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Phosphorus-containing cyclodextrins. Characteristics of the synthesis and chemical behaviour †

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Abstract. Published data on the preparation of phosphorus-containing cyclodextrins are summarized. It is demonstrated that some significant features of their synthesis and chemical behaviour are caused by specific supramolecular interactions involving the inner chiral cavity of cyclodextrins capable of incorporating various guests, which often leads to alteration of customary routes of chemical transformations. The possibilities of practical applications of phosphorus-containing cyclodextrins are briefly analyzed. The bibliography includes 89 references.

I. Introduction

The fundamental studies of Pedersen,[1] Cram,[2] Lehn[3] and their followers demonstrated good prospects of the use of cavity systems — crown ethers, cavitands, cryptands, carcerands and some other complex molecular assemblies — for the solution of topical chemical problems. As a rule, these systems attract attention for their capability for molecular recognition, resulting in the selective capture and incorporation of molecules with geometric parameters matching the size of the inner cavity.

Cyclodextrins should be added to the above list of cavity structures. These are readily available chiral polyfunctional compounds having unique properties. The key property is the presence of a chiral lipophilic cavity, which allows them to form numerous inclusion compounds with various hydrophobic 'guests' (Fig. 1). These compounds are of great practical interest, which has been reflected in special monographs and reviews [see, *e.g.*, books[4] (p. 96),[5] (p. 635),[6] (p. 489) and the dedicated issue of the journal *Chemical Reviews*[7]]. Other advantages of cyclodextrins are also noteworthy, in particular, the lack of toxicity, biodegradability and relatively low cost. Therefore, in recent years, study of cyclodextrins has been considered a rather promising area attracting attention from chemists of various schools.

Some unique properties of cyclodextrins, first of all, the solubility in water and organic solvents and the ability to form inclusion compounds can be deliberately changed by selective modification of the cyclodextrin matrix.[8,9] By now, the phosphorylation of monosaccharides and many of their derivatives has been studied rather comprehensively; however, it was found that there are no grounds to just transfer these methods to phosphorylation of cyclodextrins. This is related, first of all, to the large number of free hydroxy groups, resulting in considerable influence of the so-called 'statistical' factor (enhancement of steric hindrance upon their successive replacement)[10] and to the presence of three types of hydroxy groups, which differ in reactivity. Cyclodextrins contain primary OH groups in positions 6 of the glucosides and two sets of secondary hydroxy groups in positions 2 and 3, which complicates their targeted functionalization. Additionally, mention should be made of the substantial influence of the inner cavity of cyclodextrins, which, as has already been noted, tends to form inclusion complexes with reactants and reaction products, which may alter the usual reaction route and which restricts the use of cyclodextrins. For example, until recently, only a few works dealing with the preparation and study of organoelement derivatives of cyclodextrins, including phosphorus-containing ones, were published. In addition, one should bear in mind one more important circumstance that strongly affects the strategy of the synthesis of cyclodextrin derivatives: β-cyclodextrin is much less soluble in water (1.84 g litre^{-1}) than α- or γ-cyclodextrin (14.5 and 23.2 g litre^{-1}, respectively).[11] Conversely, β-cyclodextrin is readily soluble in pyridine and DMF, whereas α- and γ-cyclodextrins are poorly soluble in these solvents.

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† Dedicated to Corresponding Member of the Russian Academy of Sciences, Doctor of Chemical Sciences, Professor E E Nifantiev on the occasion of his eightieth birthday.

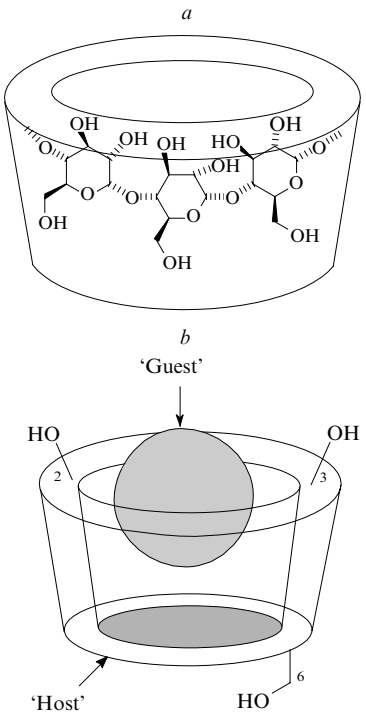
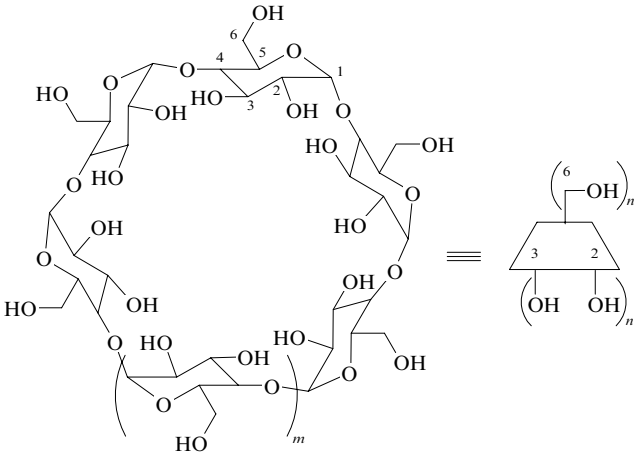


Figure 1. General view of the cyclodextrin molecule (*a*) and an inclusion complex with the participation of the inner cavity (*b*).

Cyclodextrin structures



$n = 6$ (α), 7 (β), 8 (γ); $m = n - 5$

Although active investigation of phosphorus-containing cyclodextrins started about 20 years ago, only single communications dealing with the preparation of particular compounds meant for solving a particular practical problem are encountered in the literature. There are no papers that survey the synthesis and applications of compounds of this class. In view of the unique structures and properties of cyclodextrins, it can be expected that phosphorus-containing derivatives would be of particular interest as a new class of macroheterocycles. For example, the introduction of phosphorus-containing groups into the cyclodextrin molecule changes the solubility in aqueous and organic media, enhances the coordinating ability due to an increase in the volume of the inner cavity and provides additional opportunities for the formation of host – guest complexes.

The present review is the first attempt to integrate and critically analyze the data on the synthesis and chemical behaviour of phosphorus-containing cyclodextrins. The phosphorus-containing group is most often introduced into the cyclodextrin molecule by direct phosphorylation or, more rarely, by molecular assembly in which the fragment being added to cyclodextrin already contains a phosphorus atom. Papers dealing with inclusion of phosphorus compounds into the cyclodextrin cavity, for example, those related to the study of phase transfer catalysis (see a review [12]) and the like are beyond the scope of this review. Another review [13] considers phosphorus-containing cyclodextrins as mass transfer systems and ligands for organometallic catalysis in the aqueous phase. When required, the review also touches upon the possibility of practical application of phosphorus-containing cyclodextrins.

II. P(III)-Phosphorylated cyclodextrins

Compounds of this class are of interest not only as ligands for highly selective metal complex catalysts but also since they are subject to a large variety of transformations using the huge potential of the chemistry of trivalent phosphorus.[14]

1. Selectively P(III)-phosphorylated cyclodextrins

The works devoted to selectively P(III)-phosphorylated cyclodextrins mainly refer to the synthesis of metal complex catalysts based on P(III)-ligands attached to the cyclodextrin matrix. In the case of stereoselective transformations involving such catalysts, one may expect enantiomeric enrichment of the product as a result of preferred inclusion of one of the substrate stereoisomers into the cyclodextrin chiral cavity. Note that of the variety of the possible applications of cyclodextrins as a supramolecular matrix for metal complex catalysts, this review covers only derivatives of cyclodextrins with covalently attached P(III)-containing groups. According to a proposed classification (Fig. 2),[12] cyclodextrin can act as the first- and second-coordination sphere ligand in organic metal complex (M is metal). For example, in complexes of type **A**, cyclodextrin is simultaneously a first- and a second-sphere ligand: ligand L is covalently bonded to the outer rim of cyclodextrin, while the other ligand (L′) resides in the cavity (L″ is an additional ligand). In type **B** complexes, cyclodextrin is a first-sphere ligand and a temporary second-sphere ligand,

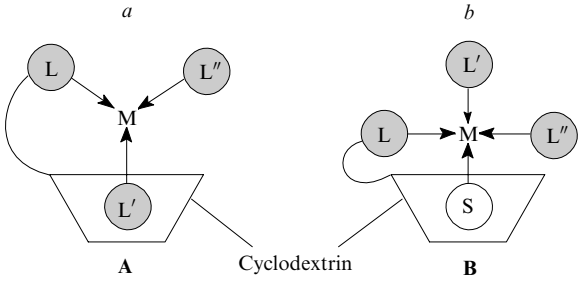
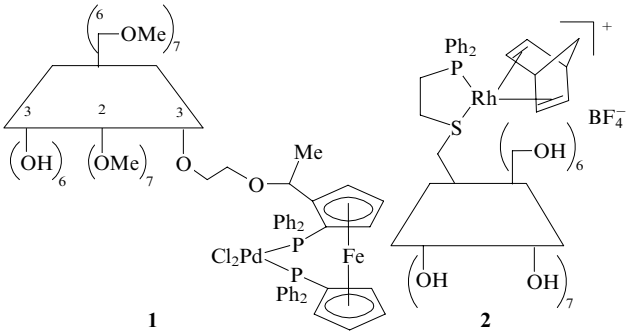


Figure 2. Two types of cyclodextrin complexes with metals (for designations, see the text).

because its cavity accommodates a substrate (S), which then reacts with the organic metal complex.

