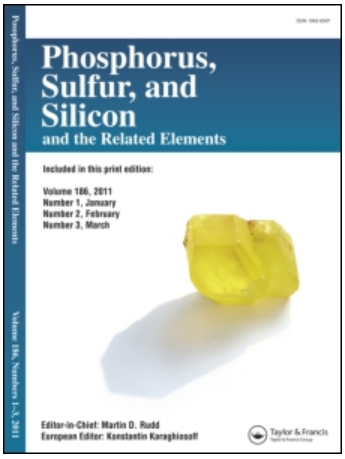

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PREPARATION AND PROPERTIES OF CYCLOPHOSPHATOPHOSPHONATES WITH 6-AND CYCLOPHOSPHATES WITH 6- TO 20-MEMBERED RINGANIONS

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Abstract Pure cyclotri-, -hexa-, -octa- and decaphosphates are prepared by topochemical controlled thermal dehydration of certain dihydrogenphosphates. Cyclophosphatophosphonates are prepared by heating geminal diphosphonic acids and phosphoric acid in molten urea. Cyclophosphatanions larger than cyclopentaphosphate are very resistant against hydrolysis. The complexing abilities of cyclophosphates increase with ring size. Phosphatophosphonates are more resistant to ring cleavage than the correspondend cyclophosphates.

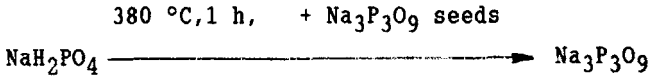
PREPARATION

The eldest [1] and most common method for the preparation of cyclo- and long chain polyphosphates is the thermal dehydration of metal dihydrogenphosphates.

$$n\ M^{I}H_2PO_4 \xrightarrow{>170°C} (M^{I}PO_3)_n + n\ H_2O \qquad n \geq 3 \qquad (1)$$

Whether the thermal dehydration of a dihydrogenphosphate leads to a ring- or a long chain polyphosphate depends mainly on
- the size of the cations
- the thermal stability of the final product
- and of the formation conditions.

The influence of the formation conditions on the ratio of cyclo- to polyphosphates in the final products is caused by amorphous and crystalline intermediates and their ability to form cyclo- or polyphosphate nuclei. In order to control these processes we use the directed nucleation, e.g. by seeding or by using topotactic reaction steps [2]. In this way we obtained pure cyclotri- (2), cyclohexa- (3,5), cycloocta- (6,7) and cyclodecaphosphates (4).



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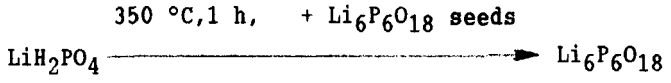

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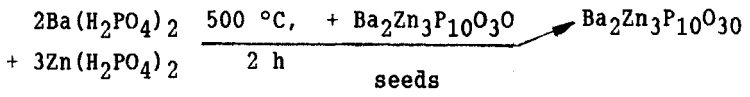

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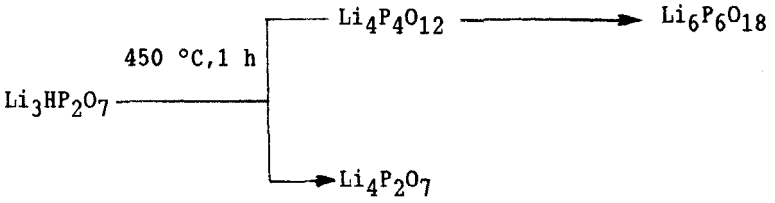

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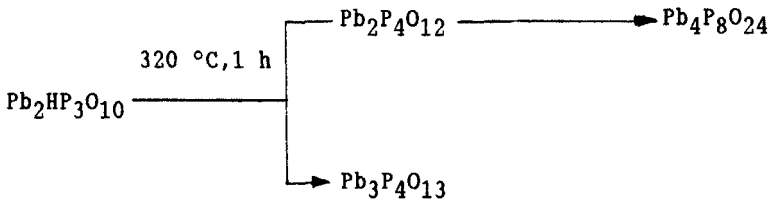

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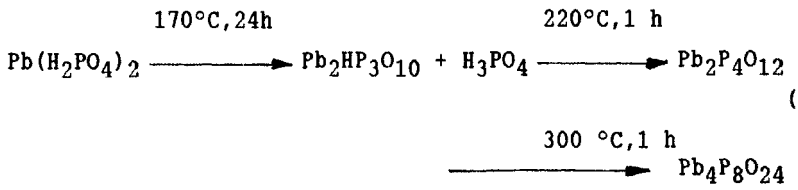

