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Carbohydrate Research 287 (1996) 263–270

CARBOHYDRATE RESEARCH

Note

The one-pot esterification of phosphoric acids with silver carbonate and alkyl halides in refluxing toluene

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Received 22 January 1996; accepted 12 March 1996

Keywords: Biodegradable phosphate esters; Acyloxymethyl esters; Silver carbonate; Inositol phosphates

Because ionic phosphates (such as biologically active inositol phosphates) do not pass readily into the cell through biological membranes, efforts have been made [1,2] to produce non-polar, membrane-permeable derivatives which could be hydrolysed by intracellular enzymes to release the native ionic phosphate.

In the original design [3–17] of such molecules the acyloxymethyl esters of phosphates (**1**) were prepared and investigated, and in the presence of esterases were shown to be hydrolysed as depicted in Scheme 1. Although the removal of one of the acyloxymethyl groups occurred readily in the presence of esterases (to give **2**) the enzymic removal of the second ester group from **2** was slow because of the negative charge close to a postulated negatively charged hydrolytic site of the enzyme [18–20].

Therefore other types of protecting groups were designed so that the enzymically hydrolysable ester group was farther removed from the anionic charge, for example, the 4-acetoxybenzyl ester (**3**, Scheme 2) [18–20] or the 4-acyloxy-1,3,2-dioxaphosphorinanes (**4**) [21,22], which are cyclic acyloxymethyl derivatives, and for which the intermediate **5** will spontaneously decompose (Scheme 3) after esterase hydrolysis of the ester group from the neutral **4**. Similarly with the acyloxymethyl triesters (**6**, Scheme 4) the ester group is removed away from the anion in the intermediate diester **7**, and compounds of this type have been described in the patent literature by Bundgaard [23].

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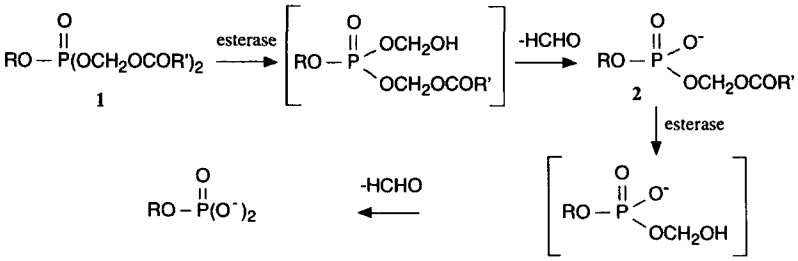
PII S0008-6215(96)00084-5

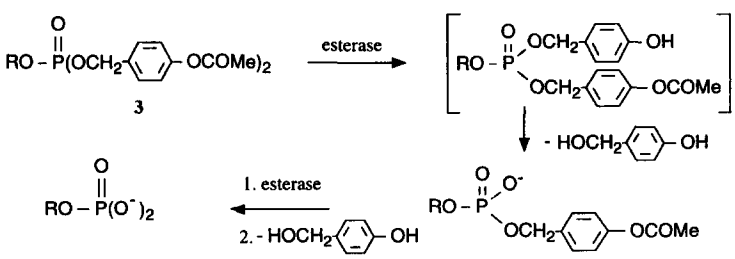


Scheme 1.

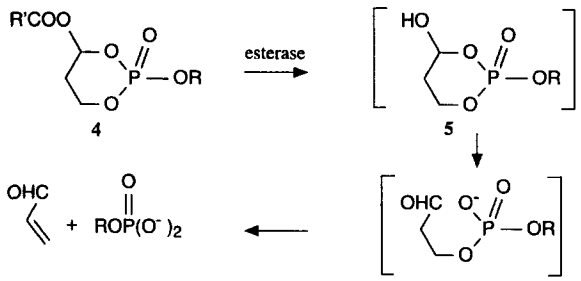
In order to synthesise acyloxymethyl phosphate esters the usual strategy has been to prepare the silver salt of the phosphate separately and to react this with the acyloxymethyl halide. Although this technique works efficiently when a single phosphate group is present, our interest was in the preparation of protected derivatives of inositol phosphates containing more than one phosphate group, and the separate preparation of the silver salts (by precipitation from an aqueous solution of the sodium salts) was not guaranteed to give complete substitution of sodium ions by silver ions.

