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Synthetic routes to carbamoylmethylphosphoryl compounds — extractants for the processing of spent nuclear fuels

E V Sharova, O I Artyushin, I L Odinets (deceased)

A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences ul. Vavilova 28, 119991 Moscow, Russian Federation

Data on synthetic routes to carbamoylmethylphosphoryl compounds are summarized. Arbuzov and Michaelis – Becker reactions are considered, as well as various methods of amidation of phosphorylacetic acids and their esters, including those using 'green' chemistry procedures. Various methods of introduction of carbamoylmethylphosphoryl moieties into calixarenes, cobalt carbollides, carboranes and other spatially pre-organized structures are demonstrated.
The bibliography includes 114 references.

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I. Introduction

Carbamoylmethylphosphoryl compounds (CMPC) or phosphorylacetic acid amides represent a large class of compounds comprising the corresponding phosphonates, phosphinates and phosphine oxides, being of high practical importance in the reprocessing of spent nuclear fuel (SNF) of nuclear power plants (NPP). A fuel cycle of NPP includes the dissolution of fuel assemblies in concentrated nitric acid, extractive recovery of uranium, plutonium and transplutonium elements (TPE) followed by the vitrification and disposal of the nuclear wastes. At the first stage of the process, where the nuclear fuels (uranium and plutonium) are recovered available monodentate organophosphorus extractants have been successfully used until now, *e.g.* tributyl phosphate (TBP) is used in the PUREX process developed back in the 1950s.[1] However, these extractants are unfit for the recovery of TPE and fission elements and especially for their fractioning at the second stage. Moreover, the spent nuclear fuel disposal without the TPE recovery is not allowed nowadays not only for the environmental reasons (vitrified blocks heat up because of high radioactivity and fracture rapidly), but also from the economical viewpoint, as many of TPE isotopes are of high demand in the modern science, technology and medicine, and are rather poorly accessible and expensive. Therefore, to recover the TPE, various types of extractants have been proposed including carboxylic acid esters and amides, crown ethers, cobalt carbollides, macrocyclic compounds and the like. However, considering the most important parameters (availability, efficacy, cost), bidentate organophosphorus compounds are absolute winners, and among them, CMPC and particularly the corresponding phosphine oxides are preferred. These compounds served as the basis for the development and application of the TRUEX process for SNF reprocessing with the recovery of TPE. In some western countries, n-octyl(phenyl)(*N*,*N*-diisobutylcarbamoylmethyl)phosphine oxide is employed in this process, whereas in Russia use is made of diphenyl(*N*,*N*-di-n-butylcarbamoylmethyl)phosphine oxide.[2]

Contrary to the other extractants of the same class, carbamoylmethylphosphine oxides are readily soluble in various organic solvents, are stable in strongly acidic medium, extract effectively TPE and, what is equally important, they are relatively cheap and readily accessible. Such valuable properties of CMPC stimulate the interest of different research groups in these compounds.

E V Sharova Candidate of Chemical Sciences, researcher of the Laboratory of Organophosphorus Compounds at the INEOS RAS.
Tel. (7-499) 135 93 56, e-mail: fos@ineos.ac.ru
O I Artyushin Candidate of Chemical Sciences, senior researcher of the same laboratory. Tel. (7-499) 135 93 56, e-mail: fos@ineos.ac.ru
I L Odinets Doctor of Chemical Sciences, head of the same laboratory.
Current research interests: chemistry of organophosphorus compounds, complexes and complexing agents, green chemistry.

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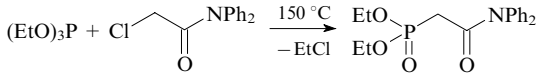
It should be noted that CMPC have been known since the 1940s; however, they received noticeable attention as late as in the 1980s when effective methods of their synthesis and modification were developed and also the peculiarities of their chemical behaviour and complexing properties were elucidated. Since then, the interest in these practically valuable compounds has permanently grown. By now, a large body of data about the synthesis and properties of CMPC has been accumulated. The extractive and complexing properties of these compounds are detailed in reviews;[3,4] as for the synthesis of CMPC, up to now, not a single review article devoted to this subject has been published. In recent years, this area of research has been rapidly developing; novel approaches appeared to both the synthesis of the desired compounds and the deposition of CMPC moieties onto polymer substrates with the aim to utilize the resulting materials in the TPE sorption.

The present review covers not only the traditional, well elaborated and developed synthetic approaches to CMPC but also those recently brought into the synthetic practice.

II. Arbuzov reaction

Arbuzov reaction is of great importance in the synthesis of carbamoylmethylphosphoryl compounds. Using this strategy, in 1940, Kazan chemists Razumov and Kashurina[5] obtained the first representative of this class bearing diphenylamide moiety starting from triethyl phosphite and chloroacetic acid diphenylamide (Scheme 1).

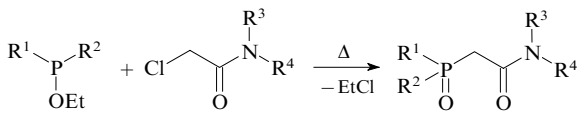
Scheme 1



(43%)

Twenty years later, Mel'nikov and co-workers[6] used the same procedure to synthesize two similar compounds having diethylamide and phenylamide substituents, however, in modest yields of 20% and 52%, correspondingly. Later, this approach was extended to the synthesis of carbamoylmethylphosphine oxides (CMPO). Although the reactions were still performed under drastic conditions without a solvent and without temperature control (heating of the reactant mixture), the yields of the target products proved to be sufficiently high due to the higher reactivity of alkylphosphinites (Scheme 2).[7]

Scheme 2

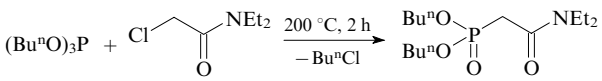


(64%–88%)

R^1, R^2 = Et, Pr^i; R^3, R^4 = H, Et, Bu^n, 4-MeC_6H_4

Till the mid-1960, all CMPC obtained were considered only as potential biologically active substances (mainly insecticides). However, in 1963 Siddall[8] pioneered in the synthesis of di(n-butyl) (*N*,*N*-diethylcarbamoylmethyl)-phosphonate (Scheme 3), which was used for quite different purposes, *i.e.*, to extract f-elements from an aqueous medium.

Scheme 3

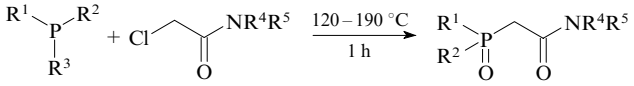


(40%)

Subsequently, elucidation of the extraction mechanism became the major area in investigating the properties of these compounds. When studying this process, it has been proposed that tris(bidentate) chelate complexes of the type $M(CMPC)_3^{3+}$ (M is metal) were formed in the organic phase. Subsequently the range of compounds obtained by Siddall was significantly extended, since these compounds were established to be very valuable Horner–Wordsworth–Emmons reagents to obtain polyunsaturated carboxylic acid amides. With the use of a solvent and at lower reaction temperature, a series of phosphonate type CMPC were prepared, the yields of the target compounds being up to 80%.[9–12]

In the 1980s, a large series of studies concerning the synthesis and complexing properties of CMPC (and particularly, CMPO) was performed under the supervision of Kabachnik[13,14] in the USSR and Horwitz[15] in the USA. The synthetic approaches to the target compounds of both research groups were based on the Arbuzov reaction. The comparative study of the reactivity of the trivalent phosphorus acid esters towards the chloroacetic acid amides accomplished by Paine and co-workers[16] revealed a direct dependence of the reaction rate on the nucleophilicity of the phosphorus-containing component. Subsequently, with the aim to study the effect of the phosphorus and nitrogen atom environment on the extraction ability of CMPC, a wide series of extractants having the general formula $R^1(OR^2)P(O)CH_2C(O)NR^3_2$ (R^1 = Ph, Me; R^2 = Et, Bu^n; R^3 = n-C_nH_{2n+1}, $n = 2-10$)[17–21] and $Ph_2P(O)CH_2C(O)NR_2$ (R = Et, Bu^n, iso-C_5H_{11}, n-C_8H_{17}, Bn; NR_2 is piperidino, morpholino) were synthesized.[22] The general reaction is illustrated in Scheme 4.

Scheme 4



(28%–88%)

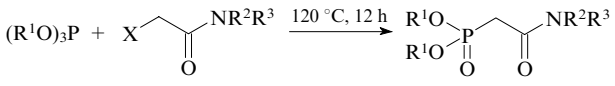
R^1, R^2 = Et, Bu^n, n-C_6H_{13}, OBu^n, n-OC_6H_{13}, cyclo-C_6H_{11}, Ph;
R^3 = OEt, OC_6H_{13}-n; R^4, R^5 = H, Et, Bu^n, *etc.*

A systematic study of extraction properties of dialkyl-substituted CMPO has shown that, being far more available than alkylenediphosphine dioxides, the former are only slightly inferior to the latter in the extraction ability. Horwitz and co-workers[15] investigated the Am^{III} and Fe^{III} extraction with a liquid–liquid system using a series of carbamoyl-substituted phosphonates, phosphinates and phosphine oxides of the general formula $X_2P(O)CH_2C(O)NR_2$, where X_2 = (n-$C_6H_{13}O)_2$, (n-C_6H_{13})(n-$C_6H_{13}O$) and (n-$C_6H_{13})_2$. Based on the partition constants obtained, the authors concluded that replacement of an alkoxy substituent at the phosphorus atom by an alkyl group results in an increase of the hydrolytic stability and improves the extraction properties of the compound

towards americium ions due to the enhancement of donating properties of the oxygen atom of the P=O group. Moreover, introduction of branched alkyl chains to the nitrogen atoms enhanced the selectivity of such extractants.[15] Generally, substituents at the phosphorus atom are mainly responsible for the extraction ability of the compounds, whereas those at the nitrogen atom are responsible for the solubility. In the case of phosphine oxides, the 'anomalous aryl strengthening' (AAS) effect was found.[23] Kabachnik and Yatsimirskii[24] discovered this effect in 1968 while studying the complex formation between tetraalkyl(aryl)methylenediphosphine oxides and alkali metal halides in non-aqueous media. Contrary to monodentate organophosphorus complexing agents (*e.g.* TBP), the extraction ability of the bidentate ones (alkylenediphosphine dioxides, carbamoylmethylphosphine oxides, *etc.*) not only does not decrease upon replacement of alkyl substituents at the phosphorus atom by more electronegative, *i.e.* aryl, groups but, on the contrary, significantly increases (in some cases, by several orders of magnitude). An impressive number of publications are devoted to the nature of AAS (see, *e.g.* studies[25–27] and the review[3]).

It should be noted that currently, especially under the influence of ever-growing application of the green chemistry methods to the synthesis of organophosphorus compounds,[28] CMPC are more often obtained by the Arbuzov reaction performed without a solvent using 1.5–2-fold excess of the phosphorus-containing reagent [usually $(EtO)_3P$ or $(MeO)_3P$]. The excess of phosphite is then distilled off and used in the subsequent syntheses. It is this approach that was used to obtain CMPC for spectral investigations[29, 30] and for performing modifications at the central carbon atom[31] (Scheme 5).

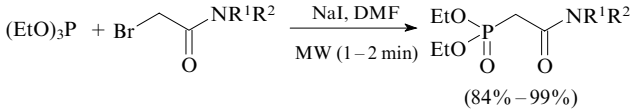
Scheme 5



X = Cl, Br; R^1 = Me, Et;
R^2 = R^3 = Me; R^2–R^3 = $(CH_2)_4$; R^2 = Me, Et, Pr^i; R^3 = Ph, Bn, 4-$MeOC_6H_4$; R^2 = H: R^3 = Pr^i, Bn, cyclo-C_6H_{11}, Ph, 4-$MeOC_6H_4$

Microwave (MW) activation of the reactants significantly reduces the duration of the Arbuzov reaction.[32] The optimal conditions found by the authors to carry out the reaction of triethyl phosphite with a large number of chloro- and bromoacetamides are as follows: 1.5-fold excess of $(EtO)_3P$, 10 mol.% of the NaI catalyst, DMF as the solvent (2 mL per mmol of acetamide), radiated power 210–280 W, time 1.5–2 min. When these conditions are met, the yields of CMPC range from 84% to 99% (Scheme 6).

Scheme 6



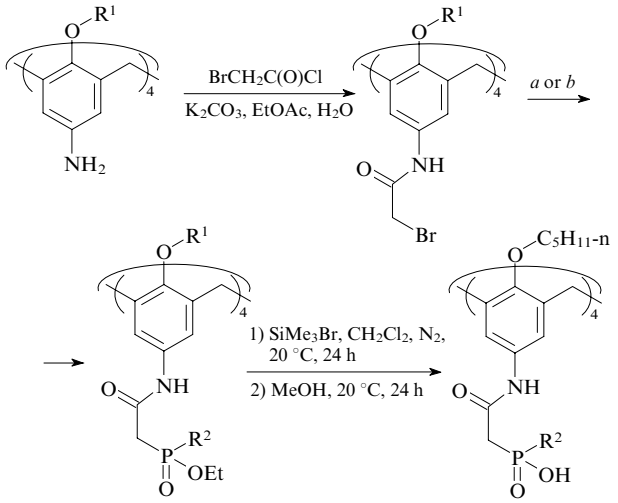
R^1 = H: R^2 = Ph, 4-BrC_6H_4, 4-FC_6H_4, 4-MeC_6H_4, 4-$O_2NC_6H_4$, 2-MeC_6H_4, $CH(Me)C_6H_5$, $(CH_2)_2$[3,4-$(OMe)_2C_6H_3$], Bu^t, Bn;
R^1 = Me: R^2 = Ph, Bn; R^1 = Et: R^2 = Ph, Bn; R^1 = Pr^i, R^2 = Bn;
R^1 = R^2 = Ph

As compared with the same reactions performed in the absence of microwave activation, catalyst or solvent (110 °C, 10 h), the process duration is reduced by more that two orders of magnitude with an increase in the CMPC yield, on average, by 20%. The above procedure is obviously a real breakthrough in the application of the Arbuzov reaction to the CMPC synthesis. However, it requires a thorough and permanent control, as in the case of too high radiated power or too long reaction time, the yields of the target products decrease down to 0%.

Since CMPO possess a high extraction ability, they have drawn attention of some researchers in relation to the preparation of effective extractants based on the modified macrocyclic molecules. Such extractants comprise preorganized complexing CMPO-groups and show an extremely high extraction ability along with the high selectivity towards various metal ions. Macrocyclic skeletons particularly suitable for the functionalization are calixarenes having cavities of different size, allowing modification of both upper and lower rims with the moieties of effective complexing agents.

Thus, introduction of carbamoylmethylphosphoryl complexing groups through the Arbuzov reaction was used to obtain a series of calix[4]arene tetraphosphonates **1a–c** and tetraphosphinates **1d**,**e** bearing various substituents at the phosphorus atom on the lower rim.[33] Note that basing on the compounds **1b**,**e**, the corresponding acids **2a**,**b** were also synthesized by the reaction with trimethylsilyl bromide followed by methanolysis (Scheme 7, the curved line denotes the calixarene rim).

Scheme 7



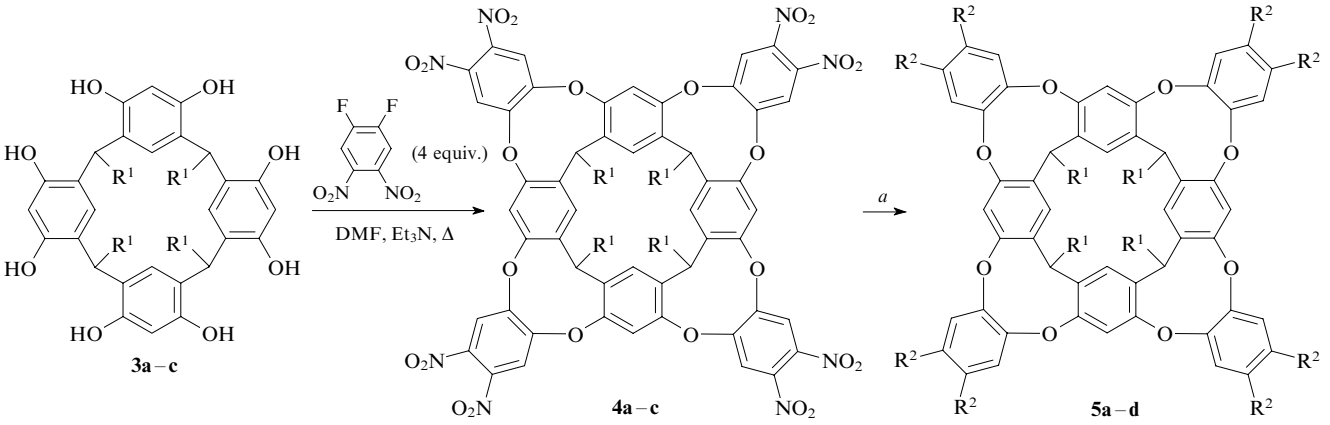
(*a*) $(EtO)_2PPh$, THF, N_2, 70 °C, 48 h;
(*b*) $(EtO)_3P$, N_2, 70 °C, 64 h

Compound **1**	Conditions	R^1	R^2	Yield (%)
a	*b*	Pr^n	OEt	77
b	*b*	n-C_5H_{11}	OEt	76
c	*b*	n-$C_{10}H_{21}$	OEt	75
d	*a*	Pr^n	Ph	65
e	*a*	n-C_5H_{11}	Ph	67

The idea to modify the macrocyclic skeleton with such effective complexing agents as carbamoylmethylphosphine

