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Polyphosphoric Acid in Cyclisation and Polycyclisation Reactions

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The literature data on the structure of polyphosphoric acid (PPA) and cyclisation and polycyclisation reactions in polyphosphoric acid whereby thermally stable polyheteroarylenes of various structures may be obtained are reviewed and the possible mechanisms of these reactions are discussed.
The bibliography includes 235 references.

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I. INTRODUCTION

Syntheses in polyphosphoric acid (PPA) are nowadays so widely employed that it is difficult to point to a branch of organic chemistry where it has not found an application.

Polyphosphoric acid was first recognised as a cyclising agent and was then extensively employed in a wide variety of reactions catalysed by acids such as condensation, esterification, hydrolysis, and acylation; polyphosphoric acid is an excellent reagent for many rearrangements, etc. The great importance which this acid has acquired in synthetic organic chemistry is shown also by numerous original papers on the subject. A number of reviews published during the period 1954–1963 give a complete bibliography on this question [1–8].

In subsequent years polyphosphoric acid found application in macromolecular synthetic chemistry. This was facilitated by a unique combination of properties in polyphosphoric acid: it is at the same time a good solvent for organic compounds, including macromolecular compounds, a proton donor which favours condensation reactions, and a cyclodehydrating agent which ensures slow intramolecular cyclisation over a wide range of temperatures. In many cases this makes it possible to carry out simultaneously two or three stages without isolating the intermediates, which is particularly important in the synthesis of polymers.

The use of polyphosphoric acid instead of other acid reagents (aluminium chloride, phosphorus pentoxide, hydrofluoric acid, and concentrated sulphuric acid) is frequently preferable, since it does not usually give rise to side reactions, in particular oxidation processes; reactions in polyphosphoric acid can be readily carried out without the need for special precautions; as a rule higher yields of the final products are obtained. Certain reactions cannot be achieved at all with other acid reagents.

This review deals with one aspect of the application of polyphosphoric acid where it has particular advantages: the cyclisation and polycyclisation reactions, which lead to the formation of low-molecular and polymeric heterocyclic compounds and which evidently take place via the same mechanism.

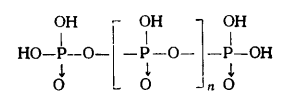
Since cyclisation processes have already been dealt with to some extent in earlier publications, this review does not quote an exhaustive bibliography on this problem. Attention was concentrated on the syntheses of heterocycles in polyphosphoric acid which have already found or may find applications in macromolecular chemistry for the synthesis of polyheteroarylenes.

II. PREPARATION AND PROPERTIES OF POLYPHOSPHORIC ACID

In the early studies phosphorus pentoxide was added to a solution of an organic compound in phosphoric acid [9,10]. Subsequently this method was improved and nowadays polyphosphoric acid is usually obtained by dissolving phosphorus pentoxide in orthophosphoric acid with heating until a homogeneous mixture is produced [10–14]. Polyphosphoric acid can also be prepared by the thermal dehydration of phosphoric acid or by treating the latter with phosphorus trioxide, but regardless of the method of preparation, polyphosphoric acid has a composition and properties which are determined by its P_2O_5 and water content [15].

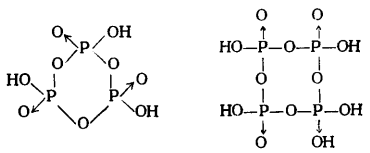
Polyphosphoric acid is a complex mixture of polymeric phosphoric acid species with different degrees of condensation. A large number of studies have been made on the structure of polyphosphoric acid, among which mention should be made in the first place of the work of Thilo and Sauer [15], Bell [16], and Huhti and Gartaganis [17]. The use of β-naphthylamine and benzidine, which are capable of precipitating chains of particular length, and also paper chromatography, ion-exchange chromatography, and nuclear magnetic resonance (NMR) led to the determination of the approximate composition and structure of the complex mixture referred to as polyphosphoric acid [18–22].

It has been shown that mixtures with 82–86% P_2O_5 contain, apart from orthophosphoric and pyrophosphoric acid, linear polyphosphoric acid with the following general structure:



The Table presents the compositions of these mixtures referred to as polyphosphoric acid, since it cannot be obtained with a uniform degree of polymerisation and is always polydisperse.