A potential solution to this problem has been reported in which various monophosphate diesters were treated with halides in acetonitrile in the presence of silver(I) oxide [24] to give phosphotriesters, but the esterification of phosphate monoesters or polyphosphates was not described. This in situ method has some advantages although the liberation of water was deleterious in certain reactions; higher temperatures lowered the yields, possibly due to the basicity of silver oxide, and the preparations of acyloxymethyl derivatives were not described.

Some years ago we prepared [25] the dibenzyl phosphate **10** by the reaction of the phosphate monoester **9** with phenyldiazomethane. This procedure was not ideal due to contamination of the product with by-products initially present in the phenyldiazomethane solution. We therefore developed (unpublished) a useful one-pot procedure (related to that described in ref. [24]) for the conversion of **9** into **10** by reaction with benzyl bromide and silver carbonate in refluxing toluene. Molecular sieve was provided, in a Soxhlet apparatus, to remove the water liberated on reaction of the phosphate with the silver carbonate. We found that this method worked very well and, more recently, because of our interest in the biologically active inositol phosphates, we have applied

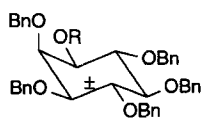


Scheme 2.

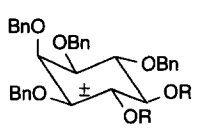


Scheme 3.

this method to the preparation of many different phosphate esters (including those from bis- and tris-phosphates). We found that the reaction was also suitable for the preparation of acyloxymethyl esters of phosphates and we describe some of the results here.



8 R = H
9 R = $P(O)(OH)_2$
10 R = $P(O)(OBn)_2$
11 R = $P(O)(OCH_2CCl_3)_2$
12 R = P(O) - OH, OBn
13 R = P(O)OBn, $OCH_2OCOCMe_3$
14 R = $P(O)(OCH_2CH_2CN)_2$
15 R = $P(O)(OCH_2OCOCMe_3)_2$



24 R = $P(O)(ONa)_2$
25 R = $P(O)(OH)_2$
26 R = $P(O)(OBn)_2$
27 R = $P(O)(OCH_2OCOCMe_3)_2$

$CH_3(CH_2)_{14}CH_2OR$

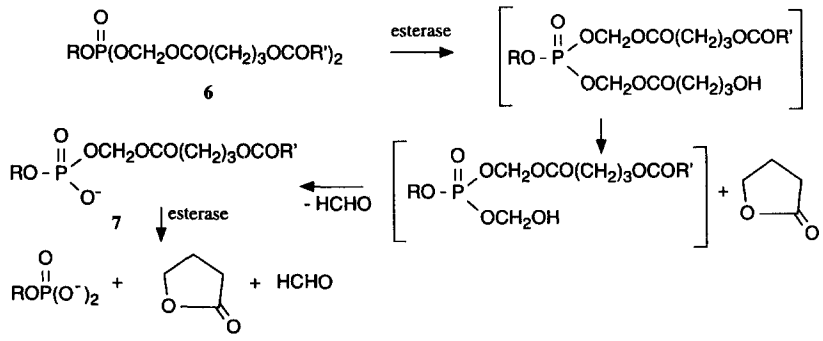
16 R = H
17 R = $P(O)(OCH_2CH_2CN)_2$
18 R = $P(O)(OH)_2$
19 R = $P(O)(OBn)_2$
20 R = P(O) - ONa, OBn
21 R = P(O) - OH, OBn
22 R = P(O) - OCH_2OCO_2Et, OBn
23 R = $P(O)(OCH_2OCOCMe_3)_2$

$ClCH_2OCOCMe_3$
28

$ClCH_2OCOOEt$
29

Bn = CH_2Ph

The reaction of the salts of phosphates with organic bases, for example, tetrabutylammonium salts [21], diisopropylethylamine salts [12,17], or *N,N'*-dicyclohexylmorpho-



Scheme 4.

linecarboxamidine salts [10,15], with halides has also been described as an alternative procedure for the preparation of esters of polyphosphates.