Water-soluble bidentate palladium (**1**)[15] and rhodium (**2**)[16] diphosphine complexes were synthesized in 1993; however, their catalytic behaviour was not disclosed.

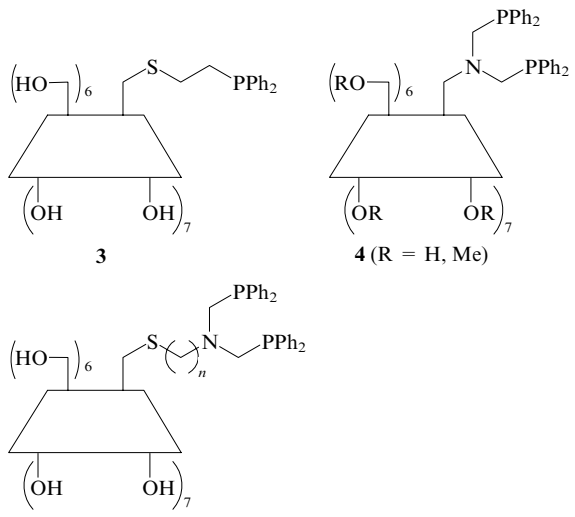
Structures **1**, **2**



1 **2**

Reetz and Waldvogel[17–19] continued studies along this line, which resulted in the preparation of a series of Rh^{I} complexes with mono- (**3**) and bidentate ligands (**4**, **5**). Compounds **5** differ in the length of the hydrocarbon bridge between the β-cyclodextrin matrix and the phosphorus-containing moiety.

Structures **3**–**5**

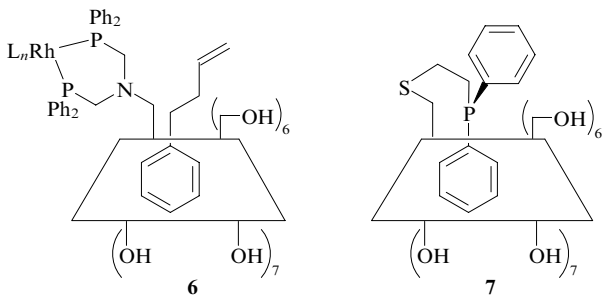


3 **4** (R = H, Me)

5 (*n* = 2–4)

A series of experiments dealing with the complexes incorporating ligands **3**–**5** with $[Rh(cod)_2]BF_4$ (cod is cycloocta-1,5-diene) showed their high catalytic activity and selectivity in hydrogenation and hydroformylation of alkenes. In the authors' opinion, this is a result of preliminary incorporation of the substrate into the cyclodextrin cavity to give structure **6**.[20] Complexes based on ligand **5** with $n = 2$ were most active.[17,18] X-Ray diffraction analysis of phosphine ligand **3** revealed selective intramolecular inclusion of one of the diastereotopic phenyl groups into the cyclodextrin cavity (structure **7**); this may also be a cause of the stereoselectivity of the transformation of guests in the presence of catalysts based on these ligands.[21]

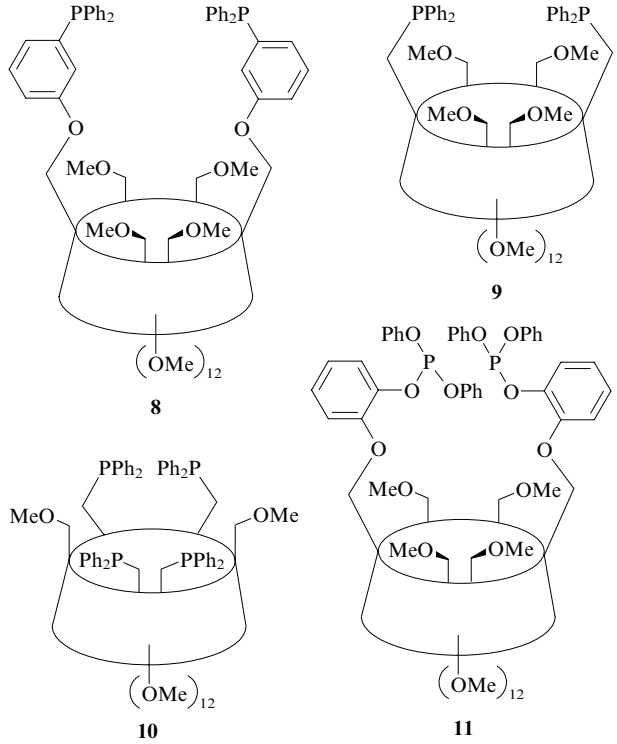
Structures **6**, **7**



6 **7**

Matt's group published a series of studies‡ on the synthesis of some metal complexes by capping the narrow rim of the permethylated α-cyclodextrin core incorporating di- (**8**,[23] **9**[24,25]) and tetraphosphine ligands **10**[26] and diphosphite ligands **11**.[27]

Structures **8**–**11**

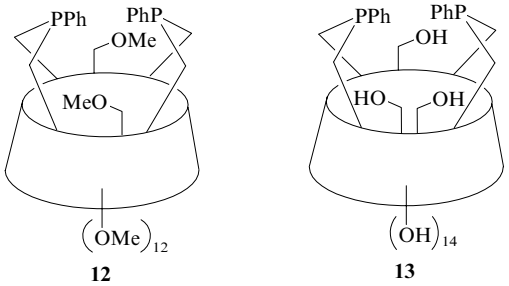


8 **9**

10 **11**

In order to rigidly fasten the chelating P(III)-containing moieties, bicyclophosphine systems based on α- (**12**)[28–32] and β-cyclodextrins (**13**) were prepared.[33] NMR spectroscopy showed the presence of through-space $\{^{31}P-{}^{31}P\}$ and $\{^{31}P-{}^{13}C\}$ spin-spin coupling in these ligands.[34] A number

Structures **12**, **13**



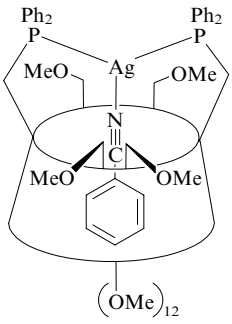
12 **13**

‡ These works are partially mentioned in the review[22] published in 2003.

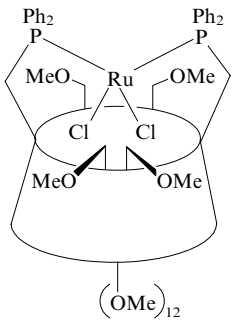
of complexes of these ligands with transition metals, metallocavitands, were prepared and some of them were used as catalysts in selective hydrogenation and hydroformylation of alkenes.