When the content of phosphorus pentoxide in the mixture is higher, cyclic compounds and compounds with a three-dimensional structure are present; as a result of reaction with water, these again give rise to linear acids:



Composition of polyphosphoric acids with different contents of phosphorus pentoxide.

Mixture component	Mixture compositions with different P_2O_5 contents, wt.%		
	80,5[23]	81,6[17]	84,2[17]
Orthophosphoric acid	14	8	4
Pyrophosphoric acid (n = 0)	38	27	11
Triphosphoric acid (n = 1)	23	22	11
Tetraphosphoric acid (n = 2)	13	17	13
Pentaphosphoric acid (n = 3)	7	11	12
Hexaphosphoric acid (n = 4)	2	6	10
Heptaphosphoric acid (n = 5)	1	4	8
Octaphosphoric acid (n = 6)	0.2	2	6
Nonaphosphoric acid (n = 7)	—	2	5
Acids with higher values of n	—	1	20

The structure of these acids has been the subject of recent studies, which led to more accurate values of the angles between different bonds and also of the bond length[24,25].

Using a flexible linear acid model, Parks and van Wazer[26,27] found the theoretical distribution of acid species in PPA; their results agree with the experimental data[24]. Pearson and coworkers[28,29] investigated the specific gravity, viscosity, refractive index, and the rate of rearrangement as a function of the concentration of phosphorus pentoxide in various PPA mixtures. The measurements of the refractive index are less accurate than those of viscosity but they are simpler and may be used to determine the concentration of phosphorus pentoxide in PPA.[28]

The dissociation constants of various phosphoric acids are quoted by Quimby[30]. The ionisation constants of ortho- and pyrophosphoric acids have not been determined with adequate accuracy and the published data do not agree[31-33].

Polyphosphoric acid exhibits simultaneously the properties of an acid and an anhydride, since it contains both the acid and the anhydride groups of the initial compound used in its preparation. The anhydride groups bind the water evolved in the process, preserving thereby the effectiveness of the reagent for some time. They are then converted into acid groups, with splitting off of orthophosphoric acid molecules.

The mechanism of the hydrolysis of polyphosphoric acid was represented by van Wazer[34] in the following way: the simultaneous rupture of several P–O–P bonds in one molecular ion is impossible; the rupture takes place exclusively at the end of the chain. Thus triphosphoric, pyrophosphoric, and orthophosphoric acids are formed in succession from tetraphosphoric acid. At room temperature and at neutral pH the time required for the hydrolysis of the P–O–P linkage is several years. A decrease of the pH and an increase of temperature appreciably accelerate the hydrolysis; for example, for each 5 deg of temperature rise, the rate of hydrolysis increases by a factor of 2.

The removal of water, which is a stronger base than many organic compounds reacting under the influence of PPA, from the reaction sphere is important for the preservation of the effective acidity of the reaction medium.

The dehydrating action of polyphosphoric acid is much milder than that of phosphorus pentoxide, which makes it possible to carry out reactions at a higher temperature. Reactions in polyphosphoric acid are much more rarely accompanied by a rearrangement with a change in the carbon skeleton than in other acid agents, although they are sometimes possible[35].

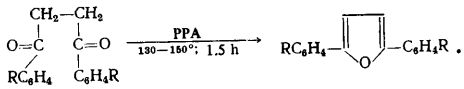
Usually polyphosphoric acid is employed in amounts such that it serves at the same time as a solvent and a reactant. However, the application of solvents in reactions with polyphosphoric acids, for example glacial acetic acid in chloroform[36], have been described. The reaction products are usually isolated by decomposing the reaction mixture with water or ice. In experiments with basic substances, it may be necessary to neutralise the dilute phosphoric acid before isolating the reaction products. Koo[37,38], Uhlig[5], and others[39,40] investigated cyclisation in polyphosphoric acid as a function of the nature of the products formed and the reactivity of the starting materials and established that the higher the melting points of the latter the more severe are the reaction conditions.