In the original preparation [25] of the dibenzyl phosphate **10** it was not characterised but was converted into the crystalline monobenzyl phosphate **12** by reaction with sodium iodide in acetone and subsequent acidification. Also in the original work [25] the phosphate **9** was obtained by phosphorylation of 2,3,4,5,6-penta-*O*-benzyl-*myo*-inositol (**8**) with phosphorus oxychloride or by deprotection of the bis(trichloroethyl) ester **11**. Here we have prepared **9** by deprotection of the bis(2-cyanoethyl) ester **14** prepared by using phosphoramidite methodology [26] and we have also prepared a reference sample of the dibenzyl ester **10** using phosphoramidites as intermediates. Using the general procedure, as described in the title, we have converted **9** into the dibenzyl ester **10** and the di-(pivaloyloxymethyl) ester **15**, and also the acid **12** was converted into the benzyl pivaloyloxymethyl ester **13**.

Hexadecanol (**16**) was converted into the dibenzyl phosphate **19** and the bis(2-cyanoethyl) phosphate **17** using phosphoramidite reagents, and **19** was converted into the benzyl phosphate **20** by reaction with sodium iodide in acetone. Basic hydrolysis of **17** gave hexadecyl phosphate **18** and this was converted into the di-(pivaloyloxymethyl) ester **23** using the general method. The monobenzyl phosphate **21** was converted into **22** using this procedure.

In order to study the preparation of esters of bisphosphates by this procedure the known [27] sodium salt (**24**) of 1,2,3,6-tetra-*O*-benzyl-*myo*-inositol 4,5-bisphosphate was converted into the free acid **25** and this was esterified to give the known [27] tetrabenzyl ester **26** and also the tetra-(pivaloyloxymethyl) ester **27**.

1. Experimental

General.—The general methods were as described [28]. NMR spectroscopy was carried out on a JEOL FX90Q instrument in $CDCl_3$ solution. All the inositol derivatives described are racemic.

General procedure for the esterification of phosphate esters by reaction of the phosphate with silver carbonate and alkyl halide in refluxing toluene.—A solution of the free phosphoric acid in aq MeOH, obtained as an eluate from an ion-exchange

column [Amberlite IR-120(H^+)] used to convert the sodium salt into the free acid, was added to an excess of silver carbonate (3 equiv) in toluene, the mixture was concentrated to azeotrope the MeOH and water, and this procedure was repeated. Alkyl halide (3 equiv) was then added to the solution which was refluxed, with a Soxhlet apparatus containing molecular sieve 3 Å, until TLC showed complete conversion of the phosphate into the product. The solution was filtered and concentrated, and the product was obtained by column chromatography.

(±)-2,3,4,5,6-Penta-O-*benzyl*-myo-*inositol 1-[bis(2-cyanoethyl) phosphate]* (**14**).—A solution of tetrazole (450 mg, 6.42 mmol) in MeCN (7 mL) was added to a solution of (±)-2,3,4,5,6-penta-*O*-benzyl-*myo*-inositol ([25], see also ref. [29]) (**8**, 2 g, 3.17 mmol) and bis(2-cyanoethoxy)(diisopropylamino)phosphine [26] (1.3 g, 4.8 mmol) in CH_2Cl_2 (15 mL) and the solution was stirred for 1 h at 20 °C. TLC (1:1 ether–light petroleum) showed conversion of **8** (R_f 0.4) into the phosphite (R_f 0.1). A solution of technical *m*-chloroperbenzoic acid (3 g) in CH_2Cl_2 (20 mL) was added and the solution was stirred for 2 h. TLC (ether) showed conversion of the phosphite (R_f 0.7) into the phosphate **14** (R_f 0.1). The solvents were evaporated, the residue dissolved in CH_2Cl_2, and the solution washed with satd aq sodium metabisulfite and satd aq $NaHCO_3$, dried ($MgSO_4$), and evaporated. Column chromatography (silica gel) and elution with ether followed by 1:1 ether–EtOAc gave the phosphate **14** (2 g, 77%) as a syrup; ^{31}P NMR data: δ −3.16. Anal. Calcd for $C_{47}H_{49}N_2O_9P$: C, 69.10; H, 6.05; N, 3.43; P, 3.79. Found: C, 68.73; H, 6.04; N, 3.09; P, 3.72.

