

SHORT
COMMUNICATIONSReaction of Hexafluoroacetone with 2,7-Diethoxybenzo-
[1,2-*d*:4,5-*d'*]bis[1,3,2]dioxaphosphinine-4,9-dione Derived
from 2,5-Dihydroxyterephthalic Acid

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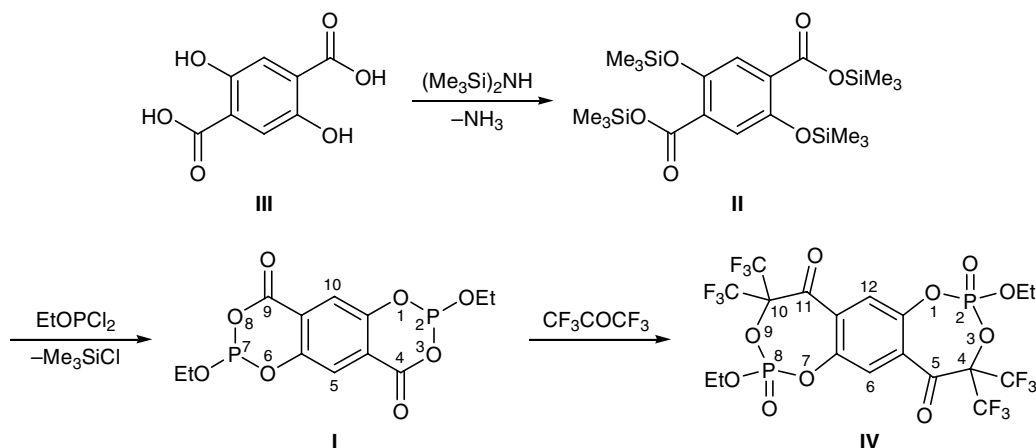
Reactions of cyclic phosphorylated derivatives of salicylic and hydroxynicotinic acids with carbonyl compounds offer a simple and convenient synthetic approach to seven-membered heterocycles such as 1,3,2- and 1,4,2-benzodioxaphosphepines [1–4]; some of these compounds may be used in the synthesis of fluorinated ketones [5]. We made an attempt to extend the above approach to more complex bis-phosphorylated derivatives of 2,5-dihydroxyterephthalic acid (**III**), namely 2,7-diethoxybenzo[1,2-*d*:4,5-*d'*]bis[1,3,2]dioxaphosphinine-4,9-dione (**I**) which was prepared by reaction of tetrakis(trimethylsilyl) derivative **II** of acid **III** with dichloro(ethoxy)phosphine in almost quantitative yield. Compound **II** was synthesized by treatment of 2,5-dihydroxyterephthalic acid (**III**) with hexamethyldisilazane.

Benzodiphosphinine **I** (CH_2Cl_2 , δ_{P} 124.9 and 125.5 ppm, a mixture of *dl* and *meso* forms at a ratio of 1:1) readily reacted with 2 equiv of hexafluoro-

acetone to give a new heterocyclic system, 2,8-diethoxy-4,4,10,10-tetrakis(trifluoromethyl)benzo[1,2-*d*:4,5-*d'*]bis[1,3,2] λ^5 -dioxaphosphepine-5,11-dione 2,8-dioxide (**IV**). The latter was formed as a mixture of two diastereoisomers at a ratio of 1:1 (CDCl_3 , δ_{P} –11.8 and –12.1 ppm, *dl* and *meso*; overall yield >90%). One diastereoisomer of **IV** gradually crystallized from methylene chloride and was isolated (δ_{P} –11.8 ppm). Its structure was proved by the ^1H , ^{19}F , and ^{13}C NMR, IR, and electron impact mass spectra.

Thus we have shown that complex bis-phosphorylated derivatives of 2,5-dihydroxyterephthalic acid like **I** are capable of reacting with hexafluoroacetone to give products of expansion of the six-membered heterorings to seven-membered. It seems promising to extend the proposed procedure to other phosphorus-containing cyclic derivatives of natural hydroxy acids.

2,7-Diethoxybenzo[1,2-*d*:4,5-*d'*]bis[1,3,2]dioxaphosphinine-4,9-dione (**I**) was synthesized by heating



a mixture of 6.0 g of trimethylsilyl derivative **II** and 4.0 g of dichloro(ethoxy)phosphine at 40–50°C under reduced pressure (100 mm); the product was isolated as a thick light yellow liquid which was freed from volatile impurities by evacuation at a residual pressure of 12 mm and was then used without additional purification.