III. SYNTHESIS OF HETEROCYCLIC COMPOUNDS IN POLYPHOSPHORIC ACID

Polyphosphoric acid proved to be an effective cyclising (condensing) agent in the synthesis of a wide variety of heterocyclic systems. Numerous derivatives of indole, quinoline, isoquinoline, and others have been obtained using polyphosphoric acid; polyphosphoric acid is important in the synthesis of intermediates for many alkaloids[41], medicinal preparations[42], steroids, and other heterocyclic compounds containing nitrogen, oxygen, and sulphur[43-45].

I. Oxygen-Containing Heterocycles

Polyphosphoric acid was used for the first time in the syntheses of oxygen-containing heterocycles by Nowlin[46], who obtained diarylfurans from the corresponding 1,4-diketones in almost quantitative yields:



Later this method was extended to the synthesis of benzofurans and dibenzofurans, chromones, and thiachromones, and a wide variety of their derivatives[48-52].

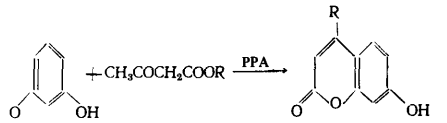
Sterically hindered 1,4-diketones are not cyclised with formation of the furan ring; an aromatic hydrocarbon and an acid are formed under these conditions. A similar phenomenon has been observed earlier by Lutz et al.[47] in other systems.

Chromanone and 6-phenylchromanone[53] and 7-methoxychromanone and 6-nitrochromanone[52] were obtained by

the cyclisation of β-phenoxypropionic acid and its derivatives in polyphosphoric acid.

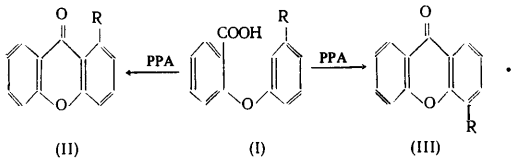
A number of substituted 1,2,3,4-tetrahydrodibenzofurans were synthesised by treating the corresponding 2-phenoxycyclohexanones with polyphosphoric acid [50].

The use of polyphosphoric acid as a condensing agent in the synthesis of coumarins by Pechmann's method [51] has been described. Thus, 4,7-dimethylcoumarin was obtained in 76% yield from *m*-cresol and acetoacetic ester [54] and the condensation of resorcinol with acetoacetic, α-methylacetoacetic, and benzoylacetic esters led to the synthesis of the corresponding hydroxycoumarins in very high yields [38]:



The mechanism of the formation of chromones and coumarins by Pechmann's method involving the interaction of β-arylcrotonic acids and β-ketoesters with phenols in the presence of polyphosphoric acid, has been investigated [55]. However, it is noteworthy that cyclisation does not always take place [56].

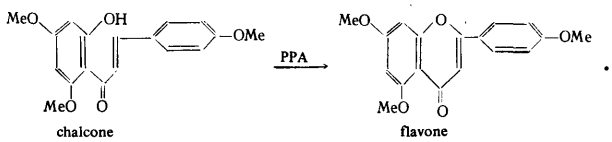
Xanthones have been synthesised with the aid of polyphosphoric acid [57]:



(II) (I) (III)

It has been shown that in the cyclisation of 3-substituted 2-carboxydiphenyl ethers (I) the mode of ring closure [(II) or (III)] depends on the nature of the substituent in the 3-position. For substituents with powerful-*I* and -*M* effects (NO_2, COOH, CN), the ratio of products of cyclisation in the 2-position (II) and 6-position (III) is about 4 : 1, for substituents with powerful-*I* and +*M* effects (NHAc, MeO), the ratio is approximately 1 : 3, and for Me or Cl as substituents the ratio is 1 : 1. The authors note that these ratios are independent of the choice of cyclising agent.

Mention should also be made of the synthesis of flavone from the corresponding chalcone in polyphosphoric acid [58]:

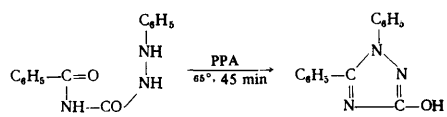


chalcone flavone

2. Nitrogen-containing Heterocycles

Among heterocyclic systems, the most widespread are nitrogen-containing heterocycles and, apart from other methods, their syntheses with the aid of polyphosphoric acid play an important role.