(±)-2,3,4,5,6-Penta-O-*benzyl*-myo-*inositol 1-(dihydrogen phosphate)* (**9**) [25].—The bis(2-cyanoethyl) phosphate **14** (1 g, 1.2 mmol) was treated with 0.2 M NaOH in aq 50% MeOH (30 mL) at 60 °C for 1 h. The solution was cooled and passed through a column of excess Amberlite IR-120(H^+) which was washed with aq 50% MeOH and MeOH. The product was eluted initially as a milky solution. This was used immediately as described below for the reactions with silver carbonate and alkyl halides.

(±)-2,3,4,5,6-Penta-O-*benzyl*-myo-*inositol 1-(dibenzyl phosphate)* (**10**) [25,30].—(*a*) The solution of the phosphate (**9**, 1.2 mmol) in aq MeOH prepared as described in the previous section was treated with Ag_2CO_3 in refluxing toluene followed by benzyl bromide as described in the general procedure for 3 h when TLC (2:1 ether–light petroleum) showed complete conversion into the dibenzyl ester **10** (R_f 0.5). At intermediate stages the monobenzyl ester **12** [25] could be detected (R_f 0.4) by TLC [100:10:1 $CHCl_3$–MeOH–concd aq NH_4OH(d = 0.880)]. Column chromatography (silica gel) and elution with 2:1 ether–light petroleum gave pure **10** as a syrup; ^{31}P NMR data: δ −1.61. Anal. Calcd for $C_{55}H_{55}O_9P$: C, 74.14; H, 6.22; P, 3.48. Found: C, 74.01; H, 6.32; P, 3.55.

(*b*) The pentabenzyl inositol **8** was treated with dibenzyloxy(diisopropylamino)phosphine and tetrazole [26], the intermediate phosphite was oxidised to the phosphate **10**, and the product isolated as described for similar products [26]. This was identical with the material described in (*a*).

(±)-2,3,4,5,6-Penta-O-*benzyl*-myo-*inositol 1-[di-(pivaloyloxymethyl) phosphate]* (**15**).—A solution of the phosphate (**9**, 1.2 mmol) in aq MeOH, prepared as described above, was treated with pivaloyloxymethyl chloride (**28**) and Ag_2CO_3 in refluxing toluene for 2.5 h as described in the general procedure; TLC (2:1 ether–light petroleum)

showed the product at R_f 0.75. Column chromatography and elution with 1:2 ether–light petroleum removed the excess of chloride, and the product **15** (1.04 g, 91%) was obtained as a syrup by elution with 2:1 ether–light petroleum; ^{31}P NMR data: δ −5.18. Anal. Calcd for $C_{53}H_{63}O_{13}P$: C, 67.79; H, 6.76; P, 3.30. Found: C, 67.85; H, 6.84; P, 3.44.

