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The synthesis of carbohydrate bicyclophosphites has been carried out using sugar derivatives as starting compounds, in which individual hydroxyl groups are protected [1]. We are the first to demonstrate the possibility of the direct bicyclophosphorylation of monosaccharides in the case of D-xylose. The tris-2,4-dimethylpyrazolide of phosphorous acid was used as the phosphorylating agent and the procedure for the bicyclophosphorylation of mutarotatory sugars was employed [2].



R = Ac(II), Bz(III).

Phosphite (I) was obtained in 40% yield as a syrup, $[\alpha]_D^{20}$ +50.0° (c 0.5, CHCl₃), R_f 0.60,* and $\delta^{31}P$ 111.2 ppm.

Bicyclophosphites (I)-(III) add selenium and sulfur in absolute dioxane at 100°C and are oxidized by ozone in CH_2Cl_2 at -70°C.



Thionephosphate (IV) was obtained in 60% yield, mp 140-142°C, $[\alpha]_D^{25}$ +13.9° (c 1.3 CHCl₃), R_f 0.86, δ ³¹P 70.9 ppm. Selenophosphate (V) was obtained in 69% yield, mp 157-158°C, $[\alpha]_D^{21}$ +29.7°C (c 1.8, CHCl₃), R_f 0.87, δ ³¹P 74.0 ppm, J_{P-Se} 1104 Hz. Phosphate (VI) was obtained in quantitative yield as a syrup, $[\alpha]_D^{21}$ +23.3° (c 0.7, CHCl₃), R_f 0.43, δ ³¹P 6.6 ppm.

As a consequence of significant strain of the phosphobicyclic fragment, bicyclophosphates (IV)-(VI) readily react with protic nucleophiles such as water in the presence of amines. Hydrolysis leads selectively to the formation of only one monocyclophosphate. The product structure was demonstrated using ¹H and ¹³C NMR spectroscopy. We should note that the hydrolysis does not affect the usually most active glycophosphate site, but rather the phosphate site.

*Chromatography using 3:1 benzene-dioxane as the eluent.

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Triethylammonium Salt of 1,4-Cyclothionephosphate-3-benzoylxylopyanoside (VII) was obtained in quantitative yield with $[\alpha]_D^{20}$ +8.8° (c 0.57, Py), R_f 0, $\delta^{31}P$ 47.5 ppm. ¹³C NMR spectrum in CDCl₃ (δ , ppm, J_{P-C}, Hz): 96.5 d (C¹, J = 11.1), 73.6 s (C²), 72.9 s (C³), 71.4 d (C⁴, J = 9.2), 64.4 s (C⁵). PMR spectrum in C₅D₅N (δ , ppm, J_{P-H}, Hz): 5.93 d.d (H¹, J = 24.9), 4.58 d.d (H²), 4.49 d.d (H³), 6.69 m (H⁴, J = 27.3), 4.50 d (H_a⁵), 4.29 d.d (H_b⁵).

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REDUCTIVE DEHALOGENATION OF HALO DERIVATIVES OF

BIS(1,1'-BICYCLO[1.1.1]PENTANE)

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[1.1.1]Propellane (I) readily undergoes a photochemical reaction with 1,3-diiodobicyclo[1.1.1]pentane to give 3,3'-diiodobis(1,1'-bicyclo[1.1.1]pentane) (II), while the irradiation of a mixture of propellane (I) and CCl₄ gives 3-chloro-3'-trichloromethylbis(1,1'-bis(1,1'-bicyclo[1.1.1]pentane (III) [1, 2].

We have found that heating iodide (II) with tributyltin hydride in ether at reflux for 3 h leads to complete reduction and the formation of hydrocarbon (IV) as the only product in 70% yield.



 $X = Y = I(II); X = Cl, Y = CCI_3(III); R = H(IV); CH_3(V).$

The dechlorination of (III) is readily achieved upon heating in ether at reflux with a 10-fold excess of both lithium and tert-butyl alcohol. Preparative gas-liquid chromatography of the reaction mixture on a Carbowax column at from 105 to 200°C gave hydrocarbon (V) as well as (VI) and (VII) in 1:3:6 ratio and 60% total yield.

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