2,8-Diethoxy-4,4,10,10-tetrakis(trifluoromethyl)-benzo[1,2-d:4,5-d']bis[1,3,2λ⁵-dioxaphosphine]-5,11-dione 2,8-dioxide (IV). Compound **I**, 4.0 g, was dissolved in a mixture of 10 ml of methylene chloride and 30 ml of carbon tetrachloride, and 4.30 g of hexafluoroacetone was recondensed thereto at –40°C. The mixture was allowed to slowly warm up to 20°C and was held for 7 days at that temperature. A crystalline material separated and was filtered off, washed with diethyl ether, and dried. Yield 37%, mp 161°C. Mass spectrum: *m/z* 678 [*M*]⁺. IR spectrum, *v*, cm⁻¹: 3030, 1726, 1488, 1409, 1315, 1297, 1235, 1184, 1147, 1080, 1023, 984, 955, 908, 905, 786, 739, 711, 691, 608, 576, 529, 510, 447. ¹H NMR spectrum, *δ*, ppm: 1.51 t.d (6H, CH₃, ³*J*_{HH} = 7.2, ⁴*J*_{PH} = 0.5 Hz), 4.53 q.d (4H, OCH₂, ³*J*_{HH} = 7.2, ³*J*_{PH} = 9.4 Hz), 7.61 d (2H, 6-H, 12-H, ⁴*J*_{PH} = 0.5 Hz). ¹⁹F NMR spectrum, *δ*_F, ppm: –72.31 q and –73.09 q (CF₃, ⁴*J*_{FF} = 9.2 Hz). ¹³C NMR spectrum, *δ*_C, ppm (signal multiplicity in the proton-decoupled spectrum is given in parentheses): 132.80 br.d.d (s) (C^{5a}, C^{11a}, ³*J*_{CH} = 4.7–5.0, ²*J*_{CH} = 2.8–3.0 Hz), 83.05 sept.d (sept.d) (C⁴, C¹⁰, ²*J*_{FC} = 30.6, ²*J*_{PC} = 5.1 Hz), 183.36 br.d (s) (C⁵, C¹¹, ³*J*_{CH} = 4.5 Hz), 145.19 d.d.d (d) (C^{6a}, C^{12a}, ³*J*_{CH} = 9.2, ²*J*_{PC} = 6.1, ²*J*_{CH} = 5.2 Hz), 124.86 d.d (d) (C⁶, C¹², ¹*J*_{CH} = 171.7, ³*J*_{PC} = 9.3 Hz), 119.45 br.q.d (br.q.d) (CF₃, ¹*J*_{CF} = 289.4, ³*J*_{PC} = 8.3 Hz), 119.50 br.q.d (br.q.d) (CF₃,

¹*J*_{CF} = 289.3, ³*J*_{PC} = 5.3 Hz), 68.83 t.d.q (d) (CH₂, ¹*J*_{CH} = 151.2, ²*J*_{PC} = 6.6, ²*J*_{CH} = 4.5 Hz), 15.89 q.d.t (d) (CH₃, ¹*J*_{CH} = 128.0, ³*J*_{PC} = 5.6, ²*J*_{CH} = 3.0 Hz).

The IR spectrum was measured on a Bruker Vector-22 instrument from a sample dispersed in mineral oil. The NMR spectra were recorded on Bruker MSL-400 (³¹P, 162.0 MHz), Bruker Avance-600 (¹H, 600 MHz; ¹³C, ¹³C–{¹H}, DEPT, 150.9 MHz), and Varian Unity-300 spectrometers (¹⁹F, 287.2 MHz) from solutions in CDCl₃ using HMDS (¹H), C₆F₆ (¹⁹F), or solvent signal (¹³C) as internal reference and H₃PO₄ (³¹P) as external reference. The mass spectrum (electron impact, 70 eV) was obtained on a Trace MS Finnigan MAT mass spectrometer with direct sample admission into the ion source (ion source temperature 200°C). The batch-inlet system was heated in a programmed mode (from 35 to 150°C at a rate of 35 deg/min).

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