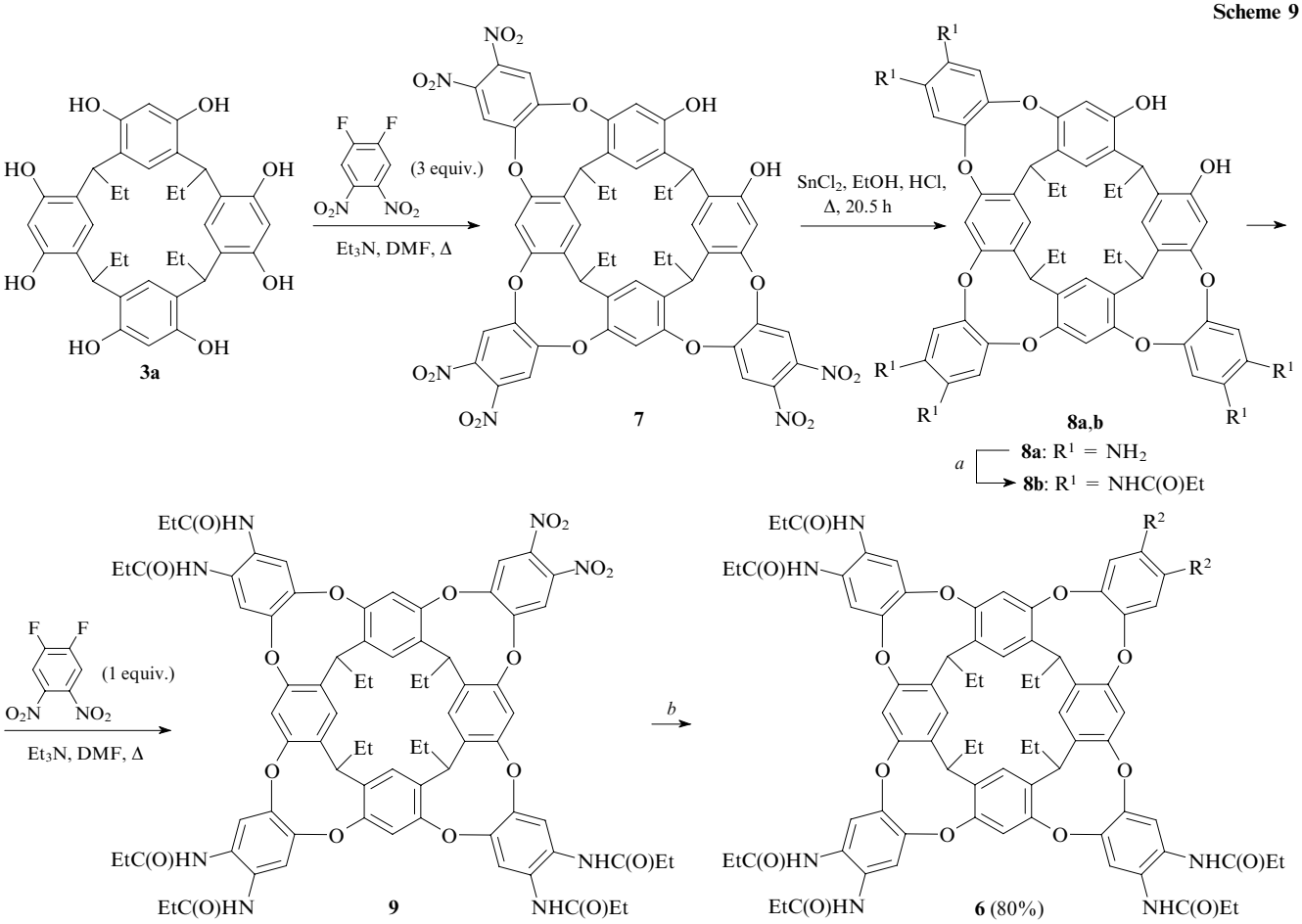
oxides has been used by Armhein *et al.*[34,35] to functionalize rigid cavitands obtained from resorcinarenes. Resorcinarene octols **3a–c** served as the starting compounds; they were made to react with 4 eq. of 4,5-difluoro-1,2-dinitrobenzene in the presence of triethylamine. This gave octanitrocavitands **4a–c**. Successive reduction of compounds **4** with $SnCl_2$ in ethanolic HCl, Schotten–Baumann acylation with bromoacetyl chloride and the Arbuzov reaction with triethyl or tripropyl phosphite yielded phosphonates **5a–d**,

Scheme 8



3, **4**: R^1 = Et (**a**), $(CH_2)_3OH$ (**b**), n-$C_{11}H_{23}$ (**c**); **5**: R^2 = $NHC(O)CH_2P(O)(OEt)_2$: R^1 = Et (**a**, 99% yield), $(CH_2)_3OC(O)CH_2P(O)(OEt)_2$ (**b**, 94%), n-$C_{11}H_{23}$ (**c**, 77%); R^1 = n-$C_{11}H_{23}$, R^2 = $NHC(O)CH_2P(O)(OPr^n)_2$ (**d**, 100%); (*a*) 1) $SnCl_2$, HCl, EtOH, Δ; 2) $BrCH_2C(O)Cl$, K_2CO_3, EtOAc, H_2O, Δ, 18.5–21.5 h; 3) $P(OEt)_3$ or $P(OPr^n)_3$, Δ, 1–2.5 h

Scheme 9



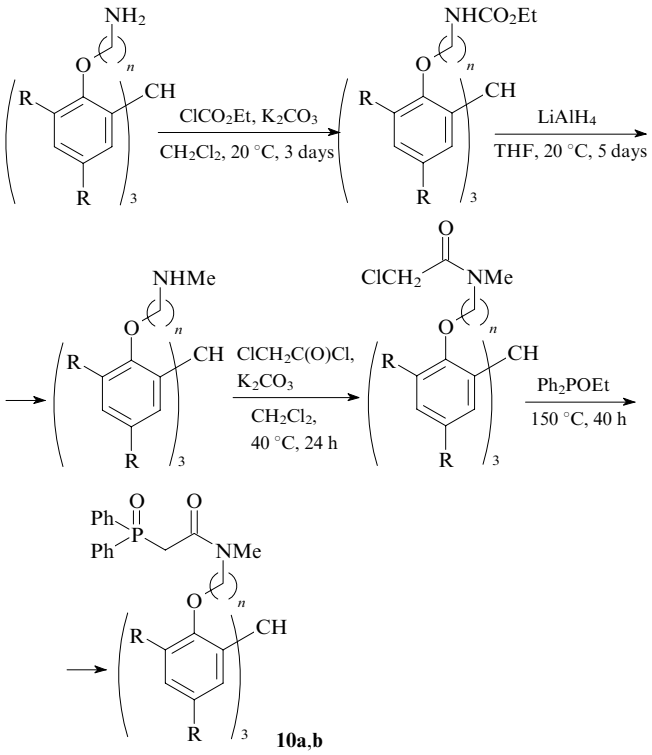
R^2 = $NHC(O)CH_2P(O)(OEt)_2$; (*a*) 1) EtC(O)Cl, PhMe, EtOH; 2) NH_2NH_2, 80 °C, 3.5 h; (*b*) 1) $SnCl_2$, HCl, EtOH, 45 °C, 17 h; 2) $BrCH_2C(O)Cl$, K_2CO_3, EtOAc, H_2O, Δ, 18.5–21.5 h; 3) $P(OEt)_3$, 105 °C, 4.5 h

comprising eight carbamoylmethylphosphonate groups (Scheme 8).

Also, the authors[35] obtained cavitand **6** (Scheme 9) having two compexing CMPO groups in the molecule. In this case, resorcinarene octol **3a** was made to react with 3 eqs. of 4,5-difluoro-1,2-dinitrobenzene in the presence of triethylamine, affording hexanitrocavitand **7**, which was then reduced to give the corresponding hexaamine **8a**. Acylation of compound **8a** with propionyl chloride followed by selective cleavage of the ester with hydrazine yielded hexaamide **8b**. Then, the reaction of the latter with 1 eq. of 4,5-difluoro-1,2-dinitrobenzene gave dinitrocavitand **9**; two carbamoylmethylphosohonate groups were introduced into this compound by successive transformations similar to those described above.

Along with other procedures, the Arbuzov reaction is successfully emloyed to modify the triphenylmethane platform with CMPO moieties (Scheme 10).[36]

Scheme 10



R = tert-C_5H_{11}, n = 2 (**a**, 85% yield); R = Bu^t, n = 3 (**b**, 57%)

Thus obtained C_3-symmetrical tripodal ligands **10a**,**b** showed excellent extraction properties on extracting uranium and plutonium from nitric acid solutions with the ligand concentrations in dichloromethane and octanol being 10^2-10^3 mol litre^{-1}.

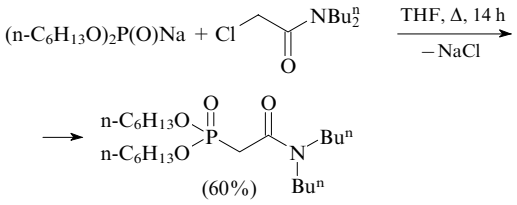
An interesting approach in applying the Arbuzov reaction to the synthesis of tripodal ligands bearing both the CMPC and CMPO moieties was shown recently by Allignol and co-workers[37] After the conventional procedures of chloroacetamide group formation in a molecule, the subsequent phosphorylation was performed with a mixture of triethyl phosphite and Ph_2POEt in a 1 : 1 ratio to give tripodal ligand **11** having one phosphonate and two phosphine oxide moieties according to the ^{1}H NMR data (Scheme 11).

As compared with a similar ligand bearing only phosphine oxide groups, compound **11** proved to be a less effective extractant. Furthermore, it was also less selective in recovering Am^{III} and Eu^{III} ions, *i.e.*, it had a lower ratio of the organic phase/aqueous phase distribution constants (D_{Am}/D_{Eu}). Therefore, further synthesis of these mixed tripodal ligands was recognized by the authors to be impractical.

III. The Michaelis–Becker reaction

The Michaelis–Becker reaction was first applied to obtain CMPC in 1964 by Siddall,[38] who published the synthetic route to di-n-hexyl *N*,*N*-n-dibutyl(carbamoylmethyl)-phosphonate depicted in Scheme 12.

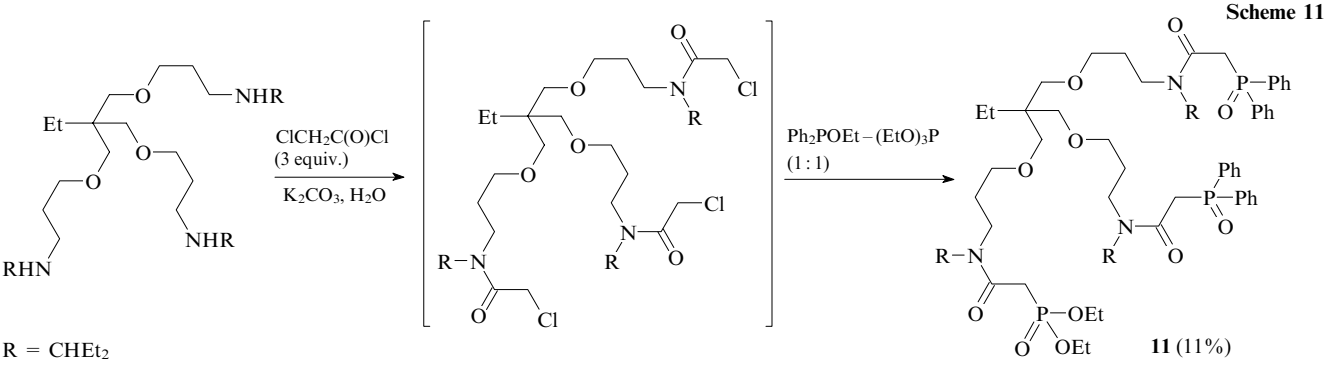
Scheme 12



Unlike the Arbuzov reaction, this transformation proceeds under relatively mild conditions (heating the reaction mixture at reflux in THF for 14 h), the sodium derivative of dihexyl phosphite being obtained *in situ* from phosphite and sodium hydride in the same reaction vessel. Such an approach to CMPC proved to be very convenient in practice and came into wide use (Scheme 13) along with the Arbuzov reaction, the yields of the products obtained by these two different methods being comparable.[11, 39, 40]

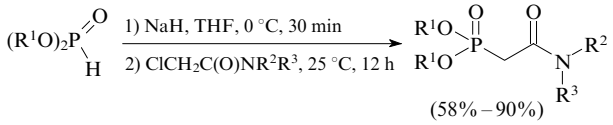
The first representative of CMPO based on n-butylphenylphosphinous acid has been synthesized[14] in a similar way (Scheme 14).

Scheme 11



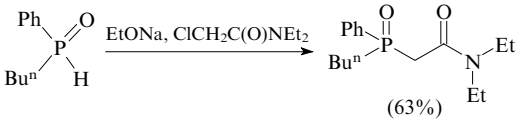
R = $CHEt_2$

Scheme 13



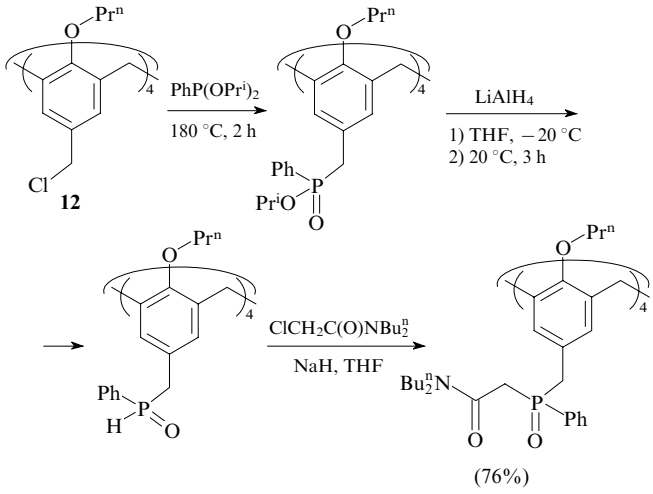
R^1 = Et, Bu^n, Pr^i, n-C_6H_{13}, Ph;
R^2, R^3 = H, Me, Bn, Ph; R^2–R^3 = $(CH_2)_4$

Scheme 14



Later, the Michaelis–Becker reaction was used to obtain CMPO-substituted calix[4]arenes starting from calix[4]arene **12**. The latter was pre-modified with four hydrophosphoryl groups attached to the upper rim through a CH_2 linker and made to react with monochloroacetic acid dibutylamide (Scheme 15).[41, 42]

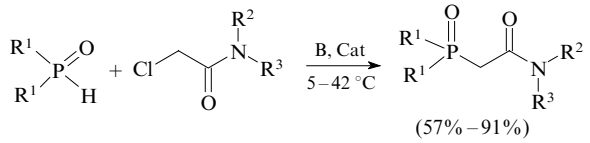
Scheme 15



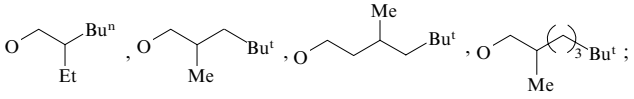
Carrying out the Michaelis–Becker reaction under phase transfer catalysis (PTC) conditions is of special interest. Kem, Nguyen and Cross[43] were the first to perform a detailed study of applying the PTC method to the Michaelis–Becker reaction. The authors used the heterogeneous system (50% aqueous NaOH solution in CH_2Cl_2) and quaternary ammonium salt as the phase transfer catalyst. The PTC procedure characterized by the practical convenience and absence of anhydrous media gave dialkyl carbamoylmethylphosphonates and -phosphine oxides in ⩾90% yields (Scheme 16), which is substantially higher than the yields obtained in this reaction under conventional conditions.

Under these conditions the major reaction rate exceeds significantly the rate of hydrolysis, the latter being responsible for the formation of the side products. The use of ammonium chlorides was shown to be more advantageous than the use of ammonium bromides, iodides and sulfonates; the authors explained this fact by higher stability of ion pairs formed by Br^-, I^- or RSO_3^- anions with the quaternary ammonium cation hampering the formation of

Scheme 16



B is base, Cat is methyltriocrylammonium or tetra-n-hexylammonium chloride; R^1 = Bu^n, OBu^n, OC_6H_{13}-n, n-C_8H_{17}, OC_9H_{19}-iso,

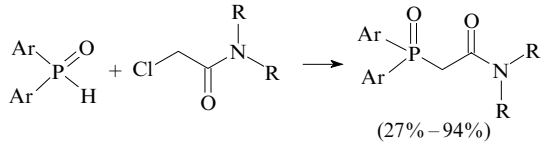


R^2, R^3 = H, Me, Et, Bu^n, $CH_2CHEtBu^n$

ammonium hydroxide. Unlike other PTC reactions, in this case, the stirring velocity has a little effect on the alkylation rate; however, rate of hydrolysis increases upon more rapid stirring.

Besides the use of 50% aq. NaOH/CH_2Cl_2 system, in some cases, good results were obtained under anhydrous conditions (the system K_2CO_3 + KOH/organic phase + Cat.). Petrov *et al.*[44] showed that under these conditions, the yields of CMPC and CMPO may be as high as 94% (Scheme 17).

Scheme 17

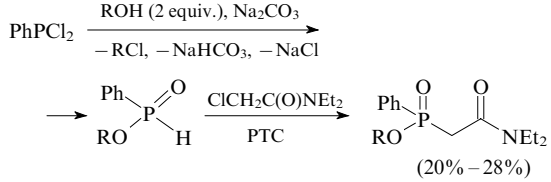


Ar = Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4; R = Et, Bu^n

The reaction involves 2 mol of KOH, 0.5 mol of the catalyst, 18-crown-6 ether (its presence dramatically accelerates the reaction), per mole of the hydrophosphoryl compound; the process is conducted at room temperature in an organic solvent (benzene, THF or dimethoxyethane). Carrying out the reaction in polar solvents, such as DMF or DMSO, lowers significantly the yield of the target compounds due to the hydrolysis of chloroacetamides and disproportionation of the hydrophosphoryl compounds. Bis(2-ethylhexyl) dialkylcarbamoylphosphonates were obtained under the same conditions.

