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The use of the phenomenon of solid-state transformations of diastereomers for the synthesis of diastereomerically pure amidophosphonates

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Previously, we established that a new phenomenon of solid-state transformations of diastereomers is observed for the series of *O*-(α-polyfluoroalkylbenzyl) methylchlorophosphonates (**1**). This phenomenon consists in the spontaneous transformation of an equilibrium mixture of two diastereomers **A*** and **B** in the crystalline state into one or the other individual diastereomer.[1–3]

However, it turned out that in a liquid phase (a melt or a solution) individual diastereomers synthesized by solid-state reactions are transformed again into diastereomer mixtures similar in composition to the initial ones, which occurs especially easily in the presence of chloride anions.

Nevertheless, we demonstrated with the synthesis of *O*-(α-polyfluoroalkylbenzyl) methylphosphonamides (**2**) as an example that under certain experimental conditions the stereochemical instability of individual diastereomers of chlorophosphonates **1** is reduced in a liquid medium to a minimum, and that methods for the synthesis of diastereomerically pure organophosphorus compounds can be developed on the basis of the phenomenon of solid-state transformations of diastereomers. Thus, according to NMR spectral data, the reaction of the individual diastereomer **B** of chlorophosphonate **1a** with liquid ammonia at −60 °C occurs almost quantitatively and leads to the corresponding diastereomerically pure amide (**2a**). Analogously, the individual diastereomer of amide (**2b**) was obtained from diastereomer A of chlorophosphonate (**1b**).

$$\underset{\mathbf{1a,b}}{CH_3P(O)(Cl)OCH(CF_3)Ar} \xrightarrow{NH_3} \underset{\mathbf{2a,b}}{CH_3P(O)(NH_2)OCH(CF_3)Ar}$$

Ar = Ph (**a**), 4-ClC_6H_4 (**b**)

It was established that the equilibrium mixtures of diastereomers of chlorophosphonates **1a,b** give under similar conditions amides **2a,b** as mixtures of two diastereomers with the ratio of components close to the initial one. In both cases, diastereomers **A** of the initial chlorides are transformed into diastereomers of amides, whose signals in the ^{31}P NMR spectra are also shifted downfield. The δ values in the ^{31}P NMR spectra* of diastereomeric mixtures are equal to 41.44 and 41.86 ppm (C_6D_6) for chlorophosphonate **1a**, 41.77 and 42.00 ppm (C_6D_6) for chlorophosphonate **1b**, 36.63 and 36.73 ppm ($CDCl_3$) for amide **2a**, and 36.27 and 36.43 ppm ($CDCl_3$) for amide **2b**.

***O*-(α-Trifluoromethylbenzyl) methylphosphonamide (2a).** A solution of the individual diastereomer **B** of *O*-(α-trifluoromethylbenzyl) methylchlorophosphonate **1a** (1.2 g, 4.4 mmol) in 15 mL of anhydrous ether was added dropwise to a mixture of 10 mL of anhydrous ether and 20 mL of liquid NH_3 at −60 °C in a flow of argon, and the reaction mixture was stirred at this temperature for 0.5 h. The excess of NH_3 and the solvent were removed, and **2a** was extracted from the residue with anhydrous THF. Yield 1.05 g (95%), m.p. 99—101 °C (from a THF—hexane mixture). Found (%): C, 42.93; H, 4.39; N, 5.48; P, 12.25. $C_9H_{11}F_3NO_2P$. Calculated (%): C, 42.70; H, 4.38; N, 5.53; P, 12.23. ^1H NMR* ($CDCl_3$), δ: 1.44 (d, 3 H, Me, $^2J_{H-P}$ = 17.0 Hz); 5.66 (dq, 1 H, CH, $^3J_{H-F}$ = 6.5 Hz, $^3J_{H-P}$ = 12.1 Hz); 7.38—7.47 (m, 5 H, C_6H_5). ^{31}P NMR ($CDCl_3$), δ: 36.65 s.