*(±)-2,3,4,5,6-Penta-*O*-benzyl-*myo*-inositol 1-(benzyl pivaloyloxymethyl phosphate)* (**13**).—The benzyl phosphate **12** [25] was treated with Ag_2CO_3 and pivaloyloxymethyl chloride (**28**) in refluxing toluene for 2 h as described in the general procedure. TLC (2:1 ether–light petroleum) showed the product at R_f 0.6. Column chromatography and elution with 1:4 ether–light petroleum removed the excess of chloride and elution with 2:1 ether–light petroleum gave the product (**13**, 90%) as an oil. Anal. Calcd for $C_{54}H_{59}O_{11}P$: C, 70.88; H, 6.50; P, 3.39. Found: C, 70.72; H, 6.55; P, 3.38.

Bis(2-cyanoethyl) hexadecyl phosphate (**17**).—A solution of tetrazole (1.4 g, 20 mmol) in MeCN (20 mL) was added to a solution of hexadecanol (**16**, 2.42 g, 10 mmol) and bis(2-cyanoethoxy)(diisopropylamino)phosphine (4.1 g, 15 mmol) in dry CH_2Cl_2 and the solution was stirred at 20 °C for 1.5 h. TLC (1:1 ether–light petroleum) showed conversion of the hexadecanol (R_f 0.5) into the phosphite (R_f 0.3). The solution was cooled to 0 °C and a solution of technical *m*-chloroperbenzoic acid (3 g) in CH_2Cl_2 (20 mL) was added slowly. After 1 h TLC (EtOAc) showed conversion of the phosphite (R_f 1.0) into the phosphate (R_f 0.5). The solvents were evaporated and a solution of the residue in CH_2Cl_2 was washed with aq 10% sodium metabisulfite and aq 10% Na_2CO_3, dried ($MgSO_4$), and concentrated. Column chromatography and elution with EtOAc gave **17** (3 g, 70%); mp 41–42 °C (from light petroleum); ^{1}H NMR data: δ 2.78 (t, 4 H, *J* 6.1 Hz, CH_2CN), 4.01–4.40 (m, 6 H, 3 × OCH_2); ^{31}P NMR data: δ −2.22. Anal. Calcd for $C_{22}H_{41}N_2O_4P$: C, 61.66; H, 9.64; N, 6.54; P, 7.22. Found: C, 61.68; H, 9.95; N, 6.45; P, 7.09.

Benzyl hexadecyl hydrogen phosphate (**21**).—Hexadecanol was treated with dibenzyloxy(diisopropylamino)phosphine and the intermediate phosphite was oxidised to the phosphate **19** [^{1}H NMR data: δ 5.04 (d, 2 H, *J* 8.6 Hz, CH_2Ph), 3.99 (ABq, 2 H, OCH_2R); ^{31}P NMR data: δ −0.81] and the product isolated as described for similar phosphorylations [26]. This was treated with NaI in acetone under reflux (as described for related compounds [25]) and the crystalline sodium salt which separated was recrystallised from acetone to give **20**; mp 118–124 °C; ^{31}P NMR data: δ +1.48. Anal. Calcd for $C_{23}H_{40}O_4PNa$: C, 63.57; H, 9.28; Na, 5.29. Found: C, 63.95; H, 9.33; Na, 5.95.

A solution of the sodium salt in water was treated with an excess of M HCl, the precipitated product was extracted with CH_2Cl_2, and the solution washed with satd aq KCl and concentrated. Recrystallisation of the product from EtOAc–light petroleum gave **21**; mp 65–66 °C; ^{1}H NMR data: δ 5.04 (d, 2 H, *J* 7.9 Hz, CH_2Ph), 3.99 (ABq, 2 H, OCH_2R); ^{31}P NMR data: δ +1.01. Anal. Calcd for $C_{23}H_{41}O_4P$: C, 66.96; H, 10.02; P, 7.51. Found: C, 66.99; H, 10.20; P, 7.1.