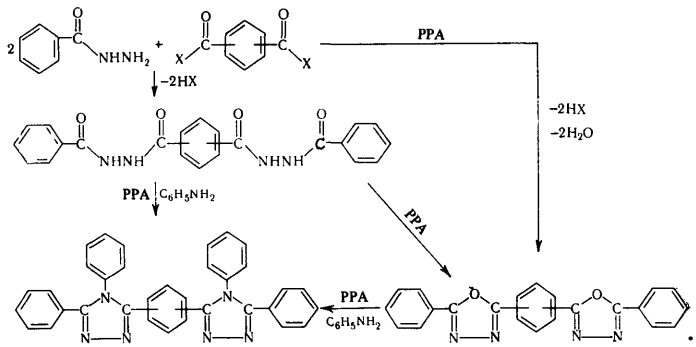
The simplest heterocycle obtained by the action of polyphosphoric acid on semicarbazide derivatives is substituted triazole:



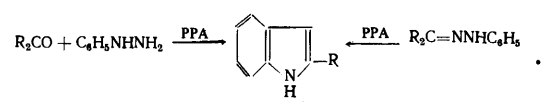
3-Hydroxy-1,5-diphenyl-1,2,4-triazole was obtained in 76% yield [59]. When the benzoyl group in the initial semicarbazide is replaced by the *p*-nitrobenzoyl group, 3-hydroxy-5-*p*-nitrophenyl-1-phenyl-1,2,4-triazole, which is unobtainable by other methods, is produced, but in the case of the 2,4-dinitrobenzoyl derivative the reaction could not be achieved [59].

3,4,5-Triphenyl-1,2,4-triazole was obtained in two ways: by treating 2,5-diphenyl-1,3,4-oxadiazole with aniline in polyphosphoric acid and by the cyclocondensation of dibenzoylhydrazine with aniline in polyphosphoric acid [60].

Holsten and Lilyquist [61] synthesised phenyl-substituted bis-1,2,4-triazoles via the following mechanism:



The Fischer synthesis of indoles, improved by the use of polyphosphoric acid, is carried out both by the cyclisation of arylhydrazones and in one stage—by the interaction of phenylhydrazine with α-ketoesters, ketones, and aldehydes [62-65]:



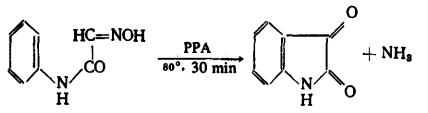
The single-stage synthesis is a general method whereby it is possible to prepare and investigate the entire series of alkyl- and aryl-substituted indoles. Thus 2-phenylindole, 3-methyl-2-phenylindole, 2-methylindole, and 3-ethyl-2-methylindole were obtained respectively from derivatives of hydrazine and acetophenone, propiophenone, acetone, and diethyl ketones in high yields [62]. Chloroindoles [66], pyridylindoles [67], nitroindoles [68,69], and carboline derivatives [70], which had not been obtainable previously by other methods, were synthesised in polyphosphoric acid.

It has also been noted that polyphosphate esters are effective in the synthesis of indoles by the Fischer method, which makes it possible to carry out the reaction in boiling chloroform [71]. There exists a patent [74] for the synthesis of 2,3-dimethylindole from *N*-butenylaniline.

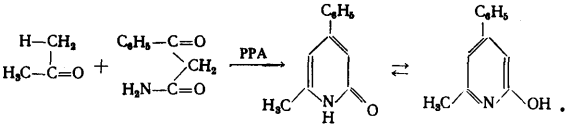
However, in many cases cyclisation to indoles does not occur [73]. Frasca and coworkers [74,75] showed that, when t-nitrophenyl hydrazones of certain acetophenones, benzaldehydes, and benzophenones are heated in polyphosphoric acid, indazoles are formed and not the expected indole derivatives; in addition, rearrangement products are isolated. Attention has been drawn to the fact that [76] polyphosphoric acid is relatively ineffective in the synthesis of indoles unsubstituted in the 2-position.