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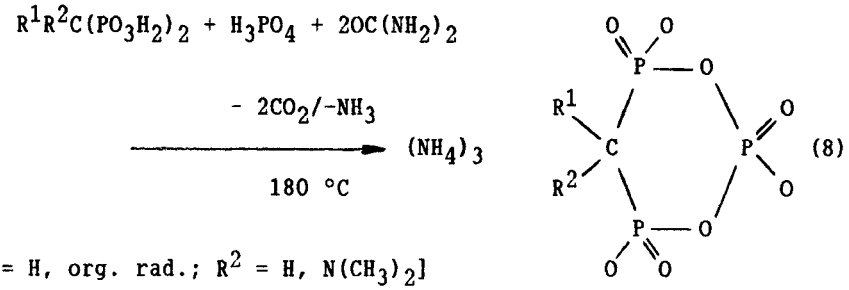
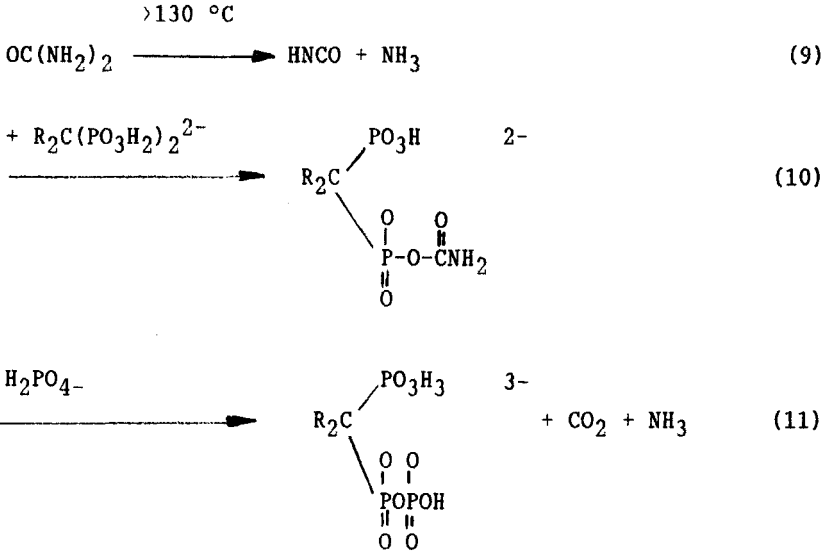
In contrast to the topochemical controlled thermal dehydration of metal dihydrogenphosphates we prepare the cyclophosphatophosphonates in amorphous phases e.g. by heating diphosphonic acids and phosphoric acid in molten urea [3].



[R^1 = H, org. rad.; R^2 = H, $N(CH_3)_2$]

Phosphoric acid and ammonium diphosphate [P(IV)-P(IV)] yield under the same conditions ammonium cyclotriphosphate, $(NH_4)_3P_3O_9$, and ammonium cyclotetraphosphate, $(NH_4)_4P_4O_{10}$, [P(IV)-P(IV)-O-]$_2$, respectively. The dehydration reactions of phosphates and phos-phonates in molten urea proceed most likely via carbamoylphosphates and-phosphonates as intermediates.

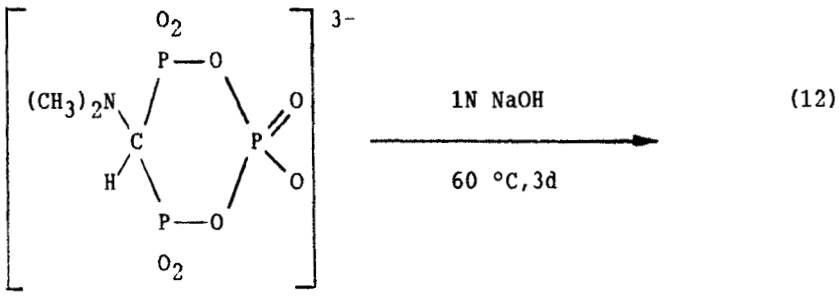


PROPERTIES

Cyclophosphates are quite stable in aqueous solutions. In alkaline solutions the ringanions are cleaved to give the correspondend linear polyphosphates. Cyclophosphate anions larger than cyclopentaphosphat are very resistant to hydrolysis (cyclotriphosphat: $\tau/2$ = 4,5 h; cyclodecaphosphat: $\tau/2$ = about 1100 h, first order, 0,4 nKOH, 30 °C).

The complexing abilities of cyclophosphates increase continuously with ring size. The complex formation of alkali cyclodecaphosphate and of long chain alkali polyphosphates with calcium ions is of exact the same magnitude [4].

The cyclophosphatophosphonate anion is more resistant to hydrolysis than the corresponded cyclophosphate.



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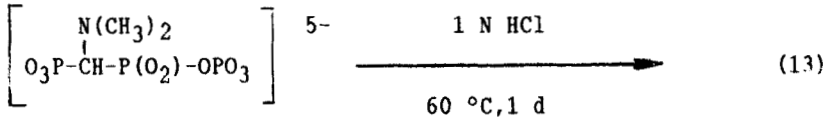

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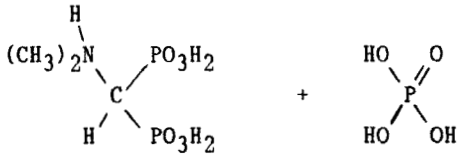

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