The structures of complexes prepared with different metals were studied in detail, namely, Ag,[23, 24, 30, 31] Au,[23, 33, 35] Ni,[27] Pd,[23, 25, 26, 28, 29, 35] Pt,[23, 28, 29] Ru[25] and Rh.[27, 35] One or two external ligands of the metal centre were found to reside in the cyclodextrin cavity to give, for example, structures **14**[24] and **15**.[25]

Structures **14**, **15**



14

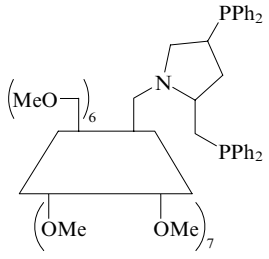


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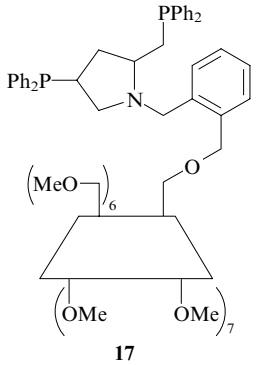
The complex of diphosphine α-cyclodextrin derivative **12** with $[Ag^{I}]^{+}$ was used to prepare a system for selective capture of guest anions, for example, the NO_3^- anion, which is encapsulated in the cyclodextrin cavity.[30]

Among bidentate diphosphine ligands, noteworthy are also derivatives **16** and **17**, which contain permethylated β-cyclodextrin.

Structures **16**, **17**



16



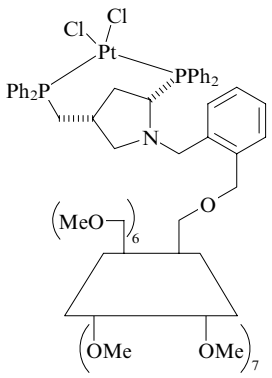
17

They differ by the spacer connecting the chelating moiety to the cyclodextrin macrocycle.[36]

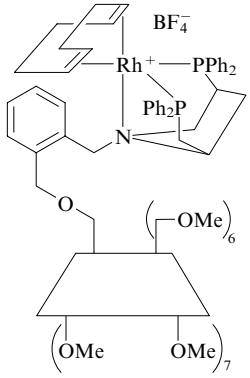
Ligand **16** reacts with $PtCl_2(cod)$ and $[Rh(cod)_2]BF_4$ to give standard four-coordinate metal complexes.[36] Meanwhile, ligand **17** with $PtCl_2(cod)$ forms four-coordinate complex **18**, while with $[Rh(cod)_2]BF_4$ it forms five-coordinate complex **19**. The latter circumstance is due to the fact that the metal centre is more remote and, hence, the steric effect of the β-cyclodextrin moiety is less pronounced.

The above-mentioned selectively substituted P(III) derivatives of cyclodextrins incorporated in complexes **1**, **2**, and ligands **3**–**5**, **8**–**13**, **16** and **17** were synthesized after the protection of hydroxy groups, which is a fairly cumbersome and complicated task.

Structure **18**, **19**

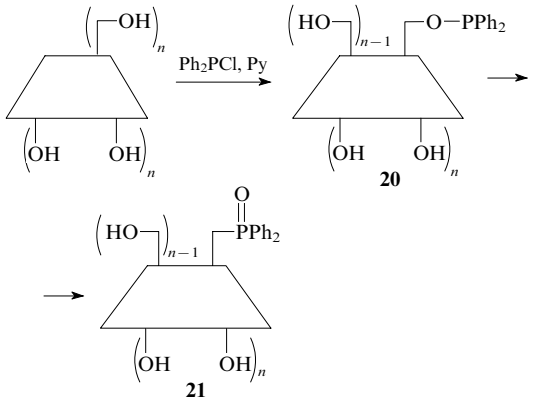


18



19

Scheme 1



20

21

n = 6 or 7; Py is pyridine

The preparation of a rhodium complex catalyst based on monophosphinite derivatives of α- and β-cyclodextrins **20** (Scheme 1) was reported.[37]

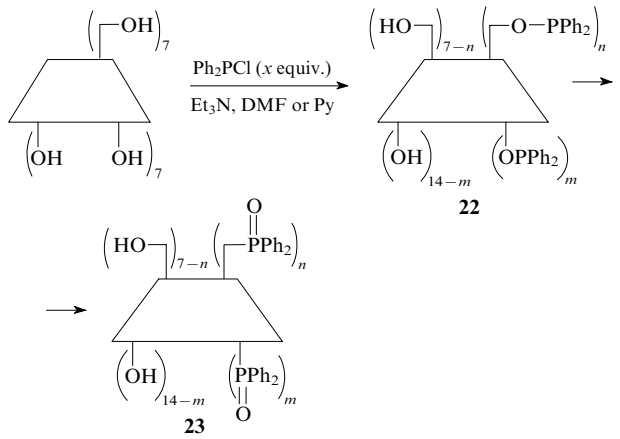
Compounds **20** were obtained by the direct reaction of diphenylchlorophosphine with α- and β-cyclodextrins in pyridine; the authors suggest that the reaction involves only primary hydroxy groups. However, note that in the study cited, the ^{31}P NMR chemical shift (19.3 ppm) of compound **20** does not correspond to the values usual for this class of compounds (105–115 ppm).[38]

Subsequently it was shown that phosphinite **20** rapidly isomerizes to phosphine oxide **21**.[39] Although the position and the nature of the phosphorus substituent in the cyclodextrin core were not exactly determined in the study cited,[37] this compound was used to prepare rhodium catalysts, which were tested in selective hydrogenation of various alkenes. The authors assert that the inner cavity of the phosphorus-containing cyclodextrin recognizes the shape and size of the substrate and is adjusted to catalytic sites through the formation of a strong inclusion complex.

Since phosphine oxides **21** can be easily reduced to tertiary phosphines attached to the cyclodextrin matrix, they present considerable practical interest, first of all, as ligands for metal complex catalysis. Attempts were made to introduce different numbers of phosphorus-containing groups ($m + n$) into the β-cyclodextrin molecule by varying the solvent and hydrogen chloride acceptor (DMF–Et_3N, pyridine) and the molar amount of diphenylchlorophosphine (from 1 to 21).[39] Unexpectedly it turned out that in all cases, intermediate phosphinite derivatives **22** rapidly iso-

merize to phosphine oxides **23**, giving rise to a difficult-to-separate complex mixture of products with rather low degrees of phosphorylation ($m + n = 3$). A ^{31}P NMR study of the course of this transformation and comparison with analogous experiments carried out in the presence of adamantane § demonstrated a higher degree of phosphorylation ($m + n = 9$) and, in addition, retardation of the phosphinite–phosphine oxide isomerization. It was concluded that the ease of this isomerization in the case of cyclodextrin derivatives is related to their structural features and specific supramolecular properties, first of all, the presence of the inner lipophilic cavity (Scheme 2).[39]

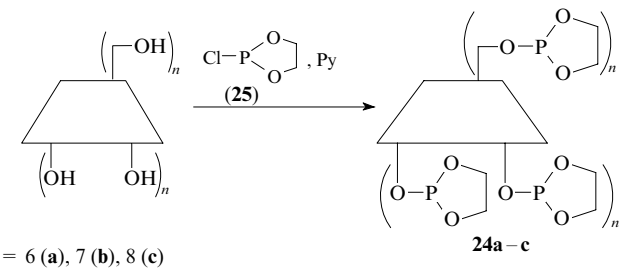
Scheme 2



2. Fully P(III)-phosphorylated cyclodextrins

The first study along this line was devoted to the synthesis of per-P(III)-phospholane derivatives of α-, β- and γ-cyclodextrin **24a–c**. The individual products formed upon treatment of a specified cyclodextrin with ethylene phosphorochloridite **25** in pyridine were not isolated but the reaction mixture was only analyzed by ^{31}P NMR spectroscopy (Scheme 3).[43]

Scheme 3

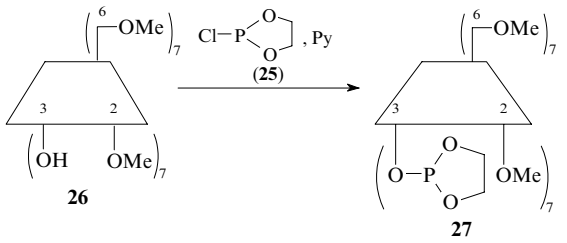


n = 6 (**a**), 7 (**b**), 8 (**c**)

The ^{31}P NMR spectrum of the reaction mixture of perphosphorylated γ-cyclodextrin **24c** exhibited three groups of signals (133.5, 135.2 and 135.8 ppm) with equal integrated intensities corresponding to the phosphorus atoms attached to oxygen in positions 6, 2 and 3, respectively. The α-cyclodextrin derivative **24a** showed one broadened signal at 135.0 ppm, while β-cyclodextrin derivative **24b** was responsible for two groups of signals at 133.5 and 135.2 ppm (integrated intensity ratio of 1 : 2), and the more intense signal was assigned by the authors to the phosphorus atoms in positions 2 and 3. In our opinion, this is at variance with the results reported in the same publication [43] and devoted to phosphorylation of methylated β-cyclodextrin **26** in positions 2 and 6 (Scheme 4).