Note that the use of PTC method to obtain carbamoylmethylphosphinates gives markedly worse results than for phosphonates and phosphine oxides.[17–21] Thus, in reaction of *O*-alkyl phenylphosphonites with chloroacetic acid diethylamide under PTC conditions following the procedure described by Kem *et al.*,[43] *O*-alkyl phenyl(*N*,*N*-diethylcarbamoylmethyl)phosphinates are formed in yields not exceeding 20%–28% (Scheme 18).

Scheme 18

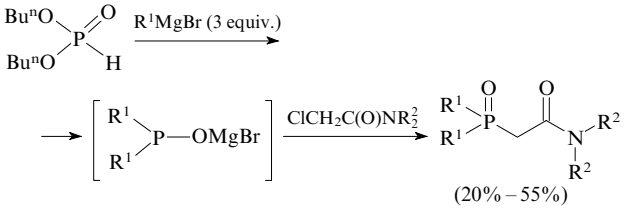


R = iso-C_5H_{11}, n-C_6H_{13}, $CH_2CHEtBu^n$, n-C_8H_{17}, n-$C_{10}H_{21}$

The decrease in the yields of the target compounds is probably due to both the inefficiency of this reaction for *O*-alkyl phenylphosphonites and the product loss during the chromatographic purification.

As an improved synthetic route to CMPO by the Michaelis–Becker reaction, an approach proposed by Horwits and co-workers [15] may be considered. It is based on the reaction of hydrophosphoryl compounds (*e.g.*, dibutyl phosphite) with 3 equiv. of alkylmagnesium bromide in diethyl ether followed by treatment of the dialkylphosphonylmagnesium bromide with the corresponding *N*,*N*-dialkyl-2-chloroacetamide (Scheme 19).

Scheme 19

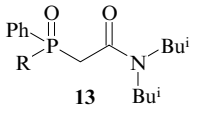


R^1 = n-C_6H_{13}, CH_2CHEt_2; R^2 = Et, Bu^n, Bu^i, Bu^s

In this case, the yields of all target compounds before the purification exceeded 50%, although these phosphine oxides were isolated in a pure state in 20%–55% yields and their purity ranged from 94% to 99%.

Similarly, the same authors [15] obtained a series of alkyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxides **13** bearing long-chain alkyl substituents (R).

Structure 13



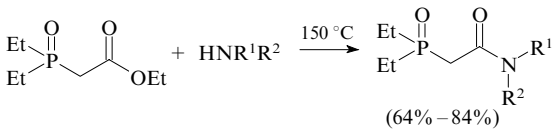
R = n-C_8H_{17}, $CH_2CHEtBu^n$, $(CH_2)_2CMe_2Pr^i$, $(CH_2)_2OC_6H_{13}$-n

Presently, compounds **13** are used in the extraction of transplutonium elements.

IV. Direct amidation of phosphorylacetic acids and their esters

Phosphorylacetic acid esters possess far more poor extractive properties than CMPC and, hence, they are not directly used in the processing of radioactive wastes. However, like the parent phosphorylacetic acids, they are valuable starting compounds to obtain CPMC due to their relative availability. Thus, as early as in 1964, a series of the first representatives of CMPO were synthesized by the reaction of the phosphorylacetic acid esters with amines without a solvent (along with the Arbuzov reaction) (Scheme 20).[7]

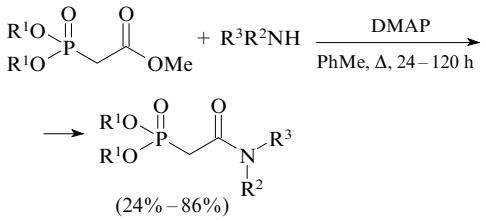
Scheme 20



R^1 = H: R^2 = Bn, Ph, 4-MeC_6H_4; R^1 = R^2 = Ph

Im a similar way, in 1987, Japanese scientists [45] obtained a series of CMPC using 4-dimethylaminopyridine (DMAP) as a catalyst (Scheme 21).

Scheme 21

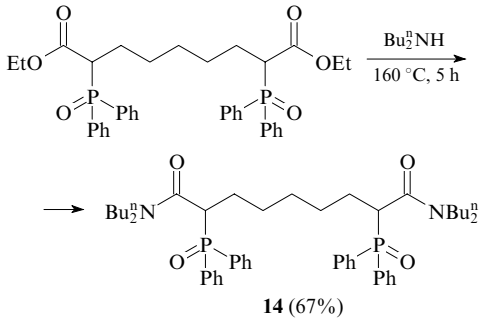


R^1 = Me, Pr^i; R^2, R^3 = H, Pr^i, Bn; R^1–R^2 = $(CH_2)_4$

Because of the drastic conditions, the reaction was complicated by displacement of alkoxy groups also at the phosphorus atom; therefore, the yields of some products were rather low.

In 1999, Russian scientists [46] used the same approach to obtain tetradentate ligand **14**. The reaction proceeded in 5 h on heating the reactant mixture to 160 °C (Scheme 22).

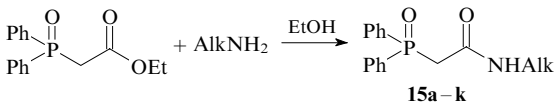
Scheme 22



14 (67%)

Though the yields of the target CMPO were sufficiently high in both cases (see Schemas 21 and 22), this method has not found wide use because of rather drastic reaction conditions (150–160 °C). Meanwhile, recently the phosphorylacetic acid esters have become commercially available and can be purchased as conventional chemicals. The development of a simple method for their amidation in order to prepare various CMPO has become a topical task. Recently, we proposed [47] an approach to CMPO **15a–k** based on direct amidation of ethyl phosphorylacetates with primary amines under very mild conditions using ethyl alcohol as the solvent (Scheme 23).

Scheme 23



15a–k

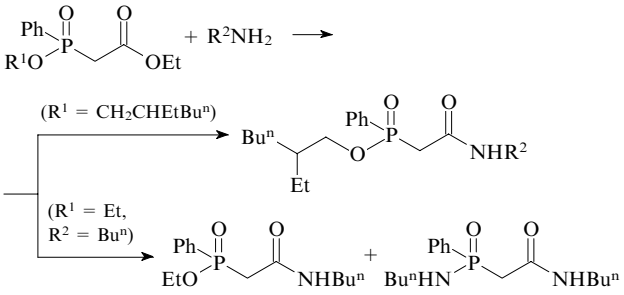
Alk = Et (**a**), Bu^n (**b**), Bu^i (**c**), n-C_6H_{13} (**d**), n-C_8H_{17} (**e**), $CH_2CHEtBu^n$ (**f**), n-C_9H_{19} (**g**), n-$C_{10}H_{21}$ (**h**), n-$C_{12}H_{25}$ (**i**), $(CH_2)_2Ph$ (**j**), $(CH_2)_3N$⟨O⟩ (**k**)

It is worth noting that although the reaction between carboxylic acid esters and amines in alcohols is well known and is widely used in the synthetic practice, it was for the first time that we applied this procedure to phosphorylacetic acid esters. The composition of products formed depends on the amine nature: secondary, alkylaryl and aromatic amines do not react. If the nitrogen atom and the heterocyclic moiety are separated by at least two methylene groups, the

reaction proceeds readily yielding the corresponding amides (*e.g.* compounds **15j**,**k**).

This approach was shown to be suitable for preparation of only carbamoylmethylphosphinates bearing sufficiently long hydrocarbon substituents in the alkoxy group at the phosphorus atom; otherwise, the reaction proceeds non-selectively (Scheme 24).

Scheme 24



R^1 = Et, $CH_2CHEtBu^n$; R^2 = Bu^n, n-C_6H_{13}, n-C_8H_{15}

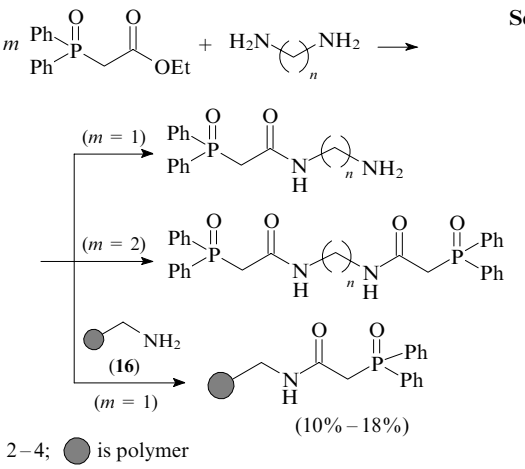
Note that the presence of long hydrocarbon substituents in the extractant molecule usually would be an asset as regards the TPE extraction, since this increases hydrophobicity and, correspondingly, the solubility of the extractant in diluents.

The above direct amidation method povided the route to not only mono-, but also di- and even polyphosphorylated CMPO [*e.g.*, using aminomethylated polystyrene **16** (Scheme 25)].[20, 47]

Low yields of the polymer-analogous transformation in the last-mentioned case are obviously connected with the steric hindrance of reagent approach, since there is only one methylene unit between the nitrogen atom and the polymeric matrix.

Apart from the reaction of amines and the phosphorylacetic acid esters, theoretically the reaction of amines and free acids may also give CMPO. However, the reaction between acids and phosphorous triamides proved to be more practically suitable. Thus, in 1989, Tsvetkov and coworkers [48] elaborated a unique one-pot procedure to obtain diphenyl(*N*,*N*-dialkylcarbamoylmethyl)phosphine oxides based on the reaction between diphenylphosphorylacetic acid and the corresponding phosphorous triamides. The

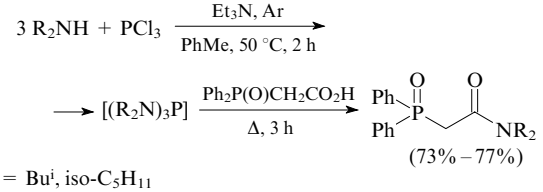
Scheme 25



n = 2–4; ● is polymer

latter are formed readily in reaction of a dialkylamine with the phosphorus trichloride in the presence of triethylamine (Scheme 26).

Scheme 26



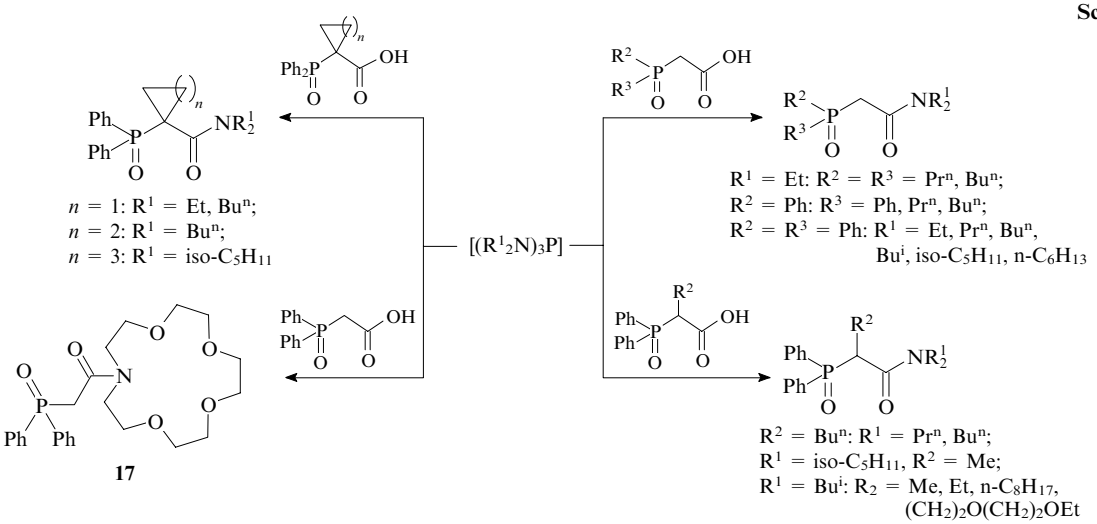
R = Bu^i, iso-C_5H_{11}

Later, the same authors applied the above method to obtain a large number of various CMPO including *N*-(diphenylphosphinylmethylcarbonyl)aza-15-crown-5 ether (**17**) (Scheme 27).[46, 49–51]

All reactions were carried out without isolation of the intermediate phosphorous triamides and without separation of the amine salt. The yields were mainly ~70%, which is quite acceptable for a two-step transformation. However, it should be mentioned that the phosphorylacetic acid esters are more available than the corresponding acids, since the latter are generally obtained through the ester hydrolysis (sometimes by a one-pot procedure, as was described for diphenylphosphorylacetic acid [49]).

In 1996, Arnaud-Neu *et al.*[52] developed a strategy for direct amidation of the phosphorylacetic acid derivatives

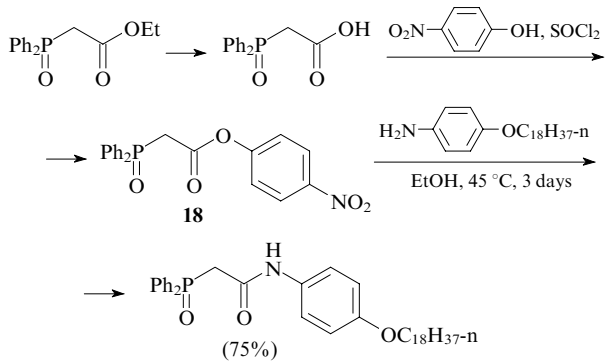
Scheme 27



17

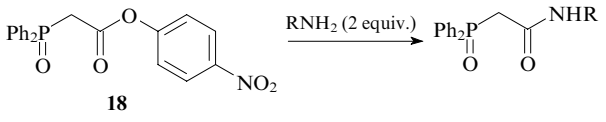
with amines, which became a basis for CMPO synthesis and modification and is still used. Direct reaction of diphenylphosphorylacetic acid or its anhydride $[Ph_2P(O)CH_2C(O)]_2O$ with amines in the presence of usual condensing agents such as dicyclohexylcarbodiimide (DCC) gave no satisfactory results, as difficult-to-separate product mixtures were formed. The authors were the first to propose a method of the direct amidation of *p*-nitrophenyl diphenylphosphorylacetate (NPDPA, **18**) containing a good leaving group (*p*-nitrophenoxy group). The above one-pot synthesis of NPDPA itself comprises the reaction of $Ph_2P(O)CH_2CO_2H$ with *p*-nitrophenol in chloroform in the presence of thionyl chloride. The *p*-nitrophenoxy group is readily replaced by the amino group, as the authors exemplified by the reaction with *p*-octadecyloxyaniline (Scheme 28). The possibility to use a single organophosphorus substrate and commercially available amines is an undoubtful advantage of the method under consideration.

Scheme 28



Later Matthews *et al.*[53] and Bernard *et al.*[54] obtained a series of phosphorylacetic acid *N*-alkylamides using this synthetic strategy. Note that the reaction with isopropylamine and isobutylamine is completed within 12–14 h at room temperature, whereas that with octylamine proceeds within 72 h at 45 °C (Scheme 29).

Scheme 29

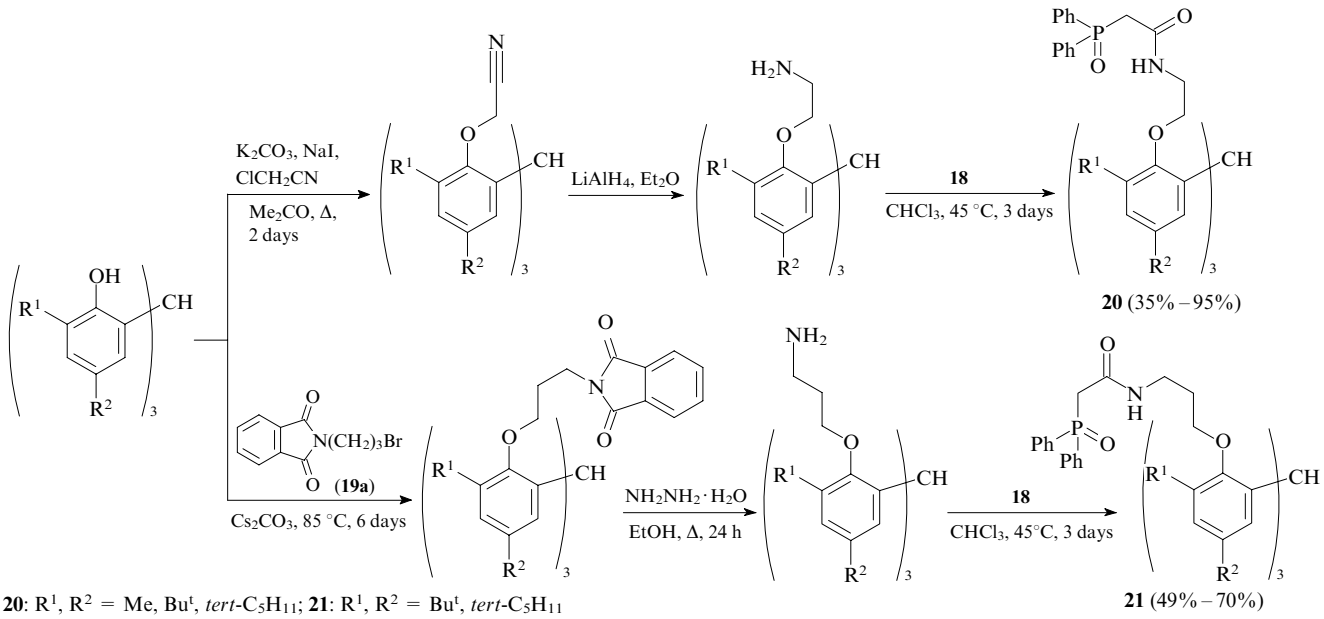


R = Pr^i, Bu^i, n-C_8H_{17}, $(CH_2)_5NH_2$

In recent years, the above method of direct amidation of NPDPA has been used very widely to obtain oligodentate CMPO ligands having pre-organized structure, advantageous for the selective complex formation with 4f and 5f elements. In other words, one of the main approaches to attach CMPO moieties to various matrices includes introduction of NH_2 group followed by the reaction with NPDPA. Since the phosphorus-containing group is introduced at the last step, the overall yield and purity of the target products increase. However, the introduction of the NH_2 group into the matrix is often a real challenge. We cite several general ways to address this problem.