Analogously, ***O*-(α-trifluoromethyl-*p*-chlorobenzyl) methylphosphonamide (2b)** was synthesized from the individual diastereomer **A** of *O*-(α-trifluoromethyl-*p*-chlorobenzyl) methylchlorophosphonate **1b** (1.4 g, 4.6 mmol). Yield 1.25 g (95%), m.p. 119—121 °C (from a THF—heptane mixture). Found (%): C, 37.78; H, 3.46; N, 4.80; P, 10.69. $C_9H_{10}ClF_3NO_2P$. Calculated (%): C, 37.58; H, 3.50; N, 4.87; P, 10.77. ^1H NMR ($CDCl_3$), δ: 1.62 (d, 3 H, Me, $^2J_{H-P}$ = 17.0 Hz); 5.66 (dq, 1 H, CH, $^3J_{H-F}$ = 6.3 Hz, $^3J_{H-P}$ = 12.1 Hz); 7.37—7.42 (m, 4 H, C_6H_4). ^{31}P NMR ($CDCl_3$), δ: 36.46 s.

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* Diastereomers, whose signals are shifted downfield in the ^{31}P NMR spectra, are named arbitrarily diastereomers A.

* ^1H and ^{31}P NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 and 161.98 MHz, respectively).

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Chemiluminescence in the reaction of sodium naphthalenide with the triphenylmethyl cation in THF

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Previously, we reported on luminescence of the $(Ph_3C^{\cdot})^*$ radical generated in reactions of Ph_3CNa with several oxidants.[1,2]

We observed chemiluminescence (CL) in the reaction of $Np^{\cdot -}Na^+$ (Np = naphthalene) with the Ph_3C^+ cation in THF. The trityl cation was obtained by mixing a solution of Ph_3CCl in THF with a weighed sample of sublimed $AlCl_3$. The Ph_3C^+ cation was identified by the UV spectrum (λ_{max} = 428.6 nm). Chemiluminescence was monitored as a rapidly descending curve : $\Delta I = 50\%$ for 30 s, $I_{max} = 6 \cdot 10^8$ photon s^{-1} mL^{-1} at $[Na^+, R^{\cdot -}] = 10^{-2}$ mol L^{-1}, $[Ph_3C^+] = 2 \cdot 10^{-2}$ mol L^{-1}, and a total volume of 5 mL.

The CL spectrum (Fig. 1) coincides with the spectrum of fluorescence (FL) of the $Ph_3C^{\cdot}$ radical generated by an independent method. Thus, the electron-excited trityl radical $(Ph_3C^{\cdot})^*$ is the emitter of CL.

During the reaction, the solution changed subsequently its green color (caused by $Np^{\cdot -}Na^+$) to brownish-yellow and yellow (typical of $Ph_3C^{\cdot}$). Then the solution was decolorized and gave a precipitate that was dissolved when several drops of water were added (NaCl and $AlCl_3$ were observed in the resulting solution). In excess water, a white precipitate was formed that contained naphthalene (identified by fluorescence, λ_{max} = 314 nm).

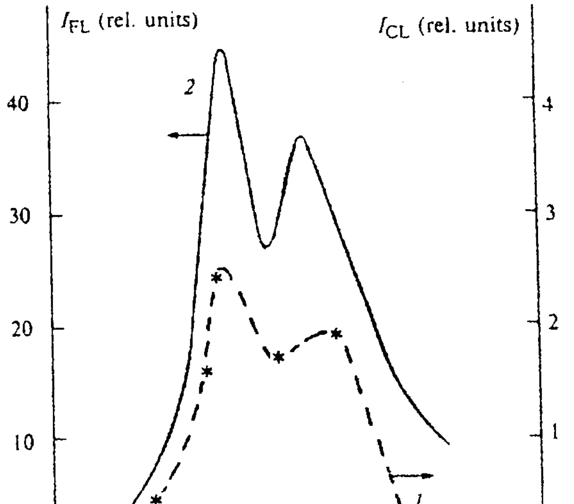

Fig. 1. *1*, CL spectrum measured by boundary light filters on the descendent region of the kinetic dependence in the reaction of $Np^{\cdot -}Na^+$ (10^{-2} mol L^{-1}) with $Ph_3C^+ \cdot AlCl_4^-$ ($2 \cdot 10^{-2}$ mol L^{-1}) in THF. *2*, Fluorescence spectrum of $Ph_3C^{\cdot}Cl$ synthesized by the reaction of Ph_3CCl with metallic zinc.

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