§ Adamantane molecule is known to closely match, as regards the structure and size, the cavity of cyclodextrin and many of its derivatives; therefore, these compounds form rather stable host–guest complexes.[40–42]

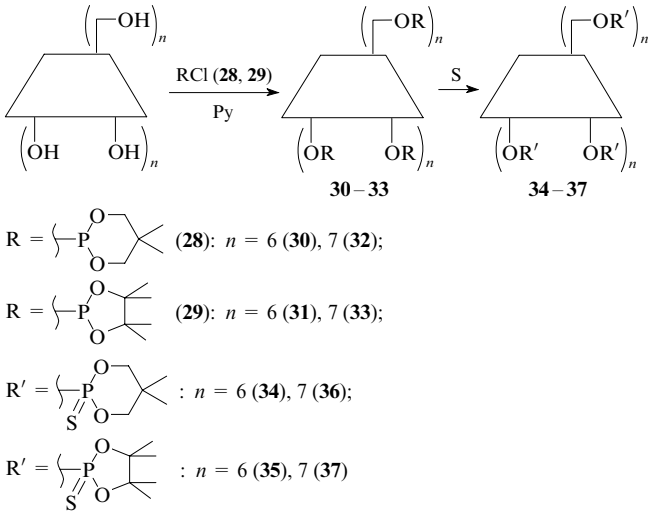
Scheme 4



The signal at 133.5 ppm observed for compound **27** has the same chemical shift as the smaller signal of persubstituted derivative **24b**. This suggests that the low-field signal (at 135.2 ppm) with double integrated intensity is rather due to the phosphorus atoms attached to positions 2 and 6, whereas the higher-field signal (at 133.5 ppm) with a lower intensity corresponds to phosphorus atoms in positions 3.

Later, systematic studies of per- and regioselective phosphorylation of α- and β-cyclodextrins with phosphorochloridites, compounds **28** and **29**, were carried out (Scheme 5).[44]

Scheme 5

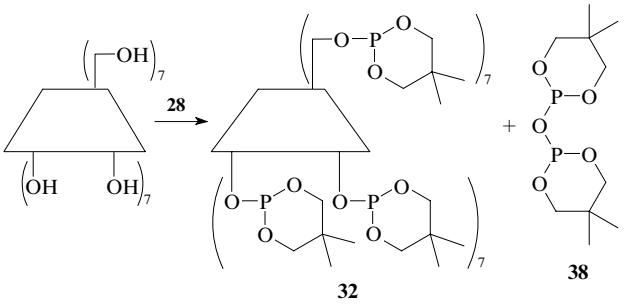


Without isolation from the reaction mixture, P(III) derivatives of cyclodextrins **30–33** were made to react with elemental sulfur being thus converted to the corresponding thiophosphate derivatives **34–37**. These products were isolated in a pure state and characterized by spectral methods (see Section III.3.). The ^{31}P NMR analysis of the reaction mixture and the course of phosphorylation during the synthesis of P(III)-containing cyclodextrin derivative **32** supported the assumption that the broadened low-field signal with double intensity belongs to the P atoms of the phosphorus-containing groups in positions 2 and 6 of glucosides [44] rather than in positions 2 and 3, as it was reported earlier.[43]

Since P(III) derivatives of cyclodextrins are important both as finished products and as starting compounds for

further functionalization, it appeared pertinent to isolate and characterize pure P(III)-perphosphorylated β-cyclodextrin **32**. However, the use of standard phosphorylation procedures involving phosphorochloridites proved inefficient. The isolation and purification of the major product **32** was accompanied by the fast formation of the side pyrophosphite **38**, which is difficult to separate due to the tight inclusion into the cyclodextrin cavity (Scheme 6).

Scheme 6

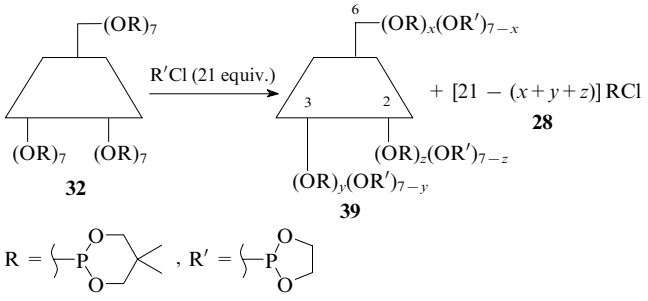


Only by means of so-called phosphotriazolide phosphorylation method,[45,46] was it possible to synthesize and isolate perphosphite **32**.[47] It is noteworthy that the individual product **32** obtained in this way exhibits one broadened signal at 122 ppm in the ^{31}P NMR spectrum recorded in $CHCl_3$ rather than two signals with 1 : 2 intensity ratio as noted above. It was shown in a separate experiment that adding an equivalent amount of pyridine hydrochloride into a solution of compound **32** (similarly to the reaction mixture in the synthesis of **32**) gives rise to two signals (at 121 and 123 ppm) with integrated intensity ratio of 1 : 2, *i.e.*, this confirms findings of the earlier work.[44] Presumably, this is a consequence of supramolecular interaction of pyridine hydrochloride with cyclodextrin derivative **32** (the result of inclusion of pyridine hydrochloride into the macrocycle cavity).[47] Thus, the formation of host–guest complexes can considerably influence the general pattern of the ^{31}P NMR spectra of phosphorylated cyclodextrins.

3. Transphosphorylation as a specific feature of P(III)-phosphorylated cyclodextrins

An unusual fact that shed light on a new aspect of phosphorylated cyclodextrin chemistry was discovered during the work with perphosphite derivative **32**. It was found that per-P(III)-derivative **32** differs considerably from other phosphorous triesters. Indeed, according to ^{31}P NMR data, treatment of compound **32** with 21 equiv. of ethylene phosphorochloridite **25** [a ^{31}P NMR signal (δ_P) at 168 ppm] leads to the partial replacement of the six-membered dioxaphosphorinane moieties (R) by five-membered dioxaphospholane moieties (R′) to release the corresponding amounts of phosphorochloridite **28** (δ_P = 147 ppm), which readily occurs in the reaction mixture even at room temperature. Cyclodextrin derivative **39** with mixed phosphorus-containing residues is formed as the only macrocyclic product (Scheme 7).[48,49]

Scheme 7

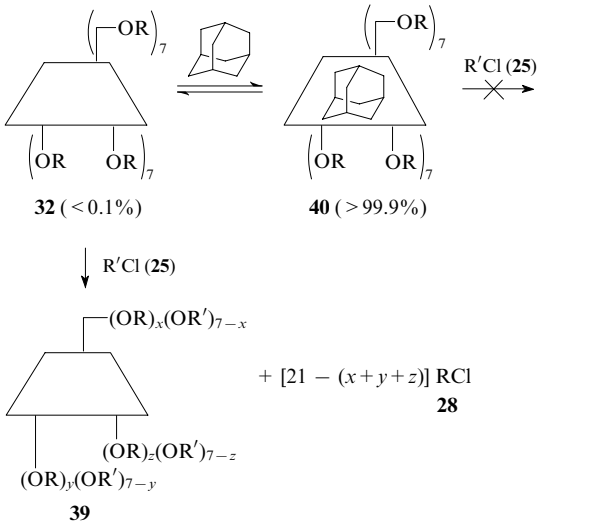


To confirm the fact that the cyclodextrin core is actually responsible for transphosphorylation in this system, similar experiments were carried out with model compounds devoid of inner cavities, namely, partially protected P(III)-phosphorylated monosaccharides. Under similar reaction conditions, no process of this type was detected for these model compounds.[48] The ability of perphosphite **32** to undergo transphosphorylation was also found for some other phosphorochloridites; however, in most cases, transphosphorylation proceeded to different degrees of substitution, which is reflected by the coefficient [21 − (*x* + *y* + *z*)] in Scheme 7.[49]

Thus, easy transphosphorylation of β-cyclodextrin phosphites is an unusual phenomenon related to the fact that the cyclodextrin core substantially changes the chemical reactivity of the phosphite groups attached to it. Presumably, the phosphorylating agent is first inserted into the cyclodextrin cavity and only after that, it is involved in the chemical reaction, which occurs at the supramolecular level.¶ The key point of this reaction is the movement of the covalently bonded host and guest phosphite groups towards each other, enabling easy redistribution of bonds (like metathesis) to give a new cyclodextrin derivative with mixed phosphite groups. This product has more compact substituents and is more stable.