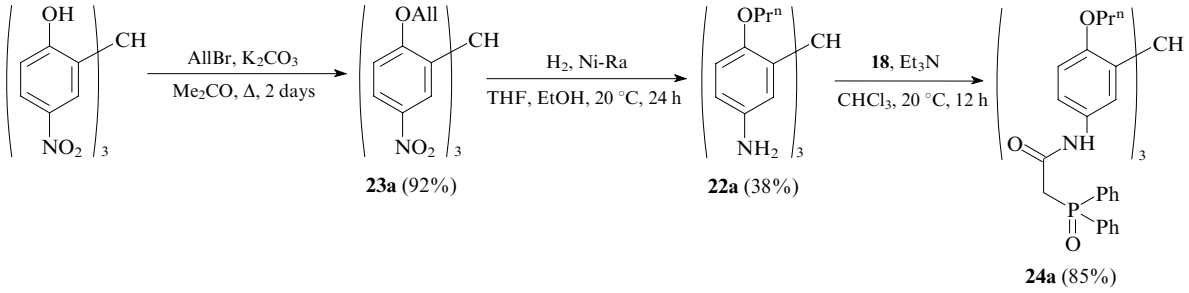
The problem is solved most easily by modification of calixarenes on the upper rim: either pre-formed calixarenes bearing *p*-nitro group are used or their nitration is carried out; in both cases, the subsequent reduction with hydrogen in the presence of Raney nickel (Ni-Ra) affords amines in high yields. Modification of calixarenes on the lower rim is far more problematic; this procedure usually includes several steps. First, the phenolic hydroxyl group is alkylated with alkyl halide bearing an amino group precursor, *e.g.*, with phthalimide derivative **19a** or with chlorocarboxylic acid nitriles $[Cl(CH_2)_nCN]$, then the amine function is formed by the hydrolysis or reduction reactions. In some cases, phenol is alkylated with an alkyl halide bearing the tosyl group, which is easily replaced by an azido group; the reduction of the latter yields the target amine. In all instances, various reducing agents ($LiAlH_4$, H_2–Pd/C, $NaBH_4 + CoCl_2$, *etc.*) are employed, their choice depending on the particular case. Since these transformations are multistep, the yields of the target amines are moderate. Several specific examples are given below.

Scheme 30

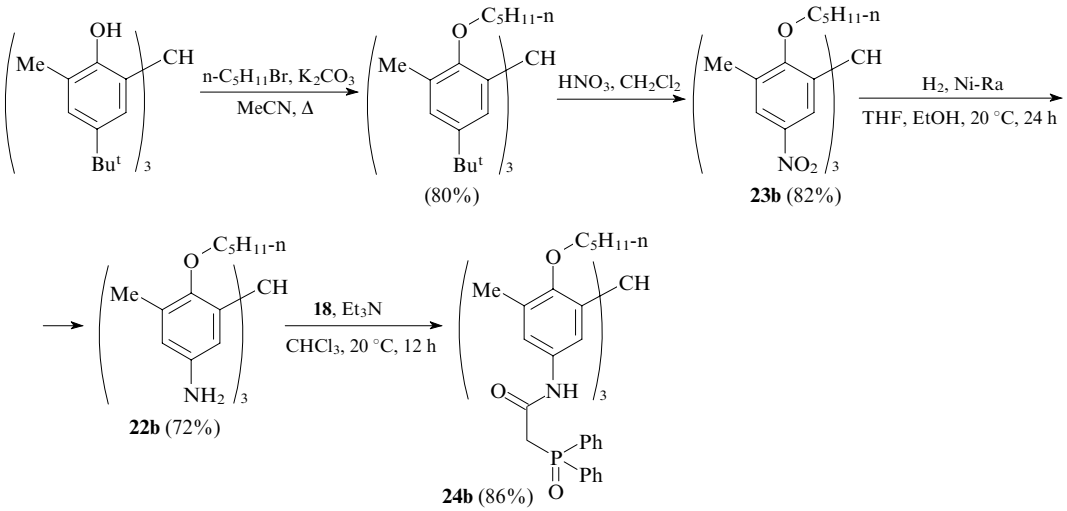


20: R^1, R^2 = Me, Bu^t, *tert*-C_5H_{11}; **21**: R^1, R^2 = Bu^t, *tert*-C_5H_{11}

Scheme 31



Scheme 32



Thus, ligands **20** and **21** based on a rigid C_3-symmetric triphenylmethane skeleton comprising three CMPO groups were synthesized (Scheme 30).[36, 55, 56] Ligands **20** and **21** were shown to quantitatively extract thorium and to exhibit low but permanent activity towards lanthanides at low pH. It should be noted that the extraction ability of ligand **21** is somewhat higher than that of ligand **20**, apparently due to higher flexibility of the trimethylene bridge. The investigation of complexes of these ligands with thorium and five lanthanides (lanthanum, cerium, neodymium, europium and ytterbium) by X-ray diffraction confirmed the participation of all oxygen atoms of CMPO moieties in the coordination, resulting in the formation of stable cationic complexes with a charge of +2.

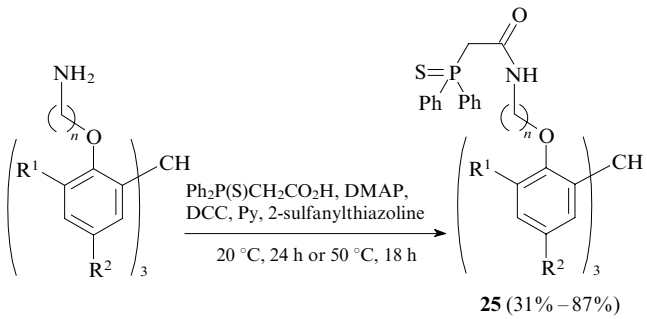
To attach CMPO groups to the upper rim of the triphenylmethane skeleton, amino-substituted triphenylmethane **22a** bearing a protected phenoxy group was used as the starting compound (Scheme 31).[57]

Since *p*-nitrophenolic rings in the substrate molecule are low reactive, the authors used highly reactive allyl bromide as an etherifying agent in the first step. The subsequent total hydrogenation of the triphenylmethane derivative **23a** furnished propyl ether **22a**, which was further acylated with active NPDPA (**18**). Contrary to the previous example (see Scheme 30) where the reaction with NPDPA proceeds upon heating for three days, the last step in the synthesis of target ligand **24a** is performed at room temperature within 12 h using triethylamine as the catalyst. Poly-CMPO derivative **24a** demonstrates high ionophoric properties towards actinides, though its extraction ability decreases dramatically with an increase in the nitric acid concentration.

An alternative reaction sequence affords CMPO-modified triphenylmethane derivative **24b** having the methyl substituent in the *ortho*-position relative to the alkoxy groups. O-Alkylation is performed with pentyl bromide due to the high nucleophilicity of the substrate. The subsequent *ipso*-nitration, reduction and N-acylation afford the target product in a high yield (Scheme 32).[57]

Interestingly, in a recent study,[58] DCC was successively used to modify the C_3-symmetric triphenylmethane platform with carbamoylmethylphosphine sulfide. In the presence of DCC, direct interaction of the acid with the amine group fixed on the lower rim of the platform takes place (Scheme 33).

Scheme 33

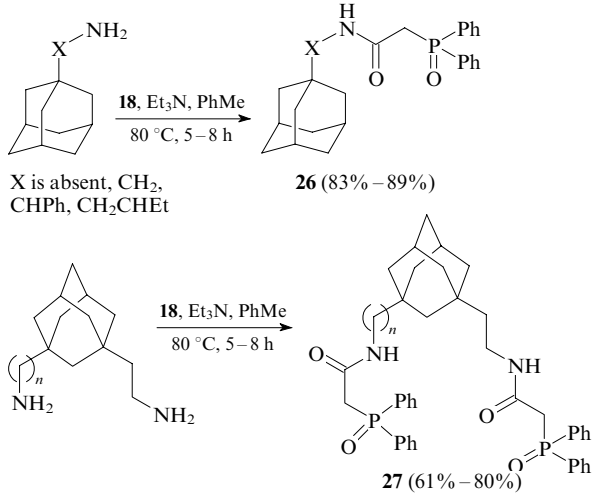


25 (31%–87%)

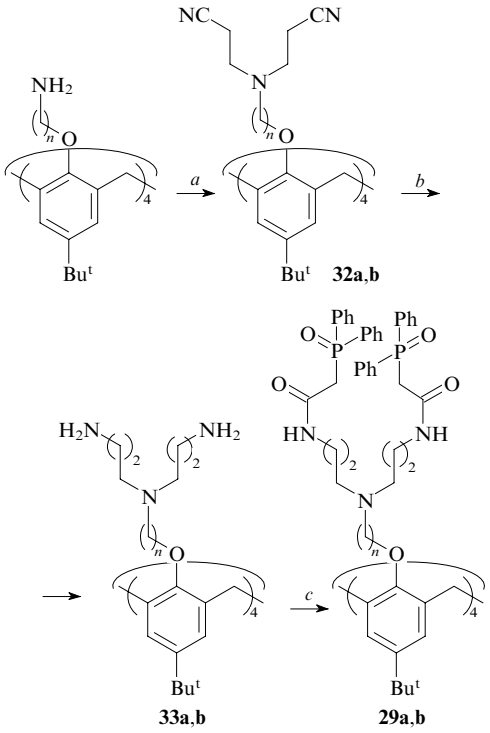
n = 2, 3; R^1, R^2 = Me, Bu^t, *tert*-C_5H_{11}; Py is pyridine

The obtained CMPC **25** showed very low efficacy towards Th^{IV} compared to CMPO, as well as nearly complete absence of the Am^{III}/Eu^{III} selectivity. Despite

Scheme 34



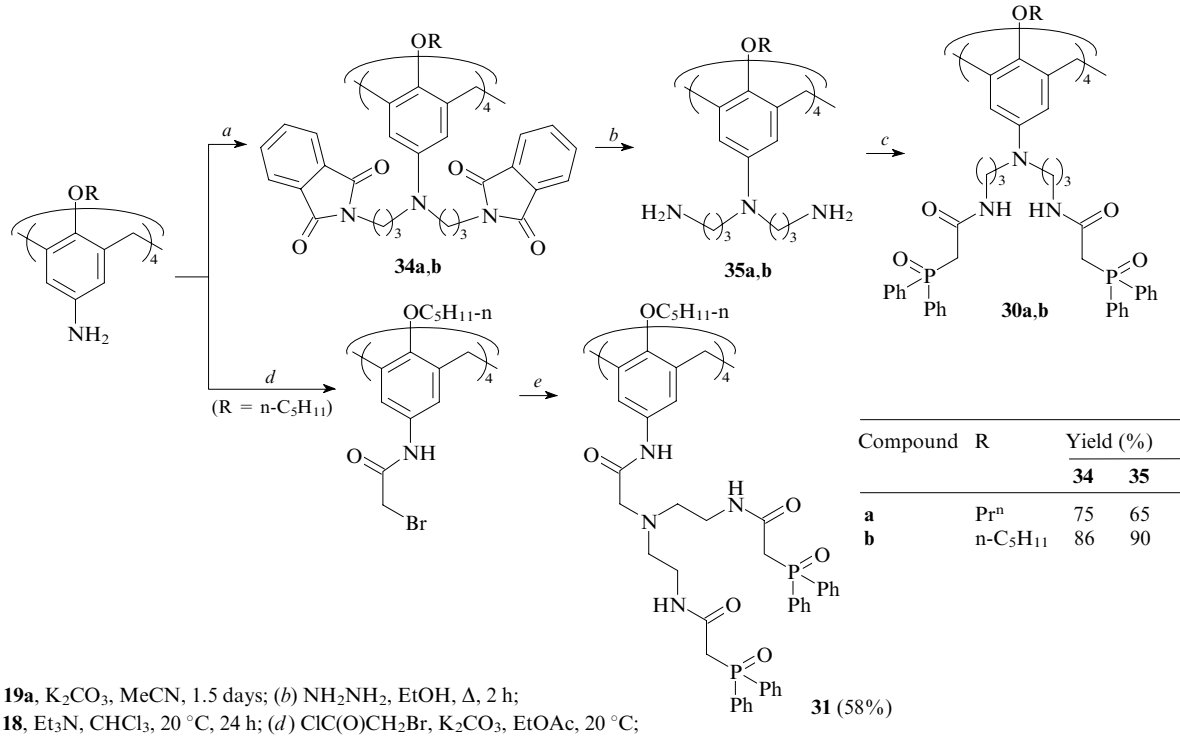
Scheme 35



(*a*) CH_2=CHCN, AcOH, Δ, 2.5 days; (*b*) Ni-Ra, NaOH, MeOH, THF, 20 °C, 24 h; (*c*) **18**, Et_3N, $CHCl_3$, 20 °C, 24 h

Compound	*n*	Yield (%)		
		29	**32**	**33**
a	3	80	87	55
b	4	51	54	51

Scheme 36



Compound	R	Yield (%)		
		34	**35**	**30**
a	Pr^n	75	65	80
b	n-C_5H_{11}	86	90	82

(*a*) **19a**, K_2CO_3, MeCN, 1.5 days; (*b*) NH_2NH_2, EtOH, Δ, 2 h;
(*c*) **18**, Et_3N, $CHCl_3$, 20 °C, 24 h; (*d*) $ClC(O)CH_2Br$, K_2CO_3, EtOAc, 20 °C;
(*e*) $[Ph_2P(O)CH_2C(O)NHCH_2CH_2]_2NH$, PhMe, 60 °C, 2 days

this, the approach described shows the significant effect of minor changes in conditions (in this instance, replacement of the P=O group by the P=S group; both groups do not directly take part in the process) on the course of phosphorylation.

A similar approach, *i.e.* acylation of amines with the diphenylphosphorylacetic acid ester **18**, has been used by a number of authors[59–62] to obtain carbamoylmethylphosphine oxide cage structures. For example, adamantane ligands **26**, **27**, derivatives of the corresponding 1-mono- and 1,3-diaminoadamantanes, and *p*-adamantylcalix[4]arenes **28** have CMPO groups in the adamantane moieties. In structures **27**, CMPO groups are attached to the 1 and 3 positions of the rigid adamantane platform through methylene or ethylene bridges (Scheme 34).

Although adamantane derivatives **27** bearing two CMPO groups extract americium and europium from 3 M nitric acid solutions† far more effectively than their monosubstituted analogues **26** and the reference diphenyl(*N*,*N*-dibutylcarbamoylmethyl)phosphine oxide, the ligands obtained are not selective to americium and europium ions ($D_{Am}/D_{Eu} < 2$).

Recently dendrimeric type derivatives of calix[4]arenes **29a**,**b**, **30a**,**b**, **31** with eight CMPO moieties on either upper or lower rim were synthesized.[63] As intermediate compounds in these transformations, calixarenes **32**–**35** were obtained (Schemes 35, 36).

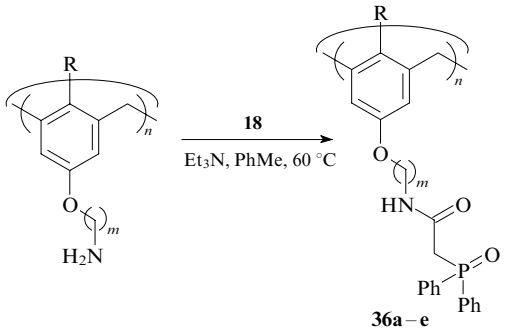
Dendrimeric calix[4]arenes **29**–**31** exhibited very low extraction ability towards Am^{III} and Eu^{III} ions, as well as nearly total absence of Am^{III}/Eu^{III} selectivity. Thus, 2-fold increase in the number of CMPO groups in a molecule of calix[4]arenes, irrespective of their positions, decreases the extraction activity by a factor of tens or even hundreds.

The above approach has been implemented in the synthesis of CMPO-modified calix[6]- and calix[8]arenes **36a**–**e** (Scheme 37).[64] The most interesting compound **36a** showed $D_{Am} > 100$ at HNO_3 concentrations >1 mol litre^{-1} and selectivity $D_{Am}/D_{Eu} > 3$, which is close to the values of the corresponding calix[4]arene derivatives.

† The highest extraction efficacy for such CMPO derivatives and reference compound is observed at this concentration.

