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A New Phenomenon in Phase-transfer Catalysis (PTC): Topoinduced Stereoselectivity in the Phase-transfer Phenolysis of Cyclophosphazenes

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An increase in the ratio of the *cis*- and *trans*-isomers of bis(aryloxy)cyclotriphosphazenes **3**—the products of the phenolysis of monoaryloxyphosphazenes in a liquid–liquid two-phase system—has been observed on passing from the reaction in the bulk of the organic phase to the reaction on the interface.

High chemoselectivity and, to a lesser extent, regioselectivity are in general characteristic of phase-transfer catalytic processes.[1,2] The increase in the stereoselectivity of phase-transfer reactions is of current interest. Attempts are presently being made to solve this problem using phase-transfer catalysts with specific activity. There have been few successes along these lines and these refer mainly to enantioselective phase-transfer processes in the presence of chiral catalysts.[2]

The role of the interface as a factor responsible for the stereoselectivity of the phase-transfer process is demonstrated for the first time in the present communication.

Thus, an increase in the ratio[†] of the *cis*- and *trans*-isomers on passing from the homogeneous reaction i to the reaction on the interface has been noted for the formation of bis(aryloxy) phosphazenes **3**.

[†] The content of the isomers in the product **3** was determined to within ±1% by two independent procedures: (1) HPLC data [Liquochrom 2010, UV, Chromsil, 4.6 × 250 mm column, particle size 10 μm, eluent hexane–benzene (95:5), 2.5 cm^3 min^{-1}]; (2) in the reaction mixture, from the ^{31}P NMR spectra of the isomers described in ref. 3: **3** (Ar = Ar′ = 4-$NO_2C_6H_4$); *cis* $\delta_P = -25.4$(t), -15.4(d); *trans* $\delta_P = -24.8$(t), -14.9(d) (121.4 MHz, relative to 85% H_3PO_4).

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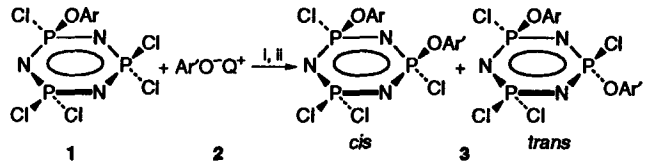

1a Ar = 4-$NO_2C_6H_4$
b Ar = 2,4-$(NO_2)_2C_6H_3$
2a Ar' = 4-$NO_2C_6H_4$, Q = Et_3BzN
b Ar' = 4-$NO_2C_6H_4$, Q = Bu_4N
c Ar' = 4-$NO_2C_6H_4$, Q = Na
d Ar' = 2,4-$(NO_2)_2C_6H_3$, Q = Na

Scheme 1 *Reagents and conditions:* i, homogeneous conditions, water-saturated PhCl or $CHCl_3$, **2a,b** (0.02 M), **1:2** = 2, 25 °C, 0.5 h; ii, 1:2 (by volume) borate buffer (pH 9) – PhCl (or $CHCl_3$) two-phase system, **2a–d** (0.02 M), 25 °C, **1:2** = 2, 2 h.

In the presence of a two-fold excess of the substrate **1**,‡ a mixture of the *cis*- and *trans*-isomers of compound **3** resulting from the non-geminal substitution with a 3% admixture of geminal bis(aryloxy)-derivatives is formed in all cases in 95% yield.§ Under homogeneous conditions i, the *cis*/*trans* ratio is independent of the structure of the reactants and the nature of the organic solvent and amounts to 57:43. The slight excess of the *cis*-isomer is usually attributed[3,4] to the manifestation of the 'through-space' interaction between the 2p orbitals of the oxygen atom in the aryloxy-group and the 3d orbital of the phosphorus atom in the initial substrate.

We showed earlier[7,8] that the phase-transfer phenolysis of the unsubstituted hexachlorocyclotriphosphazene can proceed either in the bulk of the organic phase or on the interface. Under these conditions, the conclusion concerning the site where the reaction occurs was reached on the basis of the characteristic form of the dependence of the observed rate of phenolysis on the cyclophosphazene concentration. The above dependence for the reaction on the interface assumes an anomalous form[7–9] and is observed in cases where the transfer of reagent **2** between the phases is the rate-limiting stage. We found[8] that the reactions on the interface are promoted by the high reactivity of the substrate and the poor extractability of the nucleophile **2** into the organic phase.