To confirm this hypothesis, transphosphorylation was carried out in the presence of adamantane. Evidently, an inclusion compound of adamantane into the cyclodextrin cavity (structure **40**) is initially formed, which cannot incorporate the transphosphorylating agent (Scheme 8).

Scheme 8



The experiment with the addition of two equivalents of adamantane (to provide a higher degree of conversion of derivative **32** to complex **40**) demonstrated that adamantane sharply retards (in some cases, 'switches off') the transphosphorylation under the same conditions. Thus, the

¶ A similar assumption was made in a study of regioselective acylation of β-cyclodextrin with several carboxylic acid chlorides.[50]

hypothesis about the supramolecular nature of this unusual reaction was experimentally confirmed.[49]

III. P(V)-Phosphorylated cyclodextrins

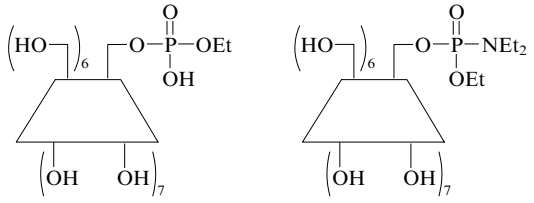
1. Selectively substituted phosphate derivatives of cyclodextrins

Selectively substituted phosphate derivatives of cyclodextrins attract especially great attention of researchers. These compounds have hydrophilic groups at the edges of the cyclodextrin core; they are highly soluble and have some other advantages, for example, they can selectively capture guest cations. In addition, they can function as biomimetic models used to study the action of phosphorylases. The first single examples on the preparation of monophosphate and phosphonate cyclodextrin derivatives were mentioned in a review.[8] Of special note is the publication [51] in which an excess of β-cyclodextrin was treated with diphenyl phosphorochloridate in pyridine to give mono(diphenyl phosphate) β-cyclodextrin **42**. The phenyl groups of the phosphorus-containing moiety were removed by subsequent hydrogenation to give monophosphate **43** (Scheme 9). In the same work, monophosphate derivatives **44** and **45** with phosphate groups at the C(2) and C(3) atoms, respectively, were synthesized by a different method: free β-cyclodextrin was kept for a long period with di(*m*-nitrophenyl) phosphate in aqueous alkali and then two isomers were separated. The last-mentioned stage was rather labour-consuming. The monophosphate derivatives were tested as general acid and base catalysts in the hydrolysis of *p*-nitrophenyl ether and enolization of β-oxo alcohol. When the substrate was captured in the cyclodextrin cavity, these compounds served as models to study the enzyme–substrate interaction.

More recently, monoethyl phosphate (**46**), *O*-ethyl *N*,*N*-diethyl phosphoramidate (**47**) and diphenyl phosphate (**42**) β-cyclodextrins were prepared by a similar procedure from the corresponding phosphoric acid chlorides.[52, 53] Compounds **42**, **46** and **47** were then used for chiral recognition of various amino acids. In particular, factors influencing the formation of inclusion complexes and enhancement of chiral recognition with the participation of these macrocycles were determined.[54]

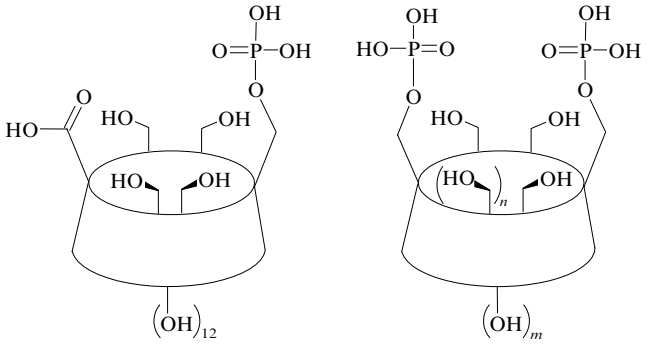
By regiospecific protection of the primary hydroxy groups of α- and β-cyclodextrins in definite positions followed by selective deprotection, α-cyclodextrin monophosphate **48** and α- and β-cyclodextrin diphosphates **49a**,**b** were prepared. Compounds **48** and **49** are of interest as cyclodextrins able to form anions to be complexed with guest cations and as models to study the biomimetic behaviour of phosphorylases.[55]

Structures **46**, **47**



46 **47**

Structures **48**, **49**



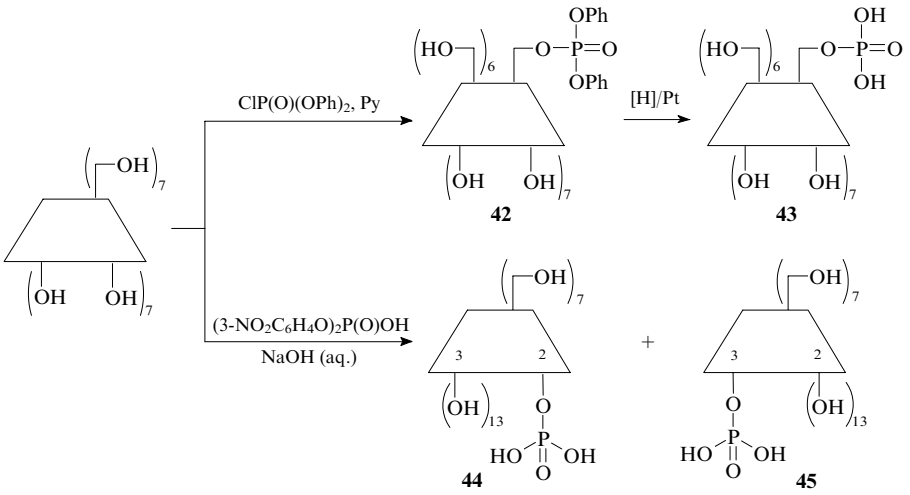
48 **49a**,**b**

$n = 1, m = 12$ (**a**); $n = 2, m = 14$ (**b**)

Another approach has been applied to prepare anionic diphosphate-containing β-cyclodextrin **50** (Scheme 10).[56] Brominated cyclodextrin **51** was used as the starting compound; the bromine atoms in it were replaced on treatment with monoaminoethyl phosphate.

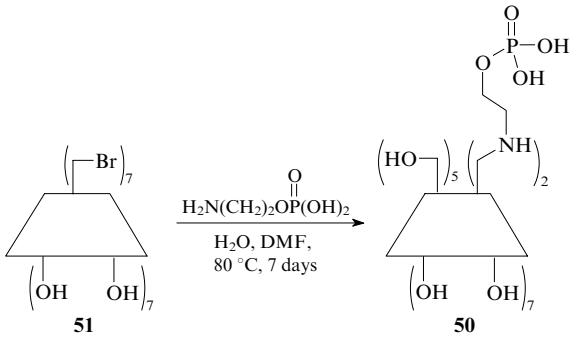
Compound **50** was converted to salt **52**, which was made to react with cationic per[6-(guanidino)-6-deoxy]cyclodextrins **53a**–**c**. This resulted in the formation of well-organized supramolecular 1 : 1 heterodimers with head-to-head orientation of the cyclodextrin cores (Scheme 11 shows dimer **54** formed from β-cyclodextrin derivative **53b**). A specific feature of these dimers is that two halves match each other to form a sort of zipper owing to the cationic guanidine moieties rigidly attached to the cyclodextrin