Calix[4]arene **37** modified with four CMPO groups on the lower rim was obtained by multistage synthesis (Scheme 38). Note that tetraamine **38** readily reacts with NPDPA even at room temperature.[65]

Scheme 37



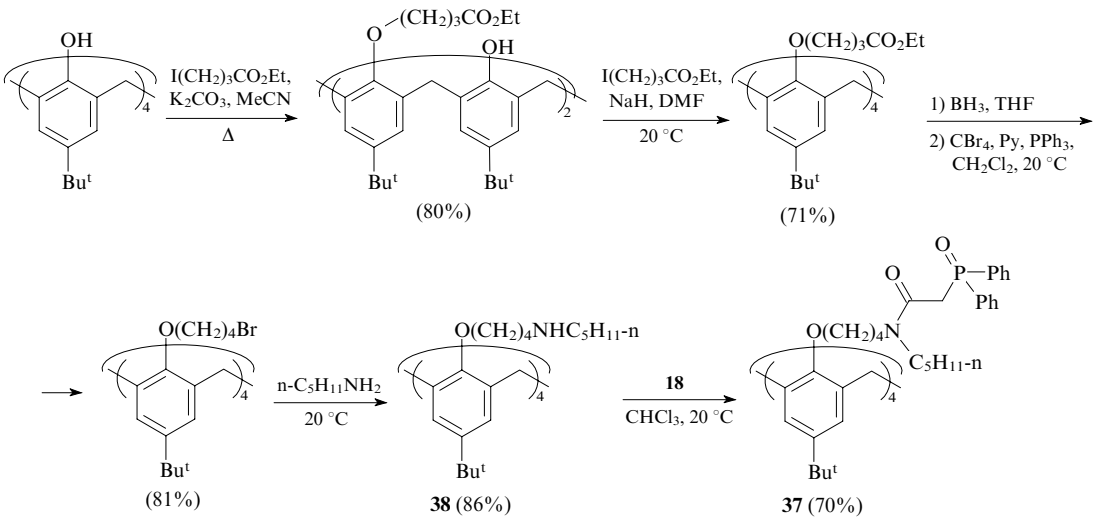
36a–**e**

Compound **36**	*n*	*m*	R	Yield (%)
a	6	3	Bu^t	66
b	6	3	H	59
c	6	4	H	78
d	8	3	H	55
e	8	3	OBn	46

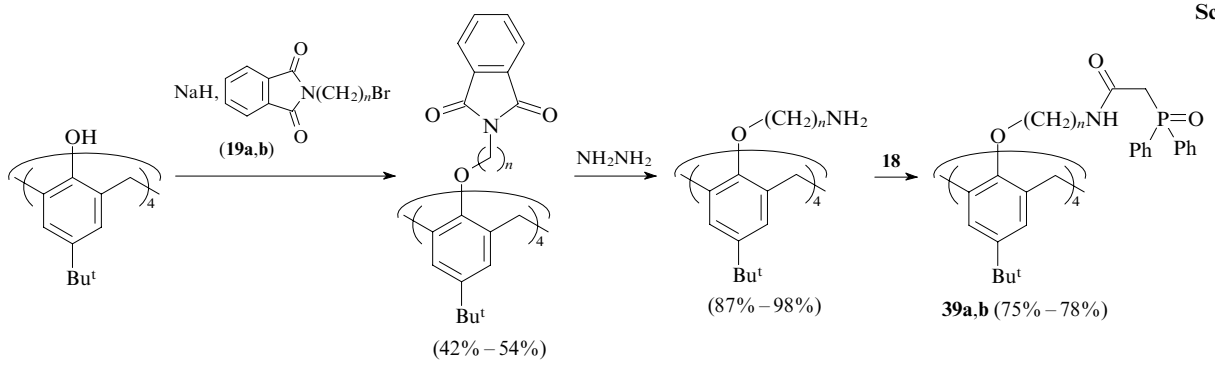
tert-Butylcalix[4]arenes **39a**–**c** with CMPO groups attached to the lower rim through linkers of different length ($n = 2–4$) were obtained in 65%–80% yields also by acylation of the corresponding aminoalkoxy derivatives.[66] The sequence of transformations used in the synthesis of CMPO-modified calix[4]arenes **39a**,**b** with $n = 3$, 4 is shown in Scheme 39. At the first step, alkylation was carried out using phthalimide derivatives with a varied linker lengths: $n = 3$ (**19a**), 4 (**19b**) and 2 (**19c**).

With a linker length $n = 2$ the alkylation agent **19c** is dehydrobrominated under the above conditions. Therefore, compound **39c** was synthesized starting from the tosyl (Ts) derivative of calix[4]arene **40**. The nitrogen-containing group was introduced through the nucleophilic substitution reaction using sodium azide, the azide group was then reduced under catalytic conditions to give an amino group, which was acylated with reagent **18** (Scheme 40).

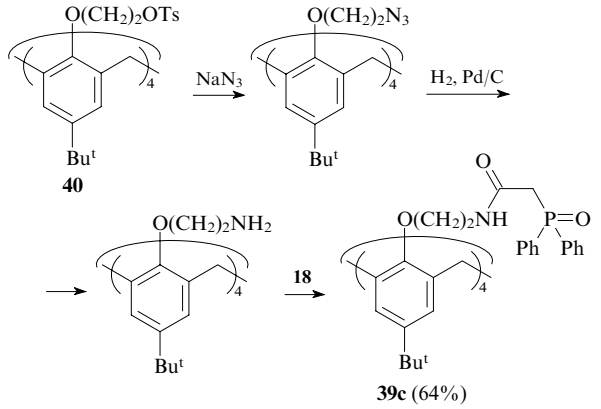
Scheme 38



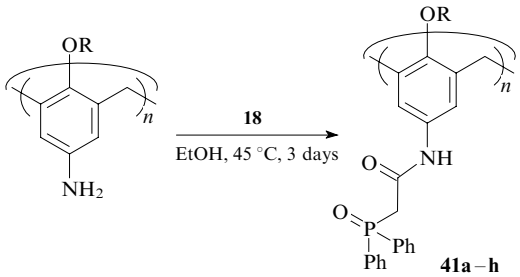
Scheme 39



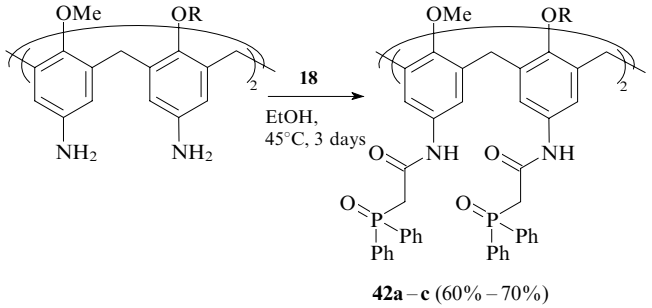
Scheme 40



Scheme 41



Compound **41**	*n*	R	Compound **41**	*n*	R
a	4	$CH_2CHEtBu^n$	**e**	4	n-$C_{14}H_{29}$
b	4	n-C_5H_{11}	**f**	4	n-$C_{16}H_{33}$
c	4	n-$C_{10}H_{21}$	**g**	4	n-$C_{18}H_{37}$
d	4	n-$C_{12}H_{25}$	**h**	5	n-$C_{14}H_{29}$

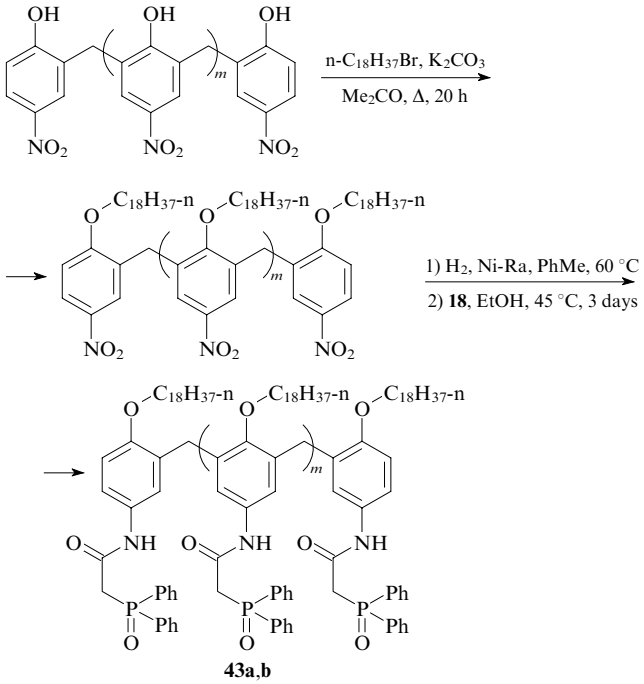


R = $CH_2CHEtBu^n$ (**a**), n-$C_{10}H_{21}$ (**b**), n-$C_{18}H_{37}$ (**c**)

In 1996, Arnaud-Neu *et al.*[52] synthesized for the first time upper-rim CMPO-modified calix[4]arene tetraalkyl ethers **41a–g** and **42a–c** and calix[5]arene pentaalkyl ether **41h**. Reactions of the corresponding poly(*O*-alkyl)poly(*p*-amino)calix[*n*]arene with a fivefold excess of NPDPA was performed in ethanol upon a moderate heating; the product yields were 60%–70% (Scheme 41). The extraction ability of the compounds **41** and **42** was found to be 1000 timer higher than that of the reference carbamoylmethylphosphine oxides.

Linear oligomeric analogues of such macrocycles, *i.e.* compounds **43a**,**b**, were obtained in a similar way starting from *p*-nitrophenol dimer and trimer in which the benzene rings were connected by a methylene bridge (Scheme 42).[52]

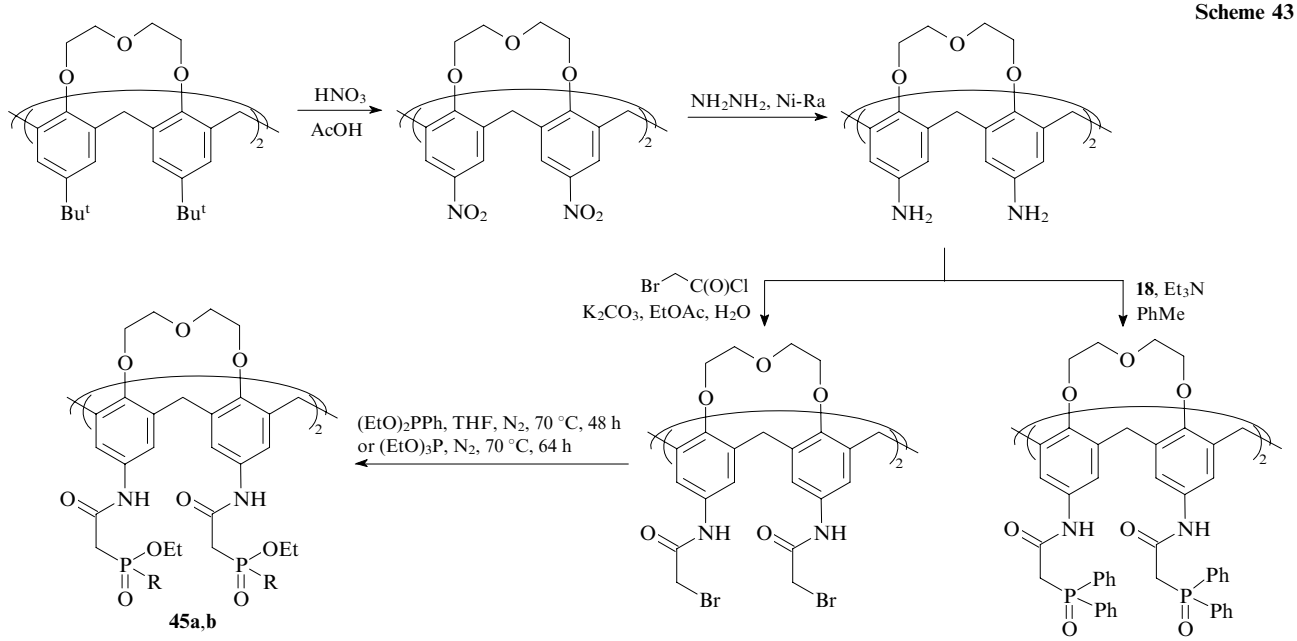
Scheme 42



m = 0 (**a**, 75% yield), 1 (**b**, 80%)

With the aim to obtain selective extractants to separate lanthanides and actinides, conformationally rigid calixarene derivatives **44** and **45** bearing four CMPO groups fixed on the upper rim were obtained, the oxygen atoms in the 1, 2 and 3, 4 positions of the lower ring being linked *via* two diethylene glycol moieties (Scheme 43).[33] In this case, NPDPA was also used to introduce diphenylphosphorylme-

Scheme 43

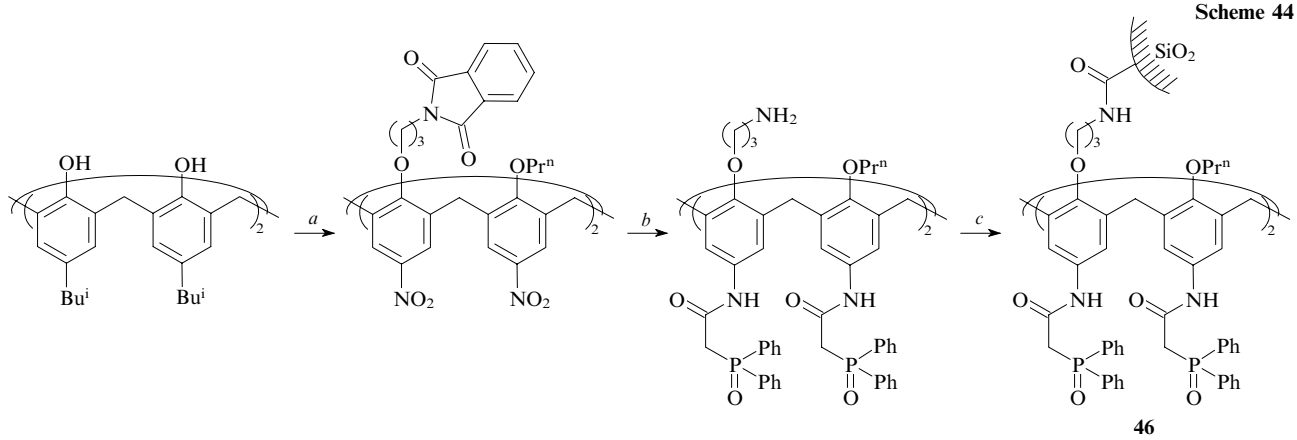


45a,b

R = Ph (**a**, 58% yield), OEt (**b**, 67%)

44 (62%)

Scheme 44



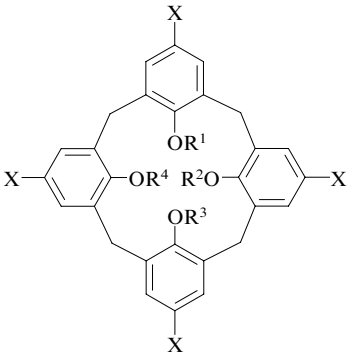
46

(*a*) 1) **19a**, K_2CO_3, MeCN, Δ, 48 h (68% yield); 2) Pr^nBr, NaH, DMF, 2 days (82%); 3) CF_3CO_2H, HNO_3, CH_2Cl_2, 30 min (65%); (*b*) 1) $SnCl_2$, EtOH, Δ, 18 h (89%); 2) **18**, PhMe, 50 °C (68%); 3) NH_2NH_2, EtOH, Δ, 1 h (96%); (*c*) linking to the substrate (99%)

thylcarbamoyl residue, whereas the corresponding phosphonates and phosphinates were synthesized by the Arbuzov reaction.

Matthews *et al.*[53] developed a novel type of extractants through the introduction of CMPO moieties under the action of NPDPA. These extractants are derivatives of calix[4]arene **46** modified with CMPO groups on the upper

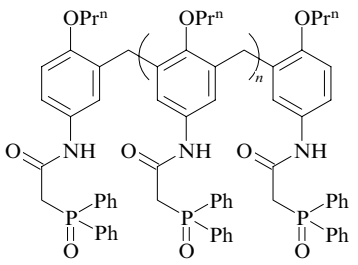
Structures 47, 48



47a–g

X = $NHC(O)CH_2P(O)Ph_2$

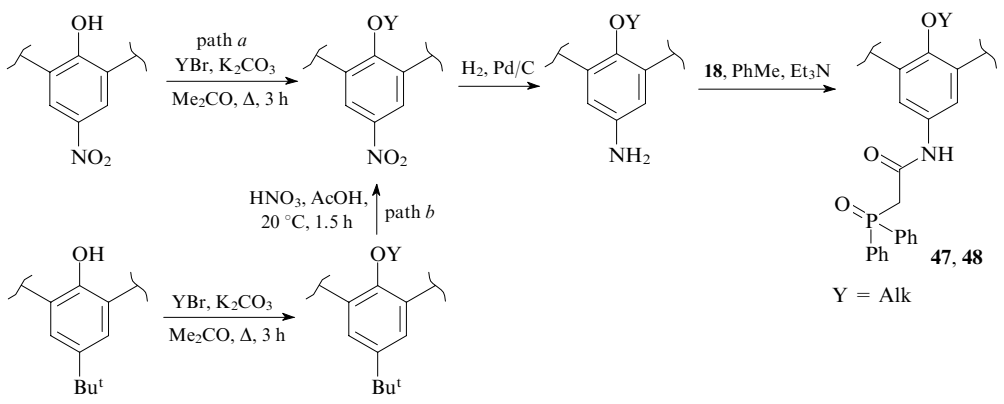
Compound **47**	R^1	R^2	R^3	R^4
a	Me	Me	Me	Pr^n
b	Me	Pr^n	Me	Pr^n
c	Me	Me	Pr^n	Pr^n
d	Me	Pr^n	Pr^n	Pr^n
e	Me	Me	Me	Me
f	Pr^n	Pr^n	Pr^n	Pr^n
g	n-C_5H_{11}	n-C_5H_{11}	n-C_5H_{11}	n-C_5H_{11}



48a–d

n = 0 (**a**), 1 (**b**), 2 (**c**), 3 (**d**)

Scheme 45



rim and with alkyleneamine linkers on the lower rim, and the linkers covalently bond the ligand to silica gel particles (Scheme 44).

Arnaud-Neu *et al.*[67, 68] synthesized a series of conformationally flexible calix[4]arenes **47a–g** having four CMPO groups on the upper rim. These compounds differ in the nature of alkoxy groups fixed on the calixarene lower rim; the derivatives **47a–f** include all possible combinations of methoxy and propoxy groups.