The action of polyphosphoric acid on isonitrosoacetanilide and its derivatives leads to the formation of isatin

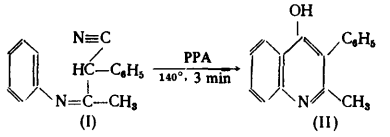
and substituted isatins in 50–60% yields via the mechanism [77]



Hauser and Eby [78] used polyphosphoric acid in the synthesis of substituted pyridones formed when β-ketoamides or β-ketonitriles reaction with ketones:



The syntheses of many derivatives of six-membered heterocyclic systems have been achieved in polyphosphoric acid. The formation of 4-hydroxyquinolines by the reaction of arylamines on β-ketoesters or β-ketonitriles (the Conrad–Limpach method) takes place smoothly in polyphosphoric acid in a single stage [79]. The anils of β-ketonitriles and β-ketoamides are also smoothly converted under the action of polyphosphoric acid into 4-hydroxyquinolines in high yields. Thus 4-hydroxy-2-methyl-3-phenylquinoline (II) was obtained from the anil (I) or directly from aniline and α-aceto-α-tolunitrile in 56% yield (instead of 4% when the usual catalysts are employed in the Conrad–Limpach method) [79]:

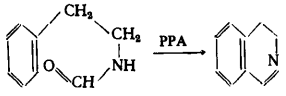


Similarly 4-hydroxy-2,3-diphenylquinoline was obtained in 34% yield.

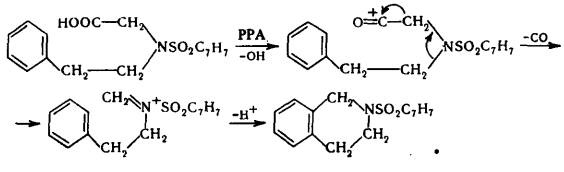
The use of polyphosphoric acid as a catalyst in the Skraup reaction was not successful [80].

6,7-Dimethoxyisoquinoline [81] and 7,8-dimethoxyisoquinoline [82,83] were synthesised in polyphosphoric acid by a modified Pomeranz–Fritsch reaction; the aminoacetyl derivatives of furfural were not cyclised under the action of polyphosphoric acid [82].

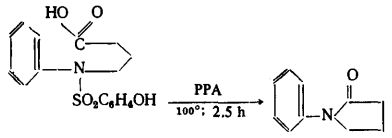
A complete study of polyphosphoric acid as a cyclodehydrating agent in syntheses of dihydroisoquinolines by the Bischler–Napieralski reaction demonstrated its high effectiveness [84]; in all cases the yields of dihydroisoquinolines in polyphosphoric acid were much higher than with other acid reagents [86–89]:



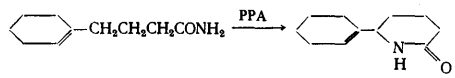
Proctor and Thompson [89] described a new method for the synthesis of tetrahydroisoquinoline derivatives. When toluenesulphonamide of *N*-β-phenylethylalanine is heated with polyphosphoric acid, the toluenesulphonamide of tetrahydroisoquinoline is formed instead of the expected product, probably by the following mechanism [89]:



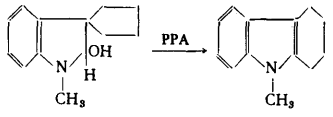
However, 1-phenyl-2-pyrrolidinone was obtained in 94% yield from the toluenesulphonamide of *N*-phenyl-γ-aminobutyric [90]:



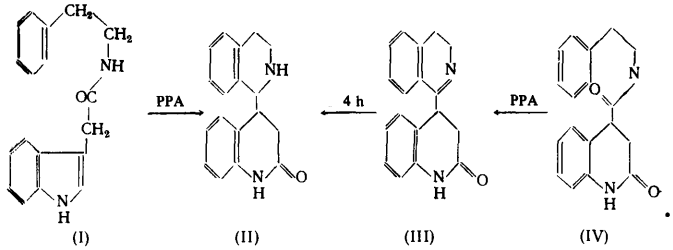
In the presence of polyphosphoric acid it proved possible to synthesise perhydro-1,4,6,9-tetraoxopyridazo-[1,2-*a*]pyridazine from succinic acid and hydrazine hydrate [91] and spiropiperidinone from γ-cyclohexen-1-ylbutyric acid amide [92,93]:



A new method has been developed for the synthesis of benz[*a*]-acridines [94]. An interesting ring expansion reaction under the action of polyphosphoric acid, consisting in the conversion of spirooxindole into 9-methyltetrahydrocarbazole and accompanied by a rearrangement of the Wagner–Meerwein type, was achieved by Witkop and Patrick [95]:

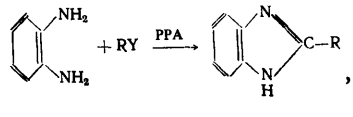


Other polynuclear heterocyclic systems synthesised in polyphosphoric acid include phenanthridine [96], 3,4-benzophenanthridine [97], 3,4-dihydro-4-phenylcarbostyril and 3,4-dihydro-4-phenylisocarbostyril [98], 2,4-dimethylindeno-[3′,2′:6,7]quinoline obtained from the anil of acetophenone and 2-aminofluorene [99], and 4-(1,2,3,4-tetrahydro-1-isoquinolyl)hydrocarbostyril, which is obtained by the rearrangement of the β-phenylethylamide of heteroauxin with subsequent cyclisation [100] according to the mechanism:



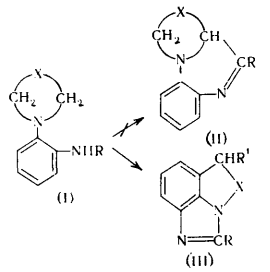
The conversion of the β-phenylethylamide (I) into the carbostyril derivative (II) can be explained only by the migration of the indoline component, which permits the formation of a six-membered ring. Structure (II) was confirmed by synthesising compounds (III) and (IV). [100] It was shown that in certain cases a mixture of polyphosphoric acid and $POCl_3$ is more effective than each component separately. In some cases the heterocycles formed were alkylated in the cyclisation process [101,102].

Polyphosphoric acid was successfully employed in the synthesis of heterocycles containing more than one nitrogen atom. 2-Substituted benzimidazoles were obtained by the following general reaction of *o*-diamines with carboxylic acids and their derivatives [103,104]:



where Y = COOH, COOR, $CONH_2$, or CN and R = alkyl, aryl, or substituted aryl. Similarly, using tetramines in reactions with carboxylic acids or *o*-diamines in reactions with dicarboxylic acids, bisbenzimidazoles of different structures were obtained [105,106].

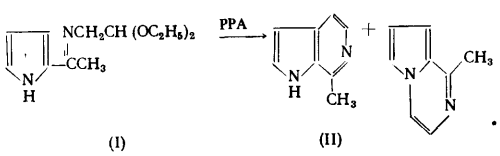
Suschitzky [83] observed an interesting and unexpected reaction involving the formation of the benzimidazole ring when *N*-2-acylaminophenyl heterocycles were treated with hot polyphosphoric acid:



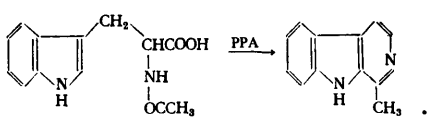
Instead of the expected 1,2-dihydroquinoxalines [(II), X = $(CH_2)_3$, $(CH_2)_4$, or $CH_2)_5$], [107] benzimidazoles (III) were obtained from the acylated amines. The authors believe that, under the action of polyphosphoric acid, the heterocyclic ring in the initial compound (I) is opened and the next stage is cyclic dehydration involving the tautomeric form of the amide N: C(OH)R, which leads to imidazole. Further alkylation of the benzene ring gives a product of type (III).

Polyphosphoric acid has found application in the synthesis of six-membered heterocycles [108-110], which could not be obtained by the Pomeranz–Fritsch and Bischler–Napieralski reactions using sulphuric acid.

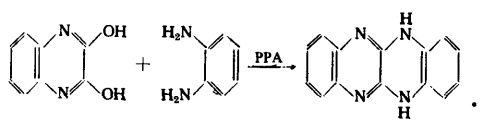
The cyclisation of Schiff bases derived from pyrrole frequently leads to a mixture of pyrazine and pyridine derivatives; for example, the aminoacetyl derivative of 2-acetylpyrrole gives a mixture of apogarmine (II) and 1-methylpyrrolo[1,2-*a*]pyrazine [108]:



Under the action of polyphosphoric acid, *N*-formyltryptophan and *N*-acetyltryptophan gave the corresponding harmans [87]:

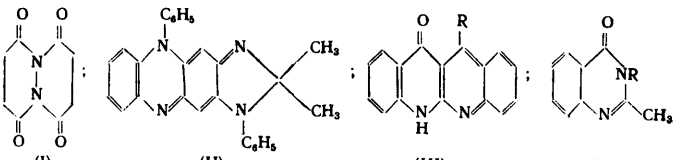


Badger and Nelson [111] obtained a new heterocycle containing four nitrogen atoms (fluoflavine) by the reaction of 2,3-dihydroxyquinoxaline with *o*-phenylenediamine in polyphosphoric acid:



From tetrasubstituted derivatives of bisquinoxaline and *o*-phenylenediamine, Marvel and coworkers [112] obtained 2,2-bisfluoflavine.