Scheme 9

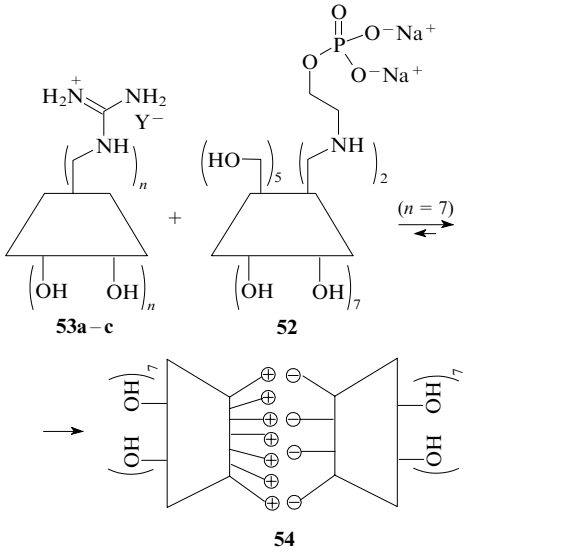


42 **43** **44** **45**

Scheme 10



Scheme 11



n = 6 (**a**), 7 (**b**), 8 (**c**); Y is picrate

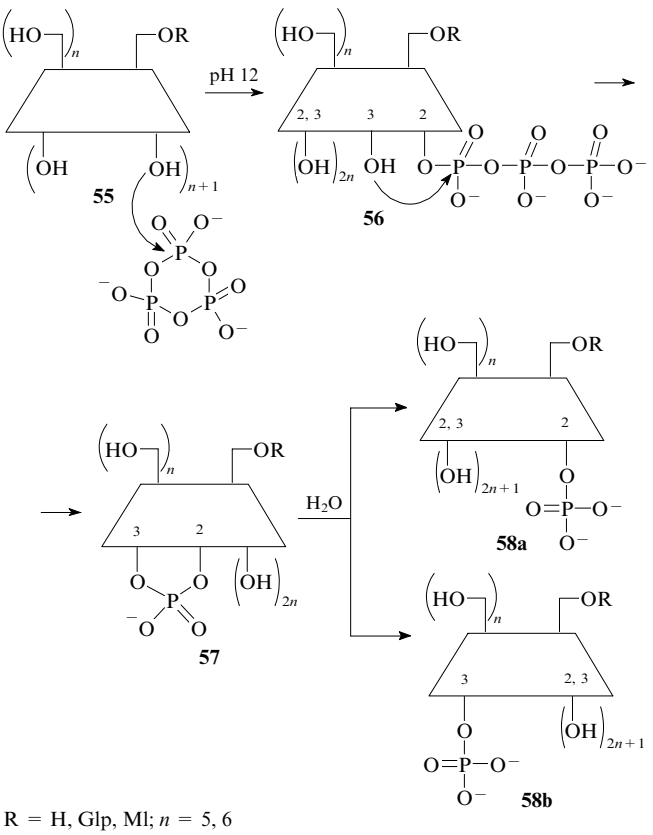
matrix and the anionic phosphate groups located on the flexible spacer and adjusted to the cationic groups. Particularly, these dimers are highly stable in solutions in DMSO, the stability decreasing upon the addition of water.

Yet another method for the synthesis of phosphate derivatives implies direct treatment of cyclodextrin with phosphorus(V) oxychloride in an aqueous alkaline medium at different pH[57–59] and different temperatures.[57] However, in this case, secondary hydroxy groups are also affected. Temperature elevation from 25 to 60 °C increases the percentage of phosphate derivatives. After phosphorylation at pH 11 – 12, the monophosphate groups are located in positions 6, whereas at pH 10, phosphorylation is mainly directed at the C(2) atom.[57] Phosphate derivatives of cyclodextrins were used to increase the water solubility of some compounds, for example, β-carotene (after inclusion into the cyclodextrin cavity);[57] owing to their anionic nature they were investigated as substrates for alkaline phosphatase while binding aromatic cationic guests.[58]

A more complex approach is non-selective ('chaotic') P(V)-phosphorylation of cyclodextrins followed by separation of the regioisomers formed. For example, monophosphates were prepared by the direct reaction of cyclodextrin with sodium metaphosphate under drastic conditions — by heating the dry residue remaining after freeze drying of an aqueous solution of cyclodextrin with sodium metaphosphate at 90 °C for 6 h in the case of α-cyclodextrin and 7 days in the case of β-cyclodextrin.[60] The authors suppose that this pronounced difference between the rates of 'dry' phosphorylation is related to a different possibility of formation of anionic host – guest complexes by α- and β-cyclodextrins. By anion exchange chromatography, the mixture was separated and the isomers were isolated. A shortcoming of this method is relatively low product yield: the overall yield of the three α-cyclodextrin isomers is 17%, while that of β-cyclodextrin is 10%. The subsequent fine separation of the isomers showed that for α- and β-cyclodextrins, the ratio of the isomers having a phosphate group at the C(2), C(3) and C(6) atoms is approximately 1 : 1 : 3, *i.e.*, sterically less hindered primary OH groups are esterified approximately three times as fast as secondary OH groups.

The phosphorylation of free α- and γ-cyclodextrins (R = H) and mono-6-O-substituted α-D-glucopyranosyl (R = Glp) and α-D-maltosyl cyclodextrins (R = Ml) **55** (Scheme 12) was studied.[61,62] The reaction was carried out in an alkaline aqueous solution at pH 12 (at pH ≈7, the reaction does not proceed) under the action of inorganic trisodium cyclotriphosphate. The phosphorylation products at the C(2)-OH groups of cyclodextrin are formed in low yields (19% – 27%). Triphosphate derivatives **56** are subjected to intramolecular attack by the neighbouring hydroxy group at C(3)† yielding cyclic phosphate **57**,

Scheme 12



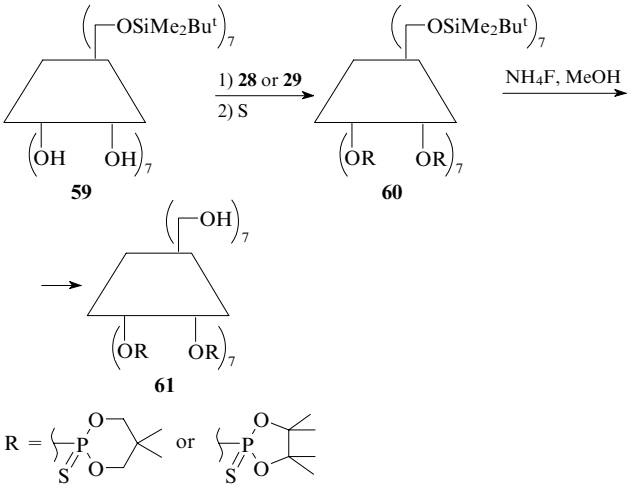
R = H, Glp, Ml; n = 5, 6

† In view of the spatial proximity of the hydroxy groups in positions 2 and 3′ of the neighbouring glucoside units of cyclodextrin and the presence of strong hydrogen bonds between them, the attack is directed most likely on the hydroxy group of the neighbouring glucoside moiety at C(3′) rather than on the vicinal OH group.[63,64]

which is then hydrolyzed to afford a mixture of products **58a**,**b** containing a phosphate group at the C(2) or C(3) atom.[61]

In order to perform regioselective phosphorylation [*i.e.*, directed only at all primary OH groups at C(6) or at secondary groups at C(2) and C(3)], it is preferable to use protecting groups. The *tert*-butyldimethylsilyl protection is used most often for cyclodextrins.[9] Thus per-6-silylated β-cyclodextrin **59** was converted to per-2,3-*O*-thiophosphate derivatives **60** on treatment with phosphorochloridites **28** and **29** and subsequent sulfurization (Scheme 13).[65]

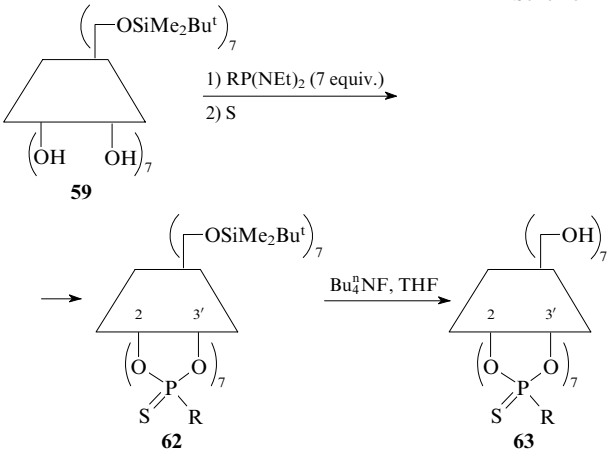
Scheme 13



The removal of the silyl protecting groups results in phosphorylated derivative **61** with free primary hydroxy groups accessible for the subsequent modification.[65]