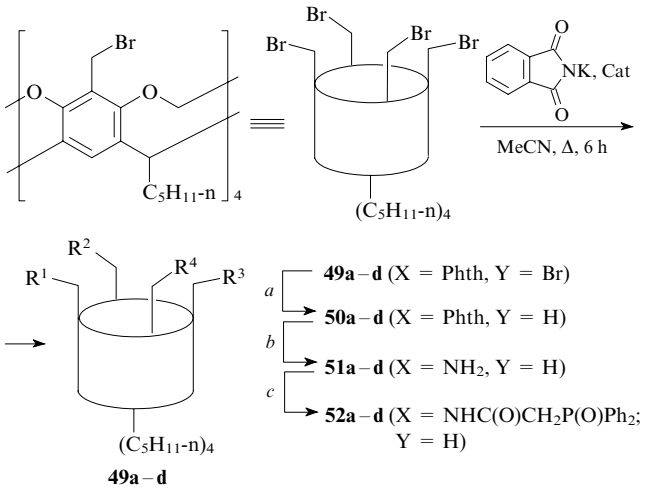
To obtain linear analogues of such calixarenes, *i.e.* compounds **48a–e**, the authors[67, 68] used linear oligomers of *p*-nitrophenols as the starting compounds.

Alkylation of these compounds with propyl bromide in acetone under reflux in the presence of potassium carbonate followed by the catalytic hydrogenation affords the corresponding amines, which react with NPDPA (the yields of **48a–e** are 53%–79%). The synthetic steps described are depicted in Scheme 45 by the example of a single phenolic unit (path *a*). Note that to obtain amino-substituted calixarenes, an alternative synthetic approach based on the *ipso*-nitration of the corresponding *tert*-butylcalix[4]arene tetraethers was applied (path *b*).

For the acyclic compounds, acylation with reagent **18** proceeds at room temperature and yields the target CMPO derivatives **47a–e** in 24 h, while for the cyclic analogues **48a–g** the acylation requires heating to 50 °C and 18 h.

Using NPDPA, Boerrigter *et al.*[69] synthesized ligands having one to three CMPO groups based on partially functionalized cavitands **49a–d**. In reaction of the starting tetrakis(bromomethyl)cavitand with potassium phthalimide in the presence of tributyl(hexadecyl)phosphonium bromide as the phase transfer catalyst, phthalimide groups are partially substituted for the bromine atoms, and four substances are formed as a result of mono- (**a**), 1,3-bis- (**b**), 1,2-bis- (**c**) and tris-substitution (**d**). These products were separated by chromatography with the yields ranging from 10% to 23%. Subsequently, compounds **49a–d** were treated with sodium tetrahydroborate in DMF at −10 °C; the debrominated phthalimido-substituted cavitands **50a–d** formed were made to react with hydrazine hydrate to give aminomethyl(methyl)cavitands **51a–d**. The latter were transformed into phosphorus-containing cavitands **52** (Scheme 46). It should be mentioned that compounds **51a–d** cannot be synthesized from the phthalimido-substituted derivatives **49a–d** , since the reaction between phthalimido groups and hydrazine hydrate in the presence of bromomethyl moieties may result in an intramolecular autoalkylation of the amino groups.

Scheme 46

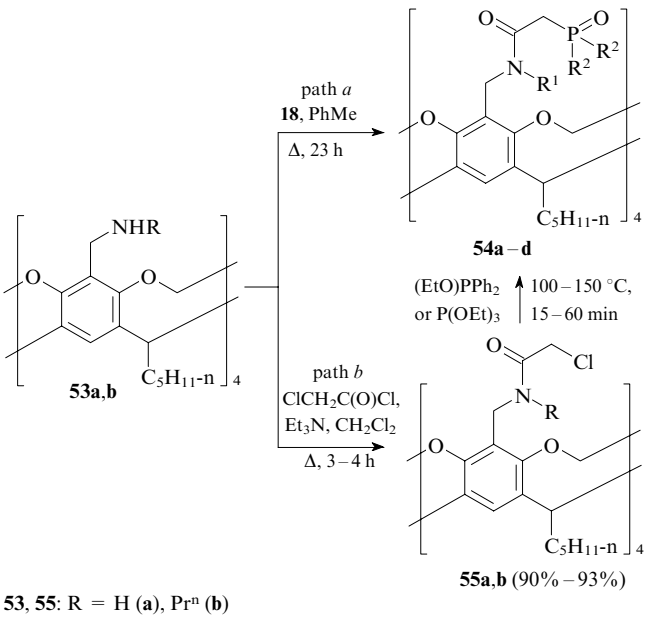


49–52: R^1 = X, R^2 = R^3 = R^4 = Y (**a**); R^1 = R^3 = X, R^2 = R^4 = Y (**b**); R^1 = R^2 = X, R^3 = R^4 = Y (**c**); R^1 = R^2 = R^3 = X, R^4 = Y (**d**); Phth is phthalimido; (*a*) $NaBH_4$, DMF, −10 °C; (*b*) $NH_2NH_2 \cdot H_2O$, EtOH, THF, Δ, 48 h; (*c*) **18**, PhMe, Δ, 5–11 h (66%–90% yields)

As applied to macrocyclic compounds, phosphorylation using NPDPA or its analogues [*p*-nitrophenyl(octyl)(phenyl)phosphorylacetate or (*p*-nitrophenyl)diphenylphosphorylpropionate][70] has obvious advantages over the synthesis of the same product by the Arbuzov reaction. Boerrigter *et al.*[71] showed this using resorcinarene derivatives **53a**,**b** as an example. Acylation of the latter with the compound **18** proceeds under milder conditions and gives higher yields of the target products **54a**,**b** (path *a*), as when employing the Arbuzov reaction the authors isolated the intermediate amides **55a**,**b** (path *b*) (Scheme 47).

For macrocyclic products, the main challenge in obtaining the compounds by the Arbuzov reaction is associated with the problems of their isolation. In this case, the purification of the target products is hampered due to the high boiling points of the starting compounds and instability of the products towards different chromatographical stationary phases (*e.g.*, silica gel or alumina). Recrystallization or reprecipitation are possible only in certain cases, but often do not improve the results. Chromatographic purification of the reaction products on Sephadex LH-20 stationary phase is suitable only in the case when the starting

Scheme 47



53, **55**: R = H (**a**), Pr^n (**b**)

Compounds **54**	R^1	R^2	Yield (%)	
			path *a*	path *b*
a	H	Ph	98	78
b	Pr^n	Ph	94	80
c	H	OEt	–	57
d	Pr^n	OEt	–	83

reactants have small molecular volume compared to the macrocyclic derivatives.

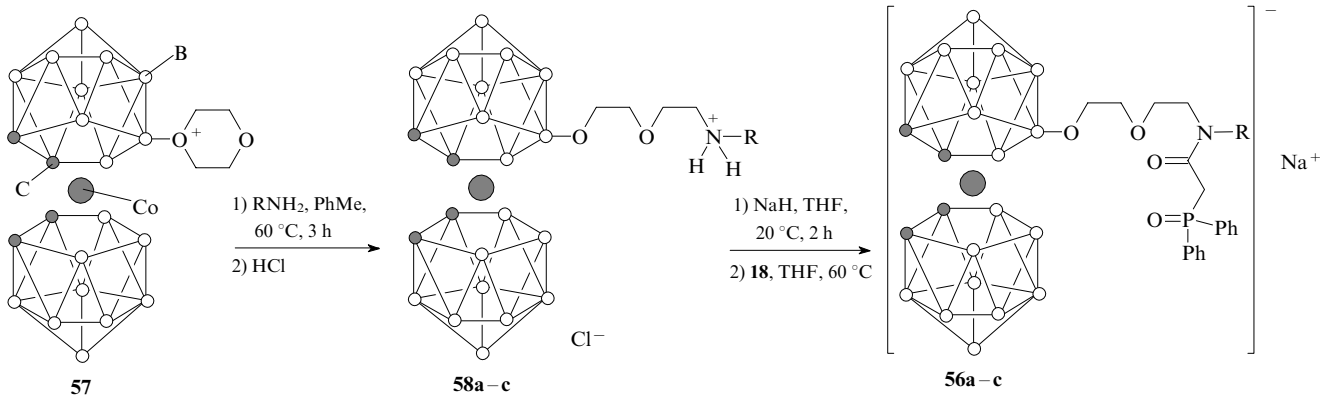
The ease of synthesis and chemical modification makes calixarenes a perfect material for designing more complex molecules. Calix[4]arenes are used particularly often as a molecular platform to attach various doping groups and thus to design cationic, anionic or even bifunctional receptors. In terms of extraction ability, CMPO-modified calixarenes outperform the ordinary phosphine oxides, the macrocyclic compounds being more powerful extractants for thorium(IV) than for europium(III). Comparison of the extraction properties of calixarenes modified with the same $Ph_2P(O)CH_2C(O)NH$ moiety on either upper or lower rim of the macrocycle showed that such functionalization contributes largely to both the extraction efficacy (in 1 M HNO_3) and selectivity. Despite the sufficiently large cavity in the cage, the more flexible is the ligand (*i.e.* the longer is the linker bonding the compexing moiety to the molecular platform), the more effectively it operates.

One more series of effective extractants **56a–c**, polyvalent cations bearing CMPO moieties, were obtained by Grüner *et al.*[72,73] based on the cobalt bis(dicarbollide) anion. The synthesis of these compounds included cleavage of dioxolane ring of cobalt bis(dicarbollide) **57** by primary amines to give zwitter-ionic intermediates **58a–c**, which were subsequently acylated with NPDPA (Scheme 48). *p*-Nitrophenyl esters of octyl(phenyl)phosphorylacetate or diphenylphosphorylpropionate were also used as phosphorus-containing acylating agents. More recently, an analogous approach allowed the authors to obtain also similar 8′-halo-substituted products (Hal = Cl, Br, I).[74] Such combination of an effective complexing moiety and a large hydrophobic cage gave excellent results in extraction of Eu and Am ions (>95%) even in strong acidic media (4 M HNO_3), though the selectivity proved to be modest. However, consideration should be given to the fact that presently, the most developed process of radionuclide recovery from the SNF is extraction using chlorinated cobalt dicarbollide (CCD) as an extractant in a polar diluent,[75] and it can be readily modified with CMPO moieties. Therefore, this extractant might be expected to find an industrial application. Moreover, it has an advantage of high solubility in non-polar solvents such as toluene and xylenes, which may eliminate the use of environmentally hazardous fluorinated and chlorinated solvents.

With the aim of obtaining effective compounds for the extraction of polyvalent cations (lanthanides and actinides) in the liquid–liquid system, Bernard *et al.*[54] has modified *closo*-dodecahydrododecaborate dianion $[B_{12}H_{12}]^{2-}$ with CMPO moieties. The authors synthesized two types of hydrododecaborate clusters — **A** and **B** (Fig. 1). The first one had a single substituent being responsible both for the ligand hydrophobicity and selectivity (*i.e.*, acting as both a hydrophobic anion and complex-selective cation). The second cluster had two substituents, each of them possessing one of the required properties.

A compound of type **A** (anion **59**) was obtained by the reaction of NPDPA with $[NH_3B_{12}H_{11}]$ in the presence of sodium hydride (Scheme 49).

Scheme 48



R = Bu^n (**a**, 95% yield), n-$C_{12}H_{25}$ (**b**, 91%), Bn (**c**, 92%)

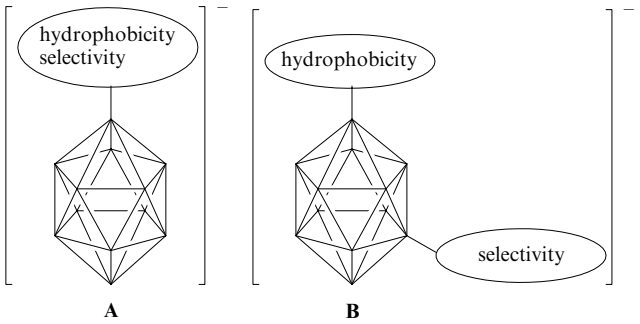
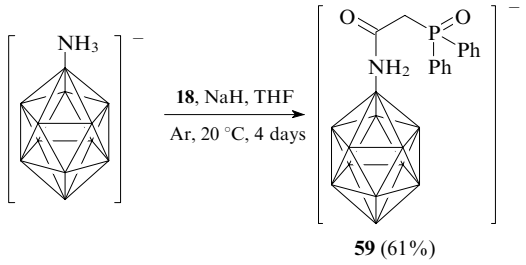


Figure 1. Two types of *closo*-dodecahydrododecaborate anion clusters (the nodes imply BH groups; for details, see the text).[54]

Scheme 49

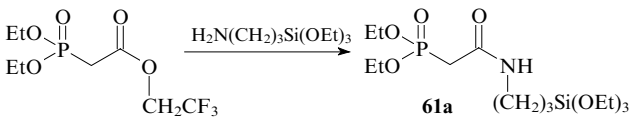


Compounds of type **B** (anions **60a–c**) were synthesized from oxonium derivatives of monosubstituted hydrododecaborates. The opening of the tetrahydrofuran or dioxane ring proceeded under the action of the phosphorylacetic acid NH-alkylamides in the presence of sodium hydride (Scheme 50).

Derivatives **60a–c** proved to be effective extractants of transuranium elements. However, high extraction ability was observed only in weak acid media (<0.1 M HNO_3) where the partition constants exceeded 100, whereas in 1–3 M HNO_3 the extraction efficacy decreased by a factor of at least 50.

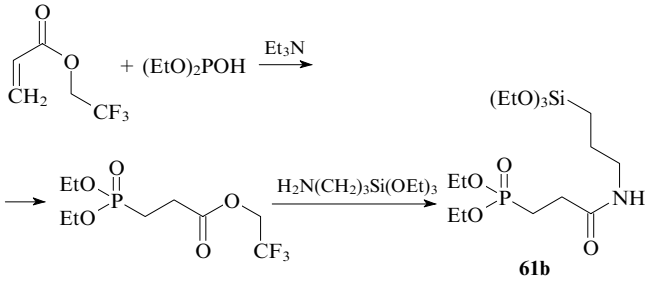
It should be noted that other esters having good leaving groups may be employed in condensation with amines, along with the NPDPA. Birnbaum *et al.*[76] suggested using the trifluoroethoxy moiety. Trifluoroethyl diethoxyphosphorylacetate reacts with aminopropyltriethoxysilane yielding CMPC silane **61a**, which the authors failed to completely purify from by-products (Scheme 51).

Scheme 51



Ligand **61b** having an ethylene bridge between the phosphonate and carbamoyl groups was synthesized in a similar way (Scheme 52).

Scheme 52

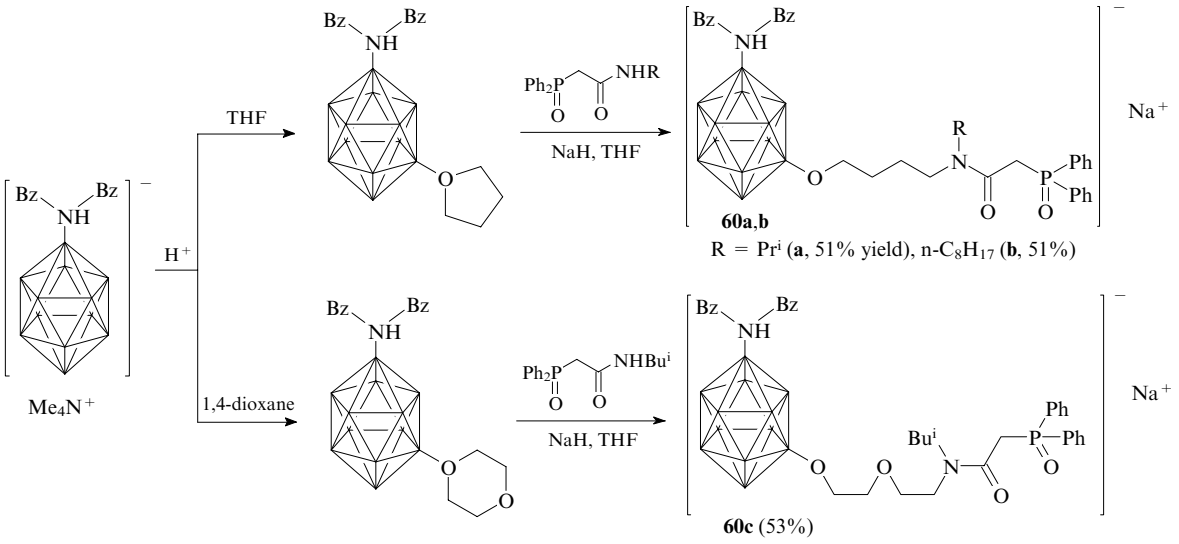


The authors showed that the reaction mixtures comprising CMPC silanes **61a**,**b**, may be applied as a monolayer in sorption processes to recover actinide cations on the silicon mesoporous substrates. With the use of such sorbents at pH < 1 and high concentration of nitrate anions, > 99% of plutonium was extracted from the model solutions.