Benzyl ethoxycarbonyloxymethyl hexadecyl phosphate (**22**).—The benzyl phosphate **21** was treated with Ag_2CO_3 and chloromethyl ethyl carbonate (**29**) in toluene under reflux as described in the general procedure for 4 h. TLC (1:1 ether–light petroleum) showed conversion of **21** (R_f 0) into the product (R_f 0.8). Column chromatography and

elution with 1:2 ether–light petroleum followed by 1:1 gave the product (**22**, 95%) as an oil; ^{1}H NMR data: δ 5.61 (d, 2 H, J 13.4 Hz, OCH_2O), 5.10 (d, 2 H, J 7.9 Hz, CH_2Ph); ^{31}P NMR data: δ −2.62. Anal. Calcd for $C_{27}H_{47}O_7P$: C, 63.01; H, 9.21; P, 6.02. Found: C, 62.61; H, 9.64; P, 6.20.

Hexadecyl di-(pivaloyloxymethyl) phosphate (**23**).—A solution of NaOH (0.4 g, 10 mmol) in water (25 mL) was added to a solution of the bis(2-cyanoethyl) phosphate **17** (1 g, 2.33 mmol) in MeOH (25 mL) and the solution was kept at 60 °C. After 10 min crystals of the sodium salt of the intermediate diester separated and water (25 mL) was added. After 30 min at 60 °C the crystals dissolved and the solution was kept at 60 °C for a further 30 min. The solution was cooled and the crystalline disodium salt, which separated, dissolved on evaporation of the MeOH. The aqueous solution was passed through a column of Amberlite IR-120(H^+) and the column was then washed with $CHCl_3$ to give a solution of hexadecyl dihydrogen phosphate (**18**) [31]. The combined eluates were concentrated in the presence of Ag_2CO_3 (3 g) and toluene was evaporated from the residue which was then treated according to the general procedure with pivaloyloxymethyl chloride (**28**, 2.5 mL, 17.3 mmol). TLC (1:1 ether–light petroleum) showed the product at R_f 0.4. Column chromatography gave **23** (1.2 g, 93%) as a syrup; ^{1}H NMR data: δ 5.65 (d, 4 H, J 13.4 Hz, 2 × OCH_2O), 4.10 (ABq, 2 H, OCH_2R); ^{31}P NMR data: δ −5.1. Anal. Calcd for $C_{28}H_{55}O_8P$: C, 61.06; H, 10.07; P, 5.62. Found: C, 61.15; H, 10.23; P, 6.03.

(±)-1,2,3,6-Tetra-O-*benzyl*-myo-*inositol 4,5-bis(dibenzyl phosphate)* (**26**) [27].—A solution of the crystalline tetrasodium salt **24** [27] in water was passed through a column of Amberlite IR-120(H^+) and the column was then eluted with 3:1 MeOH–water to give a solution of the acid **25**. The eluate was evaporated in the presence of Ag_2CO_3 and toluene, and esterified with benzyl bromide as described in the general procedure. Column chromatography and elution with 1:1 ether–light petroleum (to remove excess of benzyl bromide) followed by 2:1 ether–CH_2Cl_2 gave **26** (90%); mp 98–100 °C (from 1:10 EtOAc–light petroleum); identical with material described previously [27]. Anal. Calcd for $C_{62}H_{62}O_{12}P_2$: C, 70.18; H, 5.89; P, 5.84. Found: C, 70.22; H, 5.71; P, 5.77.

(±)-1,2,3,6-Tetra-O-*benzyl*-myo-*inositol 4,5-bis[di-(pivaloyloxymethyl) phosphate]* (**27**).—The solution of the acid **25** prepared as described in the previous section was treated as described under the general procedure with Ag_2CO_3 and pivaloyloxymethyl chloride (**28**). TLC (ether) showed the product at R_f 0.9. Column chromatography and elution with 1:1 ether–light petroleum followed by ether gave **27** (88%); mp 70–72 °C (from light petroleum); ^{31}P NMR data: δ −4.71, −5.11. Anal. Calcd for $C_{58}H_{78}O_{20}P_2$: C, 60.20; H, 6.79; P, 5.35. Found: C, 60.32; H, 6.75; P, 5.33.

Acknowledgements

We thank Perstorp Pharma, Perstorp, Sweden for support to J.G.

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