By 2,3′-interglucoside phosphocyclization by the P(III)-amide method, per-6-silylated derivative **59** was converted to silyl-substituted cyclodextrin per-2,3′-cyclo ethyl thiophosphate (**62**, R = OEt) and per-2,3′-cyclo *N*,*N*-diethyl thiophosphoramidate (**62**, R = NEt_2) (Scheme 14).[63, 64]

Scheme 14

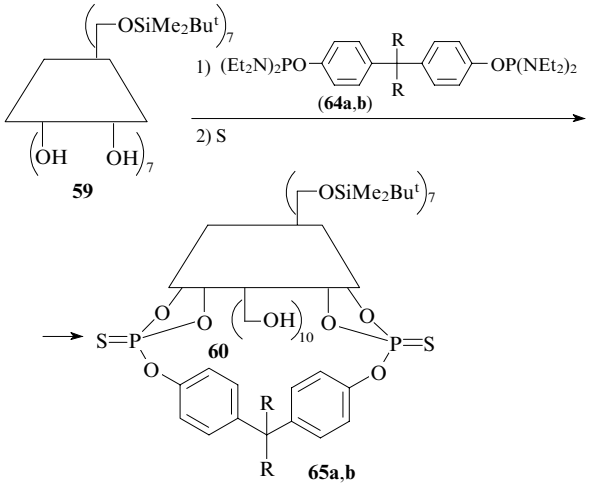


R = OEt, NEt_2

In view of the lability of 2,3′-phosphocyclic compounds **62**, deprotection was accomplished by treatment with a milder desilylating agent: tetra-n-butylammonium fluoride in THF. Due to the 2,3′-interglucoside cyclization, compounds **63** have enhanced core rigidity and enhanced hydrophilicity of the narrower cyclodextrin rim. As demonstrated for the drug Ibuprofen, the increase in the size of β-cyclodextrin molecular cavity upon phosphocyclization at the secondary hydroxy groups also enhances its ability to capture hydrophobic guests.[66]

Among cyclic cyclodextrins, special place is occupied by the above-noted capped derivatives. Presumably, capping of these hosts, which have a deep hydrophobic cavity, will provide them with enhanced capacity for capturing hydrophobic guests. For some cyclodextrin derivatives, this assumption was experimentally verified.[67–69] It is evident that study of the synthesis and properties of new phosphocapped cyclodextrins may be of particular interest. For example, they were prepared[70] using silyl derivative **59**, which was made to react with one equivalent of bis-phosphorylated 2,2-bis(4-hydroxyphenyl)propane (**64a**, R = Me) or bis(4-hydroxyphenyl)diphenylmethane (**64b**, R = Ph) (Scheme 15).

Scheme 15



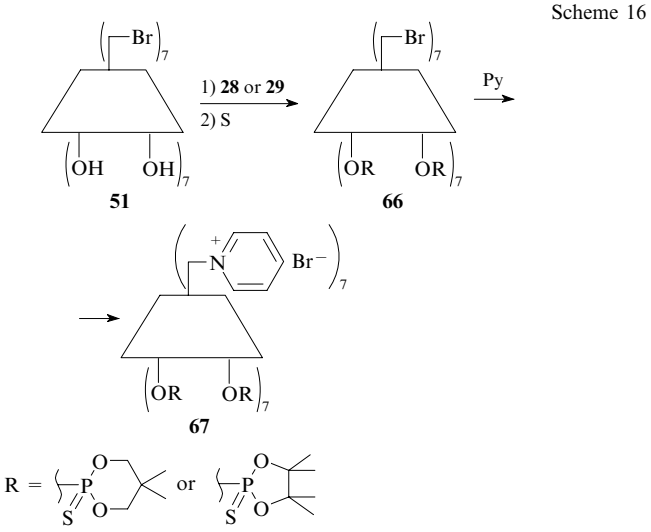
R = Me (**a**), Ph (**b**)

The addition of sulfur to intermediate cyclophosphites (not shown in the Scheme) yielded cyclothiophosphates **65a**,**b**, which were isolated in the pure form.[70] These compounds are the first representatives of phosphocyclic derivatives modified by rigid capping at the wider rim of the cyclodextrin core.

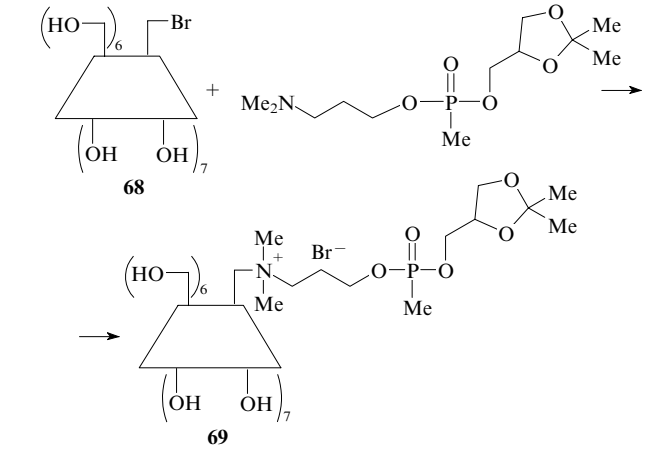
The proposed methods are also suitable for preparation of other selectively P(V)-phosphorylated cyclodextrins with ionic structure. For example, treatment of per-6-bromo-6-deoxy-β-cyclodextrin (**51**) with phosphorochloridite **28** or **29** furnished per-6-bromo-6-deoxy-per-2,3-thiophosphates **66** and per-6-deoxy-6-pyridino-per-2,3-thiophosphate bromides **67**,[71] which are cationic cyclodextrin derivatives (Scheme 16).

The alkylating properties of monobromo-6-O-substituted β-cyclodextrin **68** towards amines were utilized to prepare complex glycerophospholipid analogues of cyclodextrins **69** having a cationic alkylammonium group on the cyclodextrin core (Scheme 17).[72]

Scheme 16



Scheme 17



Cationic cyclodextrins have antibacterial properties and good solubilizing effect with respect to a number of medical drugs;[73] they are used to study the phosphatase activity and inhibition.[74, 75] Owing to the capability for self-assembly in the presence of a plasmid, these compounds can serve for complexation with DNA and DNA delivery (vectorization) into a cell, thus accelerating transfection in the presence of blood serum.[76]

2. Amphiphilic derivatives of cyclodextrins

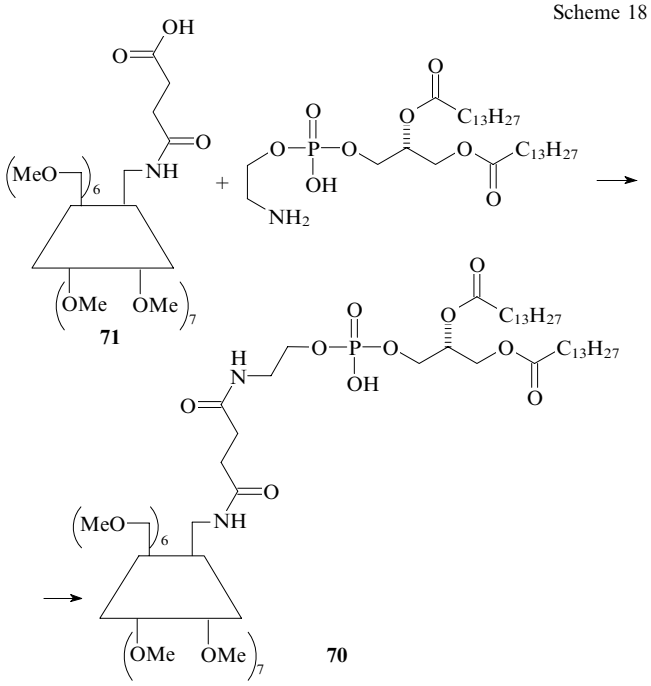
A special position is occupied by cyclodextrin derivatives containing hydrophobic lipid fragments. The conjugation of the cyclodextrin rim from the side of primary hydroxy groups makes these macrocycles amphiphilic and leaves the broad hydrophilic part free for the inclusion of guests. This ability of amphiphilic cyclodextrins has found practical application for the transport of some medical drugs (see, for example, Refs 77 – 83). By adjusting the length of the spacer connecting the lipid moiety and β-cyclodextrin, it is possible to optimize incorporation of the molecule into the lipid matrix as a so-called 'lipid anchor' and thus to induce less pronounced structural changes of the molecule. Furthermore, these conjugates used as drug delivery agents are considered to be able to penetrate the blood–brain barrier without damaging it.[80, 84]

The first representatives of phosphorus-containing amphiphilic glycophospholipid cyclodextrins **70** were obtained by condensation of β-cyclodextrin derivative **71** containing the succinamide residue with 1,2-dimyristoyl-*sn*-glycero-3-phosphoethanolamnine (Scheme 18).[80, 84]

In order to simplify the synthetic approach to cyclodextrin-based amphiphilic glycophospholipids, direct regioselective monophosphorylation of unprotected β-cyclodextrin was developed.[85] The reaction was performed by treating cyclodextrin with monophosphorochloridites **72**, **73** under specially selected conditions and subsequent oxidation of the intermediate phosphites to phosphates **74** (X = O), thiophosphates **74** (X = S) and phosphates **75** (R = Ph, CH_2CH_2CN), which were isolated (Scheme 19).