Similar relations are valid also for the phenolysis of compounds **1**, which are only 2–3 times less reactive than hexachlorocyclotriphosphazene. The results of the identification of the site of formation of product **3**, carried out by the procedure indicated, as well as its isomeric composition are indicated in Table 1.

As was to be expected, the increase in the extractability of reagent **2** (in the transitions **2a**→**2b** or PhCl→$CHCl_3$) shifts the reaction from the interface into the bulk organic phase. The stereoselectivity of the phenolysis then diminishes, becoming independent of the nature of the organic phase and the reagents and equal to that under homogeneous conditions. On the other hand, the enhancement of the hydrophilic properties of the reagent cation (**2b**→**2a**) and of the hydrophobic properties of the substrate (**1a**→**1b**) and the anion for an unchanged, very hydrophilic cation (**2c**→**2d**) displaces the reaction to the interface and leads to an increase in the process selectivity. Features of this kind suggest that a pre-reaction mutual orientation of the substrate and the reagent occurs on the interface. The hydrophobic groups of both compounds are then directed into the interior of the organic phase, while the hydrophilic cation (for which an intrinsic increase in selectivity was in fact detected) retains the arylate anion of the interface. Favourable conditions for *cis*-substitution in the monoaryloxycyclotriphosphazenes **1** are thereby created.

Table 1 The conditions for the phase-transfer catalytic phenolysis of monoaryloxycyclotriphosphazenes and the isomeric composition of the reaction products.

Substrate	Reagent	Organic phase	Reaction site	*cis*/*trans*
1a	**2a**	$CHCl_3$	organic phase	55:45
	2a	PhCl	interface	65:35
	2c	PhCl	interface	62:38
	2b	PhCl	organic phase	58:42
	2d	PhCl	interface	68:32
1b	**2d**	PhCl	interface	75:25

References

1 E. V. Dehmlow and S. S. Dehmlow, *Phase Transfer Catalysis*, 3rd edn., VCH Verlagsgessellschaft, Weinheim, 1992.
2 E. D'Incan, P. Viout and R. Gallo, *Isr. J. Chem.*, 1985, **26**, 277.
3 S. Karthikeyan and S. S. Krishnamurthy, *Z. Anorg. Allg. Chem.*, 1984, **513**, 231.
4 W. E. McEven and J. V. Cooney, *J. Org. Chem.*, 1983, **48**, 983.
5 E. Kober, H. Lederle and G. Ottmann, *Inorg. Chem.*, 1966, **5**, 2239.
6 A. E. Shumejko, A. A. Afon'kin, A. F. Popov, Zh. P. Piskunova, A. A. Yakovets and S. A. Grebenyuk, *Zh. Obshch. Khim.*, 1991, **61**, 2693 [*J. Gen. Chem. USSR (Engl. Transl.)*, 1991, **61**, 2499].
7 A. F. Popov, A. E. Shumejko, A. A. Afon'kin and Zh. P. Piskunova, *Reakts. Sposobn. Organ. Soedin.*, 1988, 313 [*Org. React. (Engl. Transl.)*, 1988, 313].
8 A. A. Afon'kin, A. E. Shumejko and A. F. Popov, *Zh. Obshch. Khim.*, 1992, **62**, 2540 [*J. Gen. Chem. USSR (Engl. Transl.)*, 1991, **62**, 2097].
9 S. S. Yufit, *Mekhanizm mezhfaznogo kataliza (Mechanism of Phase Transfer Catalysis)*, Nauka, Moscow, 1984, 264 (in Russian); M. Halpern, Y. Sasson and M. Rabinovitz, *J. Org. Chem.*, 1984, **49**, 2011.

‡ Compounds **1** were synthesised by a standard method.[5] Their ^{31}P NMR data and the results of elemental analysis are consistent with the structure presented. **1a**: m.p. 94–95 °C; ^{31}P NMR (121.4 MHz, $CHCl_3$, relative to 85% H_3PO_4), $\delta_P = -23.2$(d), -12.4(t). **1b**: m.p. 104–105 °C; $\delta_P = -23.1$(d), -13.3(t).

Compounds **2** were synthesised and described previously.[6]

§ The two-phase reactions with participation of compounds **2c** and **2d** were carried out over a period of 100 h up to 10% conversion. In such cases, the Na^+ cation was regarded as a very hydrophilic 'phase-transfer catalyst'.

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