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## LETTERS TO THE EDITOR

# Peculiarities of the Chemical Behavior of a Per-P(III)-Derivative of β-Cyclodextrin

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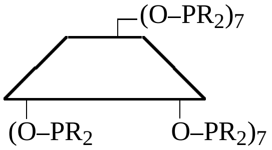
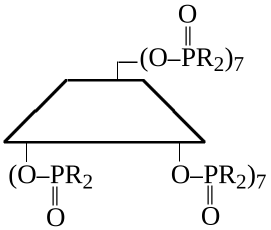
We previously found that the cyclodextrin carcass of a per-P(III)-phosphorylated β-cyclodextrine can significantly affect the chemical properties of its bound phosphite groups [1, 2]. It was shown that the unexpected transphosphorylation of per-P(III)-containing cyclodextrins is a result of intricate supramolecular interactions of per-P(III)-cyclodextrins and phosphorochloridites [2].

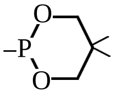
Here we report about the peculiarities of the chemical behavior of per-P(III)-phosphorylated β-cyclodextrine **I** in oxidation with nitrogen(II) oxide and sulfurization. It was found that the reactivity of P(III) fragments of compound **I** significantly depends on the possibility of insertion of the reagents and reaction products in the cyclodextrin cavity. Pure perphosphite **I** is easily and quantitatively oxidized with nitrogen(II) oxide to the corresponding phosphate, whereas attempted sulfurization of the former unexpectedly failed. Obviously, the peculiar behavior of the cyclodextrine perphospite in the first reaction is explained by the supramolecular effect of the free cyclodextrin cavity on the oxidation pathway. When the cavity is occupied, as in the case of crude perphospite, the reaction is difficult to occur. The failure of pure perphosphite **I** to add sulfur is probably associated with the fact that the hydrophobic sulfur atom is bound by the molecular cavity of the substrate. Evidence for this suggestion comes from the successful sulfurization of crude cyclodextrins whose molecular cavities are occupied by pyridine hydrochloride [3]. In addition note that the $^{31}P$ NMR spectrum of pure product **I** contains one broad signal at 122 ppm [1] rather than two signals at 121 and 123 ppm, as previously observed in the spectrum compound **I** prepared by treatment of cyclodextrin with cyclophosphorochloridite in pyridine [1]. A special experiment was performed to show that treatment of a solution of pure perphosphite **I** with 1 mol of pyridine hydrochloride results in appearance of the above-mentioned signals at 121 and 123 ppm, probably because that here, too, pyridine hydrochloride occupies the cyclodextrin cavity.



**I**



**II**

$-PR_2 =$


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Hence, the common synthetic strategy of the organophosphorus chemistry, when a P(III) compound is oxidized *in situ* to a more stable P(III) derivative and then purified and isolated as an individual compound not always works in the oxidation of P(III) cyclodextrine derivatives with nitrogen(II) oxide.

All experiments with P(III) compounds were

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carried out under dry argon in thoroughly dried solvents. The synthesis of pure β-cyclodextrin perphosphite **I** was carried out according to [1].

**Heptakis[2,3,6-tri-*O*-(5,5-dimethyl-2-oxo-1,3,2$\lambda^5$-dioxaphosphorinan-2-yl)]-β-cyclodextrin (II).** Through a solution of 0.5 g of compound **I** in 10 ml of benzene, anhydrous nitrogen(II) oxide was slowly bubbled at 20°C. Completion of the reaction was judged about by the disappearance of the signal of the starting reagent **I** at $\delta_P$ 122 ppm and the appearance of a signal with $\delta_P$ –8.5 ppm in the $^{31}$P NMR spectrum of the reaction mixture. The solvent was removed in a vacuum, and the residue was dried. Yield 0.53 g (98%), mp 212–214°C. $R_f$ 0.85 (Silufol UV-354; benzene–dioxane, 3 : 1). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 0.61–0.83 (63H, $CH_3^e$), 1.09–1.35 (83H, $CH_3^a$), 3.06–3.26 (42H, $POCH^e$), 3.95–4.53 (84H, $C^2H–C^5H$, $C^6H_3$, $POCH^a$), 5.25–5.43 (7H, $C^1H$). $^{31}$P NMR spectrum ($CHCl_3$), $\delta_P$, ppm: –8.5 br.s. Found, %: C 41.80; H 6.34, P 1519. $C_{147}H_{259}O_{98}P_{21}$. Calculated, %: C 41.59; H 6.15, P 15.32.

The $^1$H and $^{31}$P NMR spectra were registered on Bruker WP-250 (250 MHz) and Bruker WP-80 (32.4 MHz) spectrometers against external TMS and 85% phosphoric acid, respectively.

## ACKNOWLEDGMENTS

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