Since the P(III)-amide method is often more advantageous for phosphorylation of complex hydroxyl-containing compounds than the P(III)-acid chloride method,[86] an attempt was made at regioselective phosphorylation of free β-cyclodextrin with phosphorous acid diamides. Unexpectedly, the reaction of free β-cyclodextrin with three equivalents of phosphorous diamide **76** in pyridine proceeded under mild conditions (20°C) ‡ to give cyclodextrin modified at the primary hydroxy groups. It was found that under these conditions, only two equivalents of the phosphorylating agent react ($n = 2$) even when the reaction mixture is kept for a long period. After the addition of sulfur, thiophosphate derivative **77** § was isolated in the pure form. The same reaction conducted with three equivalents of phosphorous diamide **76** in pyridine at 110 °C afforded the product with the maximum possible degree of phos-

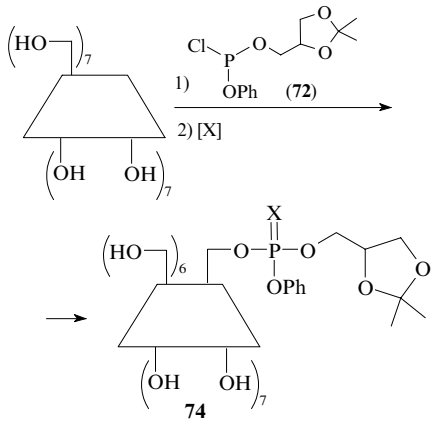
Scheme 18



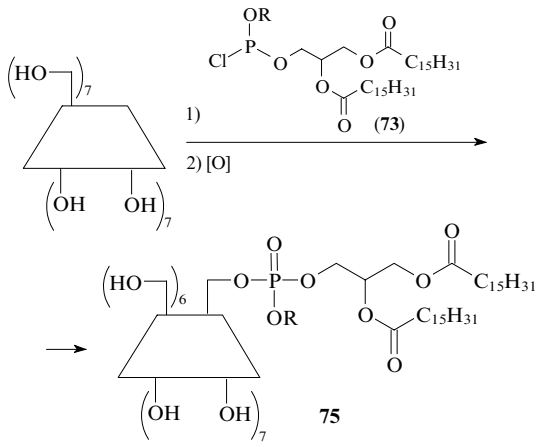
‡ Phosphorylation of most alcohols with phosphorus(III) acid amides usually occurs in the presence of catalysts at 80 – 110°C.[14]

§ The exact positions of phosphorus-containing groups among the seven possible positions of the primary hydroxy groups of derivative **77** ($n = 2$, 3) were not determined.[87]

Scheme 19



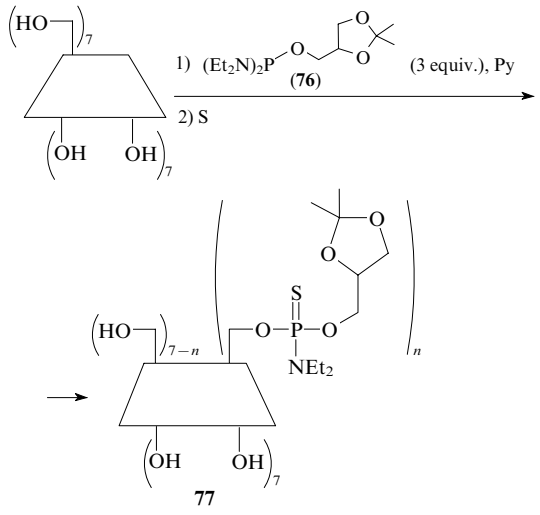
X = S or O



R = Ph, $(CH_2)_2CN$

phorylation ($n = 3$) of the primary hydroxy groups (Scheme 20).[87]

Scheme 20



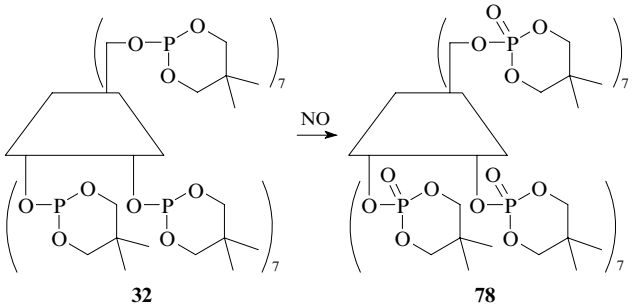
$n = 2, 3$

It is noteworthy that the reaction of free β-cyclodextrin with phosphorous triamide also occurs under mild conditions (20 °C) and involves primary hydroxy groups but yields a product mixture containing cyclophosphoramidite and phosphorodiamidite groups on the cyclodextrin core.[88] Considering the additional data on competitive phosphorylation of inclusion compounds based on β-cyclodextrin with phosphorodiamidite esters, it was assumed [89] that mild (at 20 °C) phosphorylation of cyclodextrins and some other distinctive transformations occurs owing to the preliminary inclusion (pre-organization) of the phosphorylating reagent into the β-cyclodextrin cavity. Thus, in this case, too, unusual transformations of cyclodextrin derivatives are related to its specific structural features.

3. Per-P(V)-phosphorylated cyclodextrins

It was mentioned above (see Section II.2.) that α- and β-cyclodextrin perphosphites **30** – **33** were converted to the corresponding thiophosphates without isolation from the reaction mixture.[44] Compounds **34** – **37** were prepared in the pure form in 60% – 90% yields and characterized by spectroscopy. The attempts to prepare similar perphosphate derivatives by oxidation of perphosphites **30** – **33** (also without isolation from the reaction mixture) with various reagents gave rise to a complex unseparable product mixture. Meanwhile, it was found that perphosphite **32** isolated in the pure form is easily oxidized with nitrogen(II) oxide to give perphosphate **78** in a quantitative yield. Attempts [44] to add sulfur to individual product **32** in order to prepare the above-mentioned perthiophosphate **36** failed. Sulfur added to this substrate very slowly, and this was accompanied by fast accumulation of a large amount of by-products that are difficult to separate (Scheme 21).

Scheme 21



It is evident that in this case, too, the unusual course of oxidation involving cyclodextrin perphosphite **32** is caused by the supramolecular influence of the free cyclodextrin cavity.[47] The addition of sulfur to pure perphosphite **32** follows a passive route, probably, due to the binding and strong retention of the hydrophobic sulfur in the molecular cavity of the substrate. This is also indicated by successful experiments on sulfurization of process cyclodextrin perphosphites present in the reaction mixture during the synthesis and containing pyridine hydrochloride in molecular cavities.[44] Thus, the customary synthetic strategy widely used in organophosphorus chemistry (according to which a compound of trivalent phosphorus is oxidized without isolation to a more stable derivative of pentavalent phosphorus, which is then purified and isolated in the pure form) proves to be inefficient in relation to P(III)-derivatives of cyclodextrins and needs to be corrected.[47]

* * *

Currently, phosphorus-containing cyclodextrins represent a promising class of compounds with a broad scope of

practical applications in different areas of supramolecular chemistry, metal complex catalysis, biomimetic research and pharmaceutical chemistry, biochemistry and some other interdisciplinary areas. The progress along this line is determined to a large extent by the knowledge of the possibilities of synthesis of cyclodextrin derivatives taking account of the above-considerede features of the structure and chemical behaviour of these compounds. One can hope that this review would contribute to the understanding of the role of phosphorus-containing cyclodextrins and stimulate new research in this interesting area of chemistry.

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