9.18) — chloroform was found to be sufficiently great ($\alpha_{ArO} = 3 \cdot 10^{-3}$ at $[\mathbf{2a}]_0 = 1.25 \cdot 10^{-3}$ mol L^{-1}), that is 10 times higher than in the case of chlorobenzene. At the same time the rate of the homogeneous reaction in chloroform saturated with water (mimicking the organic phase conditions) is 10 times lower than in wet chloroform. As this takes place, the observed rate constant of the phase transfer interaction does not vary with the increase in the stirring speed from 750 to 1400 rpm and is linearly dependent upon the cyclophosphazene concentration. It may be concluded that under these conditions the reaction occurs mainly in the bulk of the organic phase.

On the contrary, in the two-phase system borate buffer (pH 9.18) — chlorobenzene the dependence of the observed phenolysis rate constant on the substrate concentration is non-linear in the same concentration range. On different parts of this function the values of the activation energy of the overall process decrease from 10.8±1.2 kcal mol^{-1}, usual for chemical interaction, to 4.2±2.0 kcal mol^{-1}, typical of diffusion-controlled reactions.[24]

Table 2 lists some data showing the influence of the reaction (13) site on the *cis*- and *trans*-isomers **5** ratio.

When chlorobenzene is changed for chloroform and triethylbenzylammonium cation is exchanged for more lipophilic tetrabutylammonium one, the extractability of the phase transfer reagent increases. Similarly to the reaction of the unsubstituted substrate, it results in the transfer of the site of this process into the bulk of the organic phase and, consequently, in the decrease in the process stereoselectivity. Its value becomes the same as that in homogeneous conditions. The fivefold decrease in the absolute concentrations of substrate and the reagent (keeping their ratio constant) results in the same consequences, because in this case the conditions of equation (12) are violated and the site of the reaction is also transferred into the bulk of the organic phase (Table 2).

Considering that the results obtained may be attributed to the change of the site of the chemical interaction, we have generalized this approach to all of the reagents and substrates investigated.

It was interesting to determine the influence of the increase in the phase transfer catalyst Q^+ hydrophilicity on the *cis*-/*trans*-isomers ratio, because it is this type of the aroxide ion cariers that make preferential occurrence of the reaction (13) at the interface the most probable

Table 2. Influence of the conditions of PTC interaction of phosphazene **4** (Ar′ = 4-$NO_2C_6H_4$) with tetralkylammonium 4-nitrophenoxide on the isomeric composition of the products. 25 °C*

ArO^-Q^+	Solvent	Site of chemical reaction	*Cis/trans* isomers ratio
2a	$CHCl_3$	Organic phase	55:45
2a	PhCl	Interface	65:35
2a	PhCl	Organic phase**	57:43
2b	PhCl	Organic phase	58:42
	Homogeneous conditions		57:43

* $[(PNCl_2)_3]_0$ = 0.04 mol L^{-1}; $[ArO^-Q^+]_0$ = 0.02 mol L^{-1}.
** $[(PNCl_2)_3]_0$ = 0.008 mol L^{-1}; $[ArO^-Q^+]_0$ = 0.04 mol L^{-1}.

Table 3. Influence of reagent and substrate structures on the stereoselectivity of PTC phenolysis of monoaryloxypentachlorocyclotriphosphazenes in two-phase borate buffer (pH 9.18) — chlorobenzene system, 25°C

Substrate	ArO^-Q^+	*Cis/trans* isomers ratio
Influence of the cation Q^+		
4 (Ar′ = 4-$NO_2C_6H_4$)	**2e**	62:38
4 (Ar′ = 4-$NO_2C_6H_4$)	**2c**	65:35
4 (Ar′ = 4-$NO_2C_6H_4$)	**2d**	63:37
4 (Ar′ = 4-$NO_2C_6H_4$)	**2a**	65:35
Influence of substrate		
4 (Ar′ = 2,4-$(NO_2)C_6H_4$	**1e**	75:25
4 (Ar′ = 4-$NO_2C_6H_4$)	**1e**	68:32
4 (Ar′ = Ph)	**1e**	49:51
Influence of the anion ArO^-		
4 (Ar′ = 4-$NO_2C_6H_4$)	**1e**	68:32
4 (Ar′ = 4-$NO_2C_6H_4$)	**2e**	62:38
4 (Ar′ = Ph)	**1e**	49:51
4 (Ar′ = Ph)	**2e**	54:46
4 (Ar′ = Ph)	**3e***	58:42

* The analogous reaction between the salt **3e** and phosphazene **4** (Ar′ = 4-$NO_2C_6H_4$) failed due to the considerable contribution of the competing exchange of the phenoxy and 4-nitrophenoxy groups in the substrate.

and, consequently, increase the stereoselectivity of the process.

Contrary to the expectations, the increase in the cation Q^+ hydrophilicity in the order **2a**, **2d**, **2c** up to such a weak* "phase transfer" catalyst as Na^+ didn't result in the change of the *cis-/trans-* ratio and moreover was accompanied by the decrease in the cation catalytic activity itself.

On the other hand with the same hydrophilic Q^+ = Na^+ the increase in the hydrophobicity of the aroxide ion and of the substrate also resulted in the selectivity increase (Table 3). It seems that the interface organises the mutual orientation of both substrate and reagent according to their hydrophilic-hydrophobic features. It is known[25] that the interface is not a monomolecular formation. Its structure is close to that of the Stern layer and its thickness is estimated by different authors as 5—6 Å [25] or 8—12 Å [28]. The aroxide ion is held at the interface by the hydrophilic cation. In general, this creates the favourable situation for the formation of a *cis*-substituted product.

When the substrate molecule contains less hydrophobic fragment Ar′, the phosphazene ring is lipophilic enough,[29] which favors *trans*-substitution. This case is typical of monophenoxycyclophosphazene (Table 3).

The choice of a phase transfer catalyst is not limited to the quaternary ammonium salts. In a preliminary experiment we have also used betaines of the types $C_{16}H_{33}(CH_3)_2N^+CH_2COO^-$ (**6**) and $(CH_3)_3N^+CH_2COO^-$ (**7**) as phase transfer catalysts. Their analogs appeared to be acceptable catalysts in some PTC processes[2]. First of these betaines is hydrophobic enough and extracts 4-nitrophenoxide ion into the organic phase; phenolysis of the compound **4** (Ar′ = 4-$NO_2C_6H_4$) occurs in its bulk demonstrating the stereoselectivity usual for homogeneous conditions (*cis/trans* ratio = 56:44). On the contrary, more hydrophilic betaine is held strongly at the interface due to its carboxylate group and, with some decrease in the total catalytic activity, increases nevertheless the isomer ratio of bis(4-nitrophenoxy)cyclophosphazene up to 69:31.

Preliminary investigations of the interface influence in two-phase solid—liquid systems showed that in the dry chlorobenzene—solid ArO^-Q^+ system the following three possibilities can realize:

1) the reaction between the solid potassium aroxide and 4-nitrophenoxycyclophosphazene virtually doesn't occur;

2) in the presence of 18-crown-6 the potassium 4-nitrophenoxide is extracted in the form of its complex into chlorobenzene and colors it; the reaction occurs in the solvent bulk with the stereoselectivity usual for a homogeneous reaction (58:42).

3) in the case of the reagent **2a** the ratio of *cis/trans* isomers of phenolysis products is equal to 65:35, that corresponds to their ratio in the liquid—liquid system for the reaction occurring at the interface.

* Sodium nitrophenoxides are not in fact extracted into chlorobenzene. Two-phase reactions with them were performed for 100 h up to 10% conversion.

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