

Cyclic Phosphates Derived from 2,2,6,6-Tetrakis(hydroxymethyl)cyclohexanol Acetals in the Synthesis of New Phospholipids*

G. A. Savin¹, D. A. Predvoditelev², and E. E. Nifant'ev²

¹ Volgograd State Pedagogical University, pr. Lenina 27, Volgograd, 400131 Russia

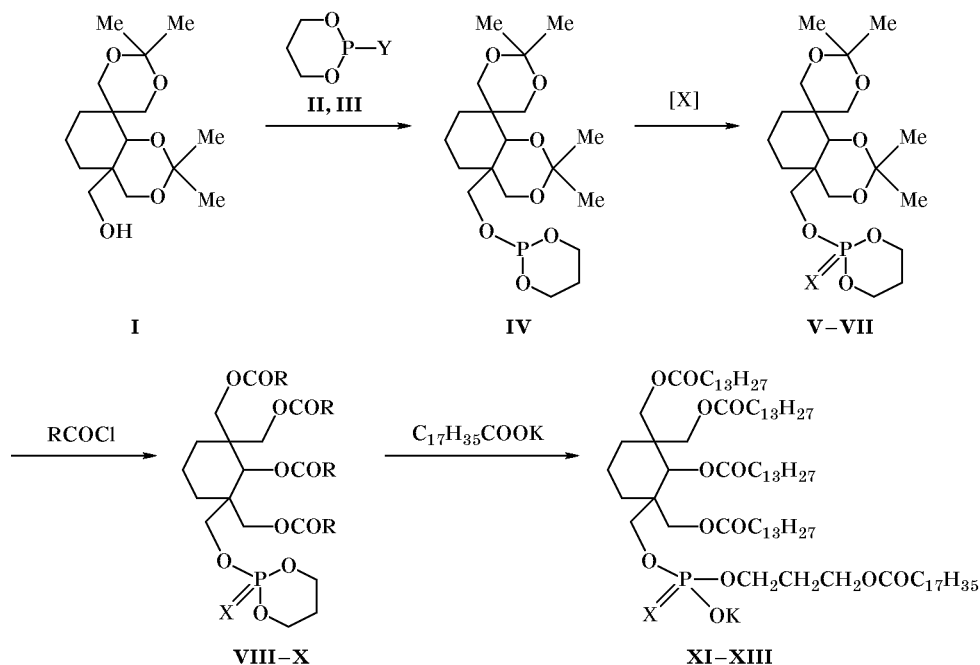
² Moscow State Pedagogical University, Moscow, Russia

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The present communication describes the synthesis of first representatives of hitherto unknown phosphatide acid analogs on the basis of cyclic phosphates derived from 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol. These compounds were synthesized with the use of cyclic P(III) and P(V) derivatives which were recently proved to be convenient reagents for lipid chemistry [1, 2]. As initial alcohol we used readily

accessible protected polyol **I** which was treated with cyclic phosphorous acid derivatives **II** and **III** to obtain cyclic phosphite **IV** (Scheme 1). Phosphite **IV** [δ_P 130 pp; R_f 0.6 (Silufol UV-254), hexane–dioxane, 5:1 (system A)] was converted *in situ* into phosphates **V–VII** by oxidation with iodobenzene or by the action of sulfur or selenium. Phosphate **V** was isolated by column chromatography on silica gel with hexane–

Scheme 1.



II, Y = Cl; **III**, Y = NEt₂; **V–X**, R = C₁₃H₂₇; **V**, **VIII**, **XI**, X = O; **VI**, **IX**, **XII**, X = S; **VII**, **X**, **XIII**, X = Se.

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dioxane (20:1) as eluent; thiophosphate **VI** and selenophosphate **VII** were purified by recrystallization from hexane.

Phosphate **V**. Yield 56%; mp 114–116°C; R_f 0.25 [benzene–dioxane, 5:1 (system B)]; δ_p –6.3 ppm.

Thiophosphate **VI**. Yield 60%; mp 136–137°C; R_f 0.7 (B); δ_p 62 ppm.

Selenophosphate **VII**. Yield 63%; mp 141–142°C; R_f 0.7 (B); δ_p 68 ppm ($^1J_{P,Se} = 990$ Hz).

Phosphates **V–VII** were subjected to direct acylation with myristoyl chloride at 20°C in the presence of anhydrous zinc chloride. Tetramyristoyl derivatives **VIII–X** were isolated in up to 55% yield by column chromatography on silica gel using hexane as eluent: phosphate **VIII**, mp 48–50°C, R_f 0.3 (A); thiophos-

phate **IX**, mp 54–55°C; R_f 0.45 (A); selenophosphate **X**, mp 61–62°C; R_f 0.45 (A).

In the final stage, acylated phosphates **VIII–X** were treated with potassium stearate at 120°C (12 h). The resulting potassium salts **XI–XIII** were purified by recrystallization from acetone (yield $\leq 50\%$). Compound **XI**, mp 16–17°C, R_f 0.0 (B), δ_p –1 ppm; **XII**, mp 57–58°C, R_f 0.0 (B), δ_p 57 ppm; **XIII**, mp 63–64°C, R_f 0.0 (B), δ_p 59 ppm ($^1J_{P,Se} = 790$ Hz).

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