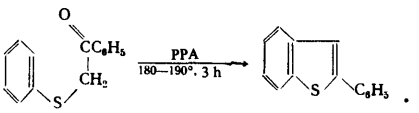
New syntheses in polyphosphoric acid of bicyclic and polycyclic nitrogen-containing systems of the following type have been developed: perhydro-1,4,6,9-tetraoxopyridazo[1,2-*a*]pyridazine (I), [113] 5,2′-dihydro-2′,2′-dimethyl-5,1′-diphenylquinoxalino[5′,4′ : 2,3]phenazine (II), [114] 4-hydroxy-1,4-quinolono[2,3 : 2′,3′]quinoline (III), [115] quinazolones (IV), [116] and others [117-119]:



3. Heterocycles Containing Sulphur and Arsenic

Only a limited number of such compounds are known and the application of polyphosphoric acid in their synthesis has been investigated in much less detail than in the reactions discussed in the preceding section.

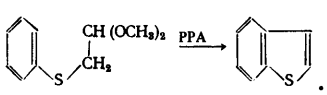
The cyclisation of α-arylthioketones of the type AR–S–CH_2COR, where R = aryl, is accompanied by a rearrangement and leads to the formation of 2-arylthionaphthene instead of the expected 3-arylthionaphthene [120]:



When, instead of the benzoyl derivative the acetyl derivative is employed, 3-alkylthionaphthenes are formed without rearrangement [121]. In the presence of hydrofluoric acid, compound (I) also rearranges to compound (II). [55]

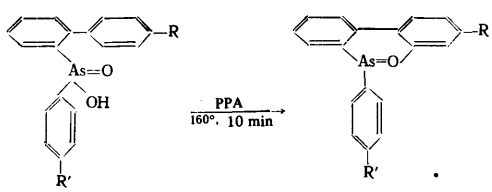
According to the data of Davies and Middleton [121], phenyl phenacyl ether undergoes an analogous rearrangement to 2-phenylbenzofuran in the presence of polyphosphoric acid. When sulphur or oxygen in the above compounds are placed by the methylene group, ring closure takes place without rearrangement [37,121].

A number of thionaphthenes were obtained in polyphosphoric acid in high yields from arylthioaldehyde acetals [122,123]:



Under the action of polyphosphoric acid, arylthiophenoxyacids also form cyclic products [124,125].

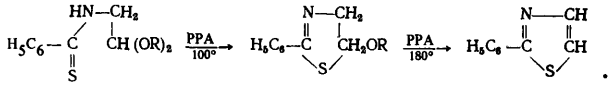
Using polyphosphoric acid, Campbell and Poller [126] synthesised arsafluorene oxide in 70% yield in one stage, while in the usual three-stage method the yield did not exceed 55%:



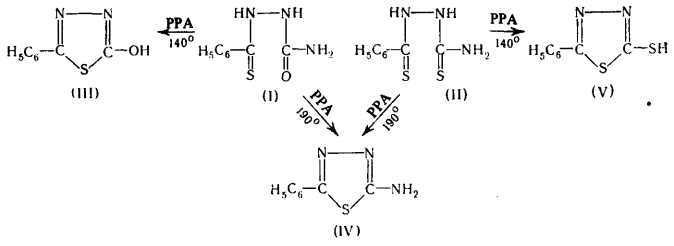
4. Mixed Heterocycles

The use of polyphosphoric acid as a condensing agent greatly extended the scope of the syntheses of a wide variety of heterocycles, including some of practical importance [127].