V. Synthesis of carbamoylmethylphosphoryl compounds by the reaction of phosphorylacetic acid chlorides with amines

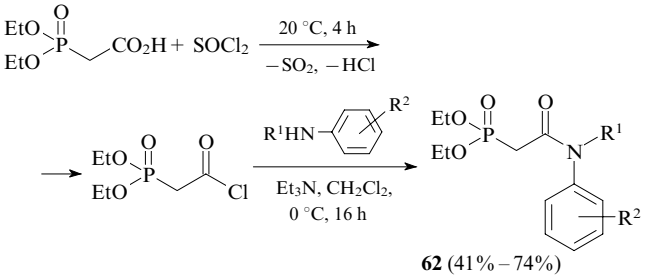
The above method, being the most general, allows one to obtain almost any CMPC starting from the preformed acid chloride and required amines, the reactions proceeding with high yields and under very mild conditions. However, this

Scheme 50



approach finds relatively low practical application. The matter is that phosphoryl acid chlorides have low stability, being prone to dehydrochlorination and polymerization due to the presence of the 'acidic' CH_2 protons. Therefore, such acid chlorides are usually obtained just before use and introduced into the reaction with amines immediately. Generally, mild chlorinating agents such as oxalyl chloride (benzene, 20 °C),[77] thionyl chloride (without solvent, 20 °C),[78] and sulfuryl chloride (CH_2Cl_2, 20 °C)[79] are used for their synthesis, and the heating of the reaction mixture is avoided. Scheme 53 shows examples of synthesis of CMPC **62** by this method.[78]

Scheme 53



R^1 = H, Me, Bu^n, Ts; R^2 = H, 2-Me, 2-OMe, 3-OMe, 4-OMe

Recently, phosphorus(III) chloride was proposed[80] for the synthesis of phosphorylacetic acid chlorides. In this case, the reactions proceed rapidly and almost quantitatively and, hence, the chloride obtained may be used not only without purification but also without isolation (one-pot procedure). Scheme 54 presents reactions of phosphorus-containing chlorides both with aliphatic mono-, di- and triamines, and with various aromatic amines.[80–84]

This methodology has no restrictions not only in the nature of the amines used in the reactions, but also in substituents in the phosphorylated acetic acid. Using this method, we have also obtained different phosphinates.[80]

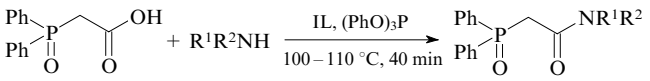
In many cases, the approach proposed affords carbamoylmethylphosphoryl compounds of sufficiently high purity, which may be used in extraction processes without further purification.

VI. Direct amidation of phosphorylacetic acids in ionic liquids

Presently, environmental aspects receive an increasing attention in the organic synthesis and especially in the synthesis of organophosphorus compounds. Nowadays, the absence of hazardous chemical effluents is of no less importance than high yields and purity of the products. Moreover, in some cases, the environmental viewpoint is of prime importance. Application of environmentally safe green chemistry methods in the synthesis of OPC is detailed in a review.[28]

In recent years, ionic liquids (IL) have found increasingly wide application in extraction preconcentration and separation of lanthanides, uranium, plutonium and thorium.[85,86] Due to their unique properties, IL, particularly those having melting point below the room temperature,[87] may be used as environmentally friendly alternative of conventional organic solvents as well as an activating medium in the synhtetic organic chemistry. Ionic liquids are characterized by a number of valuable properties: they are non-volatile, thermally stable, dissolve both organic and inorganic substances, they are non-nucleophilic but rather polar. Finally, IL may be reused in the reaction without essential losses. All these properties enable sufficiently wide application of IL in the synthesis of organophosphorus compounds.[88–90] We were the first to show that CMPO may be effectively synthesized under the conditions of green chemistry.[91–93] Thus, diphenylphosphorylacetic acid reacts with various amines in IL in the presence of triphenyl phosphite as an activating agent affording the corresponding phosphine oxides **63** in high yields (Scheme 55, Table 1).

Scheme 55



R^1 = H: R^2 = Ph, Bn, Bu^n; R^1 = R^2 = Bu^n

Scheme 54

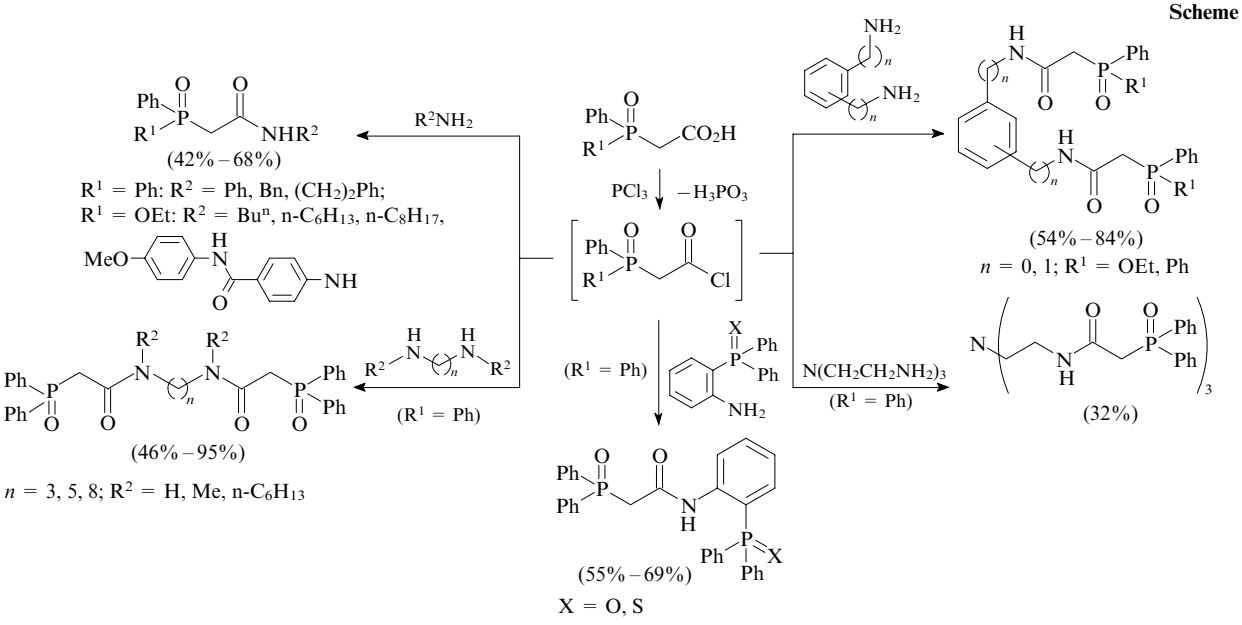


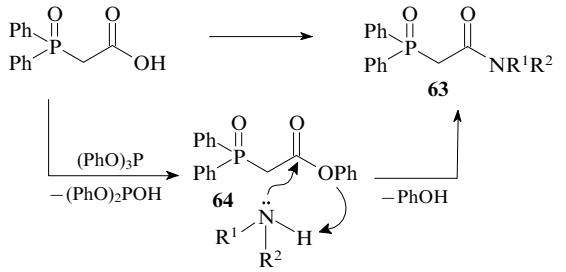
Table 1. Yields of carbamoylphosphine oxides **63** in the reaction of diphenylphosphorylacetic acid with amines in various ionic liquid media.[92]

Ionic liquid	Yield (%)			
	$PhNH_2$	$BnNH_2$	Bu^nNH_2	Bu^n_2NH
[bmim]Br	100	100	100	99
[bmim]PF_6	83	100	88	88
[bmim]BF_4 (see [a])	67	91	87	96
[bmmim]BF_4 (see [a])	–	–	–	81
[P(n-C_6H_{13})$_3$(n-$C_{14}H_{29}$)]Cl	90 [b]	100	95 [c]	100
[P(n-C_8H_{17})$_4$]Br	93 [d]	75 [c]	–	68
[P(n-C_6H_{13})$_3$(n-$C_{14}H_{29}$)]BF_4 (see [a])	–	72 [c]	–	–

Note. bmim is 1-n-butyl-3-methylimidazolium, bmmim is 1-n-butyl-2,3-dimethylimidazolium. [a] MeCN as cosolvent; the reaction proceeds quantitatively: [b] within 1.5 h, [c] within 2.5 h, [d] within 2 h.

It should be noted that removing IL from the reaction medium almost results in termination of the amidation (upon replacement of the medium by inert toluene, the yield of CMPO did not exceed 15%). The mechanism of the transformation obviously comprises the formation of phenyl diphenylphosphorylacetate **64**, bearing a good leaving phenoxy group and reacting readily with N-nucleophiles (Scheme 56).

Scheme 56

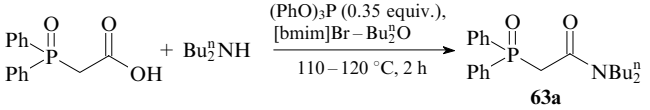


A ^{31}P NMR spectral study of the process confirms the above mechanism. The reaction does not take place in the absence of triphenyl phosphite.

All phenoxy groups of triphenyl phosphite were shown to participate in the reaction, and, hence, its amound could be reduced to 0.35 equiv. This change in the reactant ratio had no effect on the reaction rate or the yield of product **63a** (Scheme 57).

To isolate the target CMPO, application of a two-phase system IL – Bu^n_2O proved to be convenient. Dibutyl ether was chosen only due to its high boiling point. After the completion of the reaction, phosphorus-containing product

Scheme 57



was contained mainly in the ether layer, the phases were separated, and IL was reused in the process (recycle). As shown in Table 2, CMPO yields did not decrease even after five cycles.

Table 2. Yields of compound **63a** upon repeated reuse of the two-phase system IL – Bu^n_2O.[92]

Cycle number	Time /h	Yield [a] (%)
1	1/3	92
	1	95
	2	99 (94)
2	2	99 (93)
3	2	99 (95)
4	2	99 (95)
5	2	99 (95)

[a] According to ^{31}P NMR spectroscopy; the yield of the isolated product is given in parantheses.

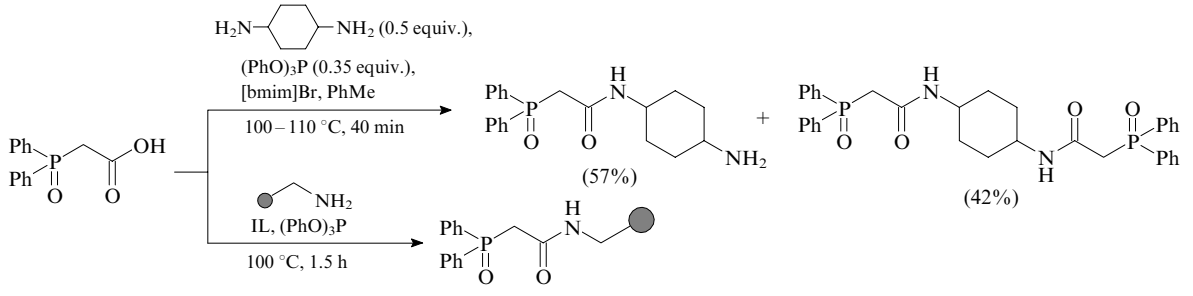
The above methodology of IL application allowed for the synthesis of also bi- and poly-CMPO-substituted products including those immobilized on the polymeric support (Scheme 58).

In the last-mentioned case, the degree of aminomethylpolystyrene phosphorylation exceeded significantly the value obtained during the amidation of ethyl diphenylphosphorylacetate in ethanol (100% and 18%, respectively).

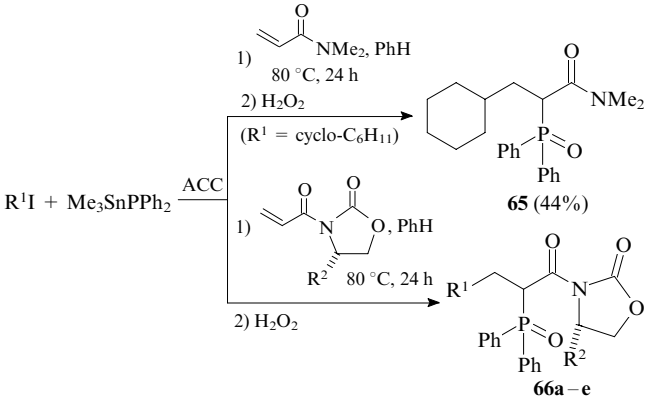
VII. Other synthetic routes to carbamoylmethylphosphoryl compounds

Certain effective synthetic routes to CMPC have been discovered during the search for approaches to other classes of compounds. As a rule, these methods are not general, but in some cases, they are useful for obtaining specific representatives of CMPC. Thus, German authors [94] have studied a three-component radical reaction of alkyl iodides, trimethylstannyl(diphenyl)phosphine and various acrylic acid amides in the presence of an initiator such as 1,1′-azobis(cyclohexane-1-carbonitrile) (ACC). Under these conditions, carbamoylmethylphosphine oxides **65**, **66a–e** substituted at the central carbon atom were found to form in yields ranging from moderate to high (Scheme 59).

Scheme 58



Scheme 59

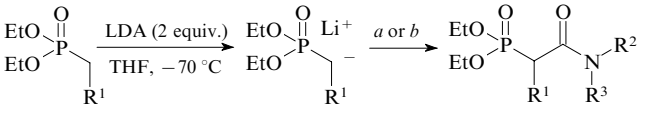


R^2 = H: R^1 = cyclo-C_6H_{11} (**a**, 74% yield), 1-adamantyl (**b**, 64%), Bu^t (**c**, 62%), n-C_5H_{11} (**d**, 19%); R^1 = cyclo-C_6H_{11}, R^2 = Bn (**e**, 47%)

Using chiral substituents in the amide moiety results in the formation of a diastereomeric mixture in the 1 : 1 ratio. The reaction is rather easy to perform; tin is separated as trimethyliodostannane after the treatment of the reaction mixture with hydrogen peroxide. Note that the synthesis of the stannylated phosphine presents the main challenge in this approach.

During elaboration of the synthetic routes to α,β-unsaturated amides, a group of French researchers headed by Savignac and co-workers,[95,96] proposed an approach to CMPC that were Horner–Wadsworth–Emmons reagents in this case. The approach is based on the fact that due to the increased acidity of the α-hydrogen atoms, alkyl phosphonates may be easily deprotonated by lithium diisopropylamide (LDA) (the required amount is 2 equiv.), and the complex carbanion thus formed reacts with ethyl(*N*-alkyl)-carbamates or isocyanates to furnish CMPC **67**, which are either mono- (**67a–g**) or disubstituted (**67h–m**) at the nitrogen atom (Scheme 60).

Scheme 60



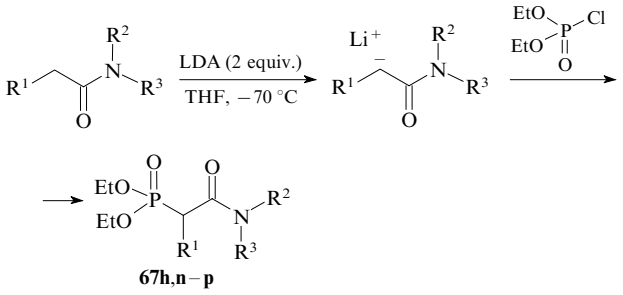
(*a*) $R^2R^3NCO_2Et$, (*b*) $R^3N{=}C{=}O$ (for R^2 = H)

Compound **67**	R^1	R^2	R^3	Yield (%)
a	H	H	Ph	40
b	Me	H	Ph	62
c	Me	H	Pr^i	85
d	Et	H	Pr^i	76
e	Et	H	Bu^t	59
f	Pr^n	H	Pr^i	65
g	Pr^n	H	Bu^t	82
h	H	Me	Me	68
i	Me	$(CH_2)_4$		77
j	Me	$(CH_2)_5$		86
k	Et	$(CH_2)_3$		77
l	Et	$(CH_2)_5$		81
m	Pr^n	$(CH_2)_3$		79

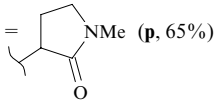
The yields of CMPC are rather high; however, this synthetic route is easy to perform only with the low-cost starting alkyl phosphonates; otherwise, the corresponding carbamoylmethylphosphonates are more easily accessible through the modification on the central carbon atom.

Also possible in an assembly of the CMPC molecules in a different order, that is, deprotonation of the α-carbon atom of the acid amide followed by the reaction of the carbanion with dialkyl phosphorochloridate. Such approach has been implemented by Savignac and co-workers[96] and demonstrated good results in the synthesis of compounds **67h,n–p** (Scheme 61). However, the fact that this is the only example and that other researches have not employed this approach to the synthesis of CMPC before or after Savignac may be a warning sign.

Scheme 61

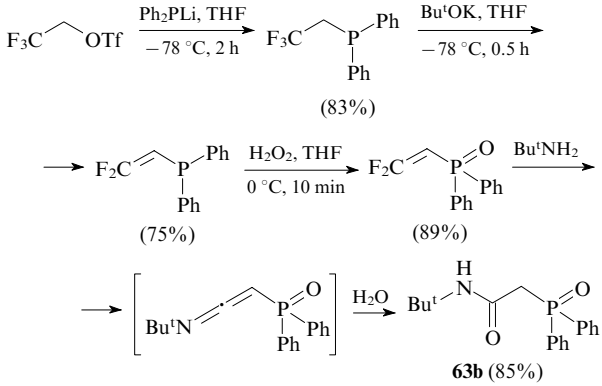


R^1 = H, R^2 = R^3 = Me (**h**, 61% yield); R^1 = R^2 = H: R^3 = Me (**n**, 64%), Bu^n (**o**, 67%),

$CHR^1C(O)NR^2R^3$ =  (**p**, 65%)

Sometimes CMPO are formed in unique reactions, for example, in demonstration of the high reactivity of exotic building blocks. Thus, Japanese authors[97] demonstrated the possibility to obtain compound **63b** starting from 2,2-difluorovinylphosphine (Scheme 62).

Scheme 62



Undoubtedly, other CMPO may also be synthesized by this method if the appropriate amine is chosen, but since the parent phosphines are difficult to obtain, the above method is only illustrative.

VIII. Modification of carbamoylmethylphosphoryl compounds

Taking into consideration the practical significance of the ligands of the CMPC series, some researches modified their structures with the aim of searching for more effective and selective extractants. In principle, the CMPC molecule may

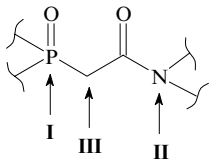


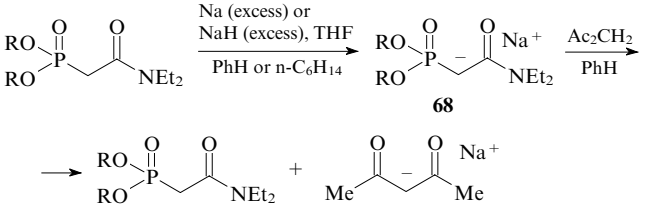
Figure 2. Modification sites of carbamoylmethylphosphoryl molecules.

be modified in three ways, namely, by the change of substituents at the phosphorus atoms (path I), at the nitrogen atoms (path II) and at the central carbon atom (path III) (Fig. 2).