2-Phenylthiazoline was obtained by the cyclisation of a 2-thiobenzamidoacetal under the action of polyphosphoric acid. 5-Ethoxy-2-phenylthiazoline is formed similarly at 100°C; at a higher temperature (180°) 2-phenylthiazole is formed [128]:

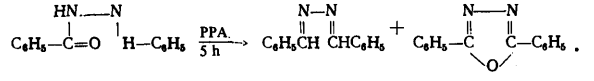


On treatment with polyphosphoric acid, 1-thiobenzoylsemicarbazide gives thiadiazole derivatives in high yields. The reaction conditions are very important for cyclisation in polyphosphoric acid; the temperature and duration of the reaction frequently determine the nature of the compound obtained. Thus in the cyclisation of thiobenzoylsemicarbazide (I) and thiobenzoylthiosemicarbazide (II) at different temperatures, various substituted 1,3,4-thiadiazoles are formed [228]:

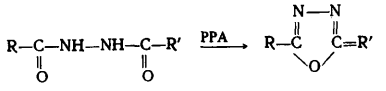


After isolation and purification, the yields were 88% of 2-hydroxy-5-phenyl-1,3,4-thiadiazole (III), 65% of 2-amino-5-phenyl-1,3,4-thiadiazole (IV), and 83% of 2-mercapto-5-phenyl-1,3,4-thiadiazole (V).

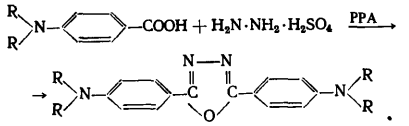
When 1-benzoyl-2-benzylidenehydrazine was treated with polyphosphoric acid under mild conditions (reaction temperature below 100°C), a mixture of benzaldazine and 2,5-diphenyl-1,3,4-oxadiazole was obtained [129]:



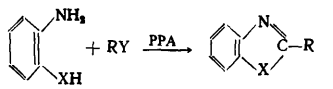
Cyclisation of hydrazine derivatives under more severe conditions (180–205°C) gives rise to derivatives of 1,3,4-oxadiazoles in quantitative yields [130,131]:



2,5-Di-(*p*-aminophenyl)-1,3,4-oxadiazole was obtained by treating *p*-aminobenzoic acid with hydrazine sulphate in polyphosphoric acid [132,133]:



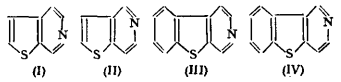
Hein et al. [104] achieved the synthesis of benzimidazoles, benzoxazoles, and benzothiazoles substituted in the 2-position by the condensation of carboxylic acids, their esters, amides, and nitriles with *o*-amino-, *o*-hydroxy-, and *o*-mercapto-anilines in polyphosphoric acid:



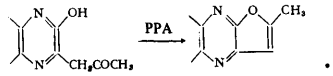
where X = NH, O, or S, Y = COOH, COOR, $CONH_2$, or CN, and R = alkyl or aryl.

Advances have been achieved in the synthesis of bisazoles and bisbenzazoles in polyphosphoric acid [134,135].

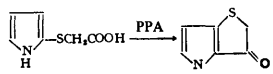
Thieno[2,3-*c*]pyridine (I) and thieno[3,2-*c*]pyridine (II) were synthesised by the cyclisation of the Schiff bases (Pomeranz–Fritsch reaction) obtained by the reaction of formylthiophencarboxylic acids and aminoacetals in polyphosphoric acid. Thianaphtheno[2,3-*c*]pyridine (III) and thianaphtheno[3,2-*c*]pyridine (IV) were obtained in low yields. A mixture of polyphosphoric acid and phosphorus oxychloride is recommended for these syntheses [108]:



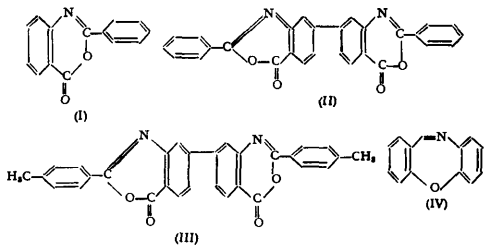
On treatment with polyphosphoric acid, xanthopterin derivatives are cyclised with formation of natural dyes—pteridines [136,137]:



A convenient method has been described for the synthesis of thieno[3,2-*b*]pyrrole, the first stage of which is the formation of 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one as a result of the rearrangement and cyclisation of 2-pyrrolylthioacetic acid under