The first two paths are generally implemented by the choice of the starting compounds, as detailed previously. Only the third path, *i.e.* the change in the environment of the central carbon atom, is usually carried out using preformed CMPC. In most cases, this refers to alkylation of the central carbon atom.

The problem of alkylation of the compounds with the activated methylene group is closely allied to the acidity of the corresponding protons. Bowen *et al.*[98] was the first to determine quantitatively the CH-acidity of CMPC by the example of reactions between diethyl carbamoylmethylphosphonates and sodium metal or sodium hydride and subsequently with acetylacetone. It is difficult to estimate the relative efficacy of reagents used to deprotonate the central carbon atom of CMPC, since in both cases, the authors isolated sodium salts of the corresponding carbamoylmethylphosphonates **68** in the form of colourless or slightly yellowish substances, soluble in THF, hexane and benzene. Salts **68** are readily protonated not only by water but also by acetylacetone, that is to say, CMPC ligands are stronger CH-acids than acetylacetone (Scheme 63).

Scheme 63

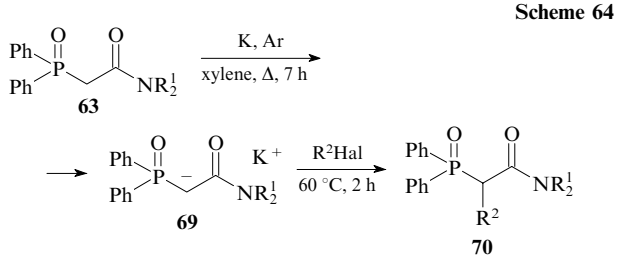


R = Et, Pr^i, Bu^n, n-C_6H_{13}

Later, the CH-acidity of CMPC in DMSO was determined experimentally by Kabachnik and co-workers [99, 100] It proved to be modest (pK value from 22.4 to 25.7), thus precluding the alkylation of these substrates under phase transfer catalysis conditions.[101]

A theoretical possibility to alkylate CMPO at the central carbon atom was shown by Kabachnik and co-workers back in the first publication [13] concerning the synthesis of these compounds. The results of an extended study of the same subject were published later.[23] In both cases, the authors alkylated potassium salts **69** of such CH-acids obtained at 140 °C during 7 h from CMPO **63** and potassium metal dispersed according to Bruhl with alkyl halides. Along with the drastic conditions in obtaining the potassium salts, low yields of the products **70** are due to nonselectivity of the process (mono- and dialkylation competition) as well as with heterogeneous character of the reaction (Scheme 64).

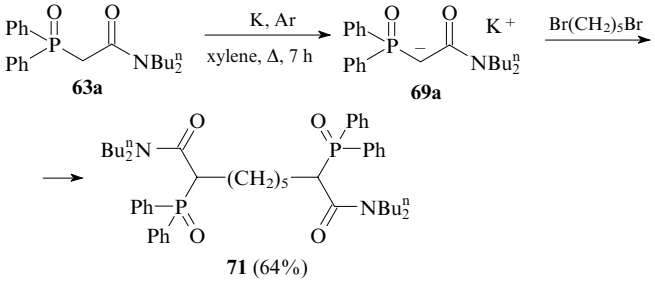
Scheme 64



R^1 = Et, Bu^n; R^2 = Me, Et, n-C_7H_{15}; Hal = Br, I

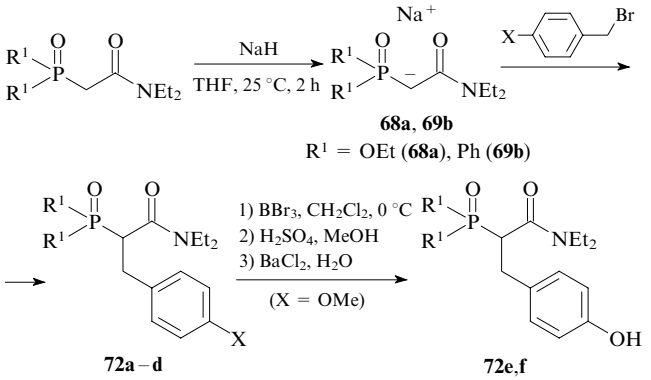
Using1,5-dibromopentane as an electrophilic component, the same authors [23] obtained tetradentate ligand **71** (Scheme 65).

Scheme 65



Sodium hydride proved to be more preparatively suitable deprotonation agent to obtain CMPO carbanions. Its application allowed Conary *et al.*[102] to synthesize a series of benzyl-substituted CMPO derivatives **72a–d** in high yields (Scheme 66).

Scheme 66



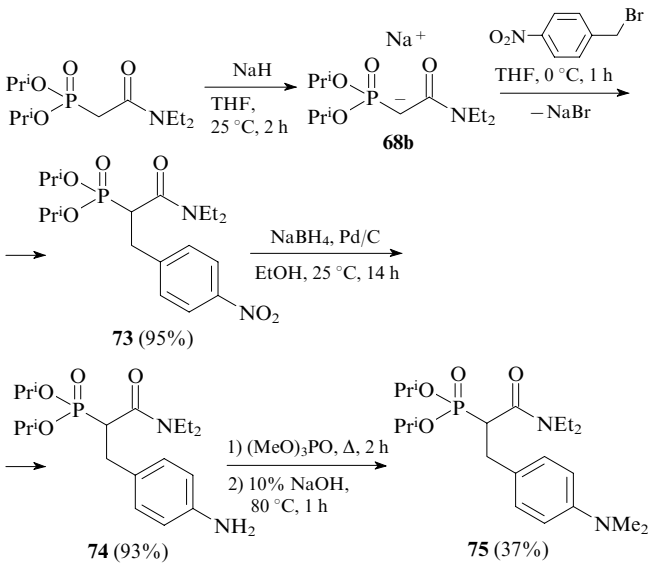
Compounds **72**	R^1	X	Yield (%)
a	OEt	H	95
b	OEt	OMe	82
c	Ph	H	85
d	Ph	OMe	89
e	OH		67
f	Ph		80

The subsequent reactions of compounds **72b**,**d** with boron tribromide proceeding with the decomposition of the intermediate compex under the action of H_2SO_4 in MeOH afford hydroxybenzylphosphonates **72e**,**f**. Along with the methoxy group, dealkylation of the ester groups

at the phosphorus atom takes place under such drastic conditions.

With the use of *p*-nitrobenzyl halides based on nitro-substituted alkylation products **73** as alkylating agents, the CMPO derivatives bearing *p*-aminobenzyl (**74**) and *p*-dimethylaminobenzyl (**75**) moieties were obtained (Scheme 67).[103]

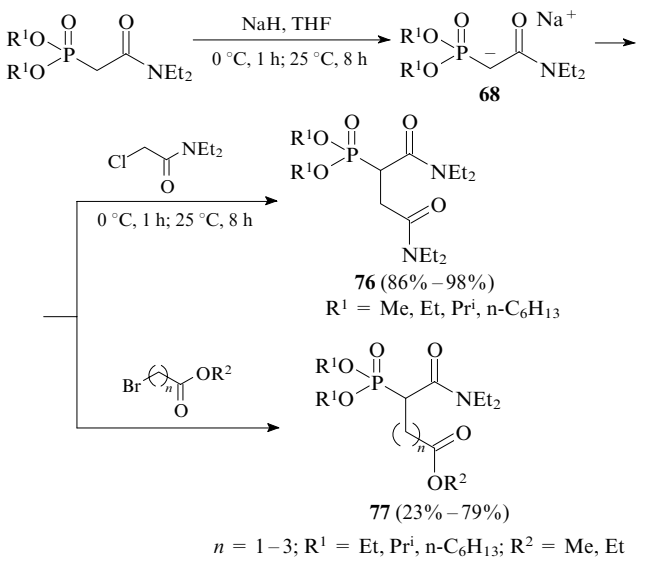
Scheme 67



As a reducing agent for the nitro group, the authors used sodium tetrahydridoborate in the presence of a catalyst such as palladium on activated charcoal, and trimethyl phosphate was used as a methylating agent for the amino group.

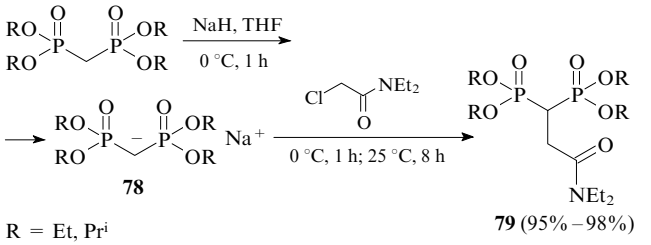
Deprotonated sodium salts **68** react with *N*,*N*-diethylchloroacetamide or ω-bromocarboxylic acid esters to give phosphonates **76** and **77**, which may serve as tridentate ligands (Scheme 68).[104–106]

Scheme 68

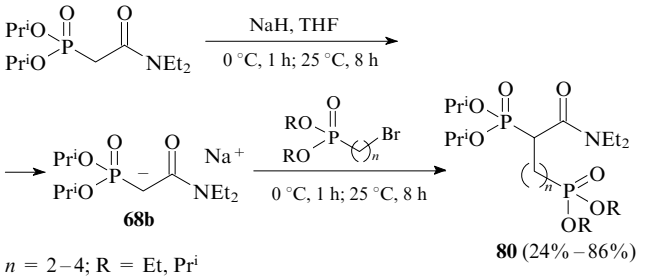


Starting from salts **78** and **68b**, tridentate ligands of different types, namely 1,1-bis(phosphono)-2-carbamoylethanes **79** (Scheme 69) and 1-carbamoyl-1-phosphono-1-phosphonoalkylmethanes **80** (Scheme 70) were synthesized by similar reaction schemes.[107]

Scheme 69

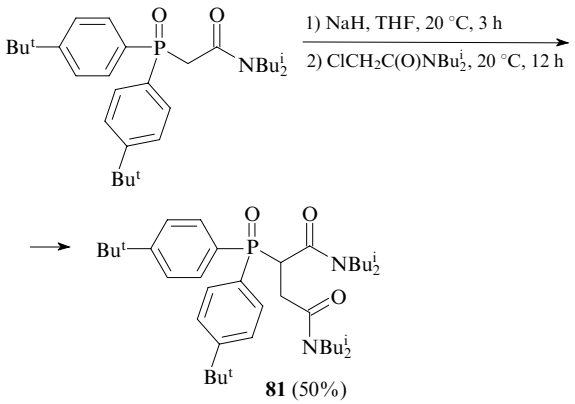


Scheme 70



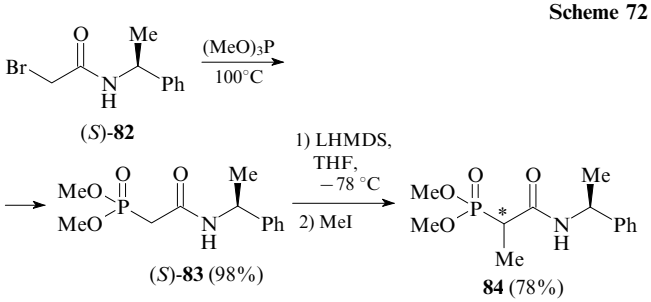
Tridentate CMPO **81** proved to be a suitable model for studying complexes with lanthanides by mass spectrometry (Scheme 71).[108]

Scheme 71



Of interest is the synthesis of two diastereomers of substitued carbamoylmethylphosphonates having (*S*)-α-methylbenzylamine moiety as the only one chirality inducer.[109] First, the amide (S)-**82** was subjected to the Arbuzov reaction with trimethyl phosphite to give *N*-[(*S*)-α-methylbenzyl]acetamide (*S*)-**83** in a quantitative yield. The subsequent alkylation of compound (*S*)-**83** with methyl

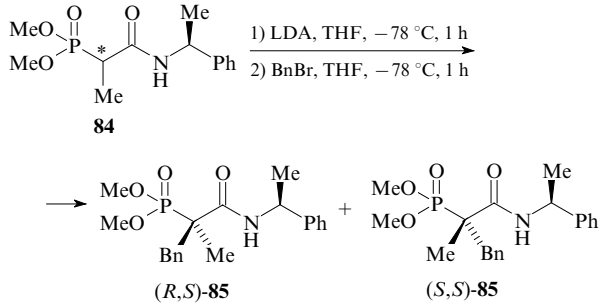
Scheme 72



iodide in the presence of lithium bis(trimethylsilyl)amide (LHMDS) as a base at −78 °C in THF yielded a single monomethylation product, namely, β-phosphonoamide **84** in a 47 : 53 diastereomer ratio (Scheme 72).

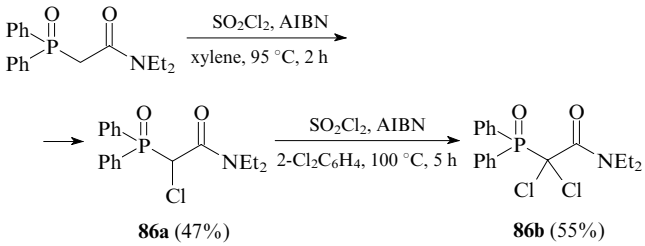
Treatment of the diastereomers **84** with lithium diisopropylamide taken in different amounts (from 1 to 4 equiv.), at −78 °C in THF followed by the addition of benzyl bromide (1 equiv.) resulted in α,α-disubstitued β-phosphonamides (*R*,*S*)-**85** and (*S*,*S*)-**85** in satisfactory yields. Diastereomer ratio depends on the amount of LDA used in the reaction (Scheme 73).

Scheme 73



Only few examples of the synthesis of mono- and dichloro derivatives (*e.g.*, of the compounds **86a**,**b**) by the reaction of CMPO with sulfuryl chloride under rather drastic conditions of radical substitution were reported (Scheme 74).[23]

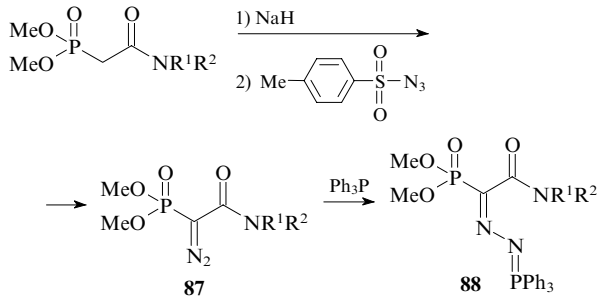
Scheme 74



AIBN is azobis(isobutyronitrile)

Bartlett *et al.*[31] have utilized a reaction of CMPC sodium salts with tosyl azide to obtain diazophosphonacetamides **87**, which were fully characterized by spectral and analytical methods. The structure of these compounds was confirmed by the reaction with triphenylphosphine yielding phosphazene **88** (Scheme 75).

Scheme 75



R^1, R^2 = H, Me, Pr^i, Bn

In conclusion we consider the extraction properties of modified ligands obtained from CMPO through the introduction of an additional substituent to the central carbon atom. A comparison of the extraction characteristics of three compounds, namely, $(n\text{-}C_6H_{13}O)_2P(O)CHRC(O)NEt_2$ with R = H, Me and Bn showed that the partition constants for the first two compounds increase with the rise of the medium acidity (from 0.01 up to 5 M HNO_3), whereas for the benzyl derivative, the quite opposite dependence was observed.[110] Based on this fact, the authors[110] suggested that the extraction mechanism changes upon the introduction of benzyl group in the CMPO molecule and studied the specific nature of the complexes formed with such extractants. At low concentrations, tridentate ligands **77** are comparable in characteristics with their unsubstituted precursors; however, as the acidity increases, they become significantly inferior to the latter.[107] Thus, the introduction of any substituents to the central carbon atom in a CMPO molecule generaly affects adversely the extraction properties of the compounds.

This fact is confirmed by the special study performed by Russian authors[111,112] who investigated U^{VI}, Th^{IV}, Pu^{IV}, Am^{III} and rare earth element extraction from nitric acid solutions with diphenyl(dialkylcarbamoyl)methylphosphine oxides bearing substituents in a methylene bridge. In the presence of IL [bmim]Tf_2N, the compounds having a methine group linking the donor centres possess the highest extraction ability towards U^{VI} ions, with $D_U > D_{Th}$.[113] In contrast, the compounds having unsubstituted methylene group are more effective in extracting Th^{IV} under the above conditions.

The introduction of coordinating substituents to the central carbon atom in the CMPO molecule may have a favourable effect depending on the nature of the extracted ion. In particular, introduction of dialkylaminomethyl substituents into the methylene bridge results in effective extractants towards Pd^{II} (see Ref. 112).

Carbamoylmethylphosphine oxides modified with dialkylamidomethyl coordination group in the methylene bridge, were recently described[114] as physiologically active substances. However, among them, also effective extractants for reprocessing of SNF may be found, since some of these tridentate compounds show extraction properties towards lanthanide ions.[108]

* * *

Our analysis of published data shows that presently CMPO may be obtained using a number of well elaborated and practically proven procedures (Arbuzov and Michaelis–Becker reactions both in traditional and phase transfer modes, amidation of *p*-nitrophenyl phosphorylacetates), as well as a number of novel approaches of considerable promise (*e.g.*, direct amidation of phosphorylacetic acids in ionic liquids or ethyl esters of these acids in an alcohol). Modification of CMPO at the central carbon atom with the aim of searching for novel extractants seems to be of very little promise. In general, development of novel synthetic routes to CMPO and investigation of their properties is progressing effectively, as connected with an extremely practical importance in the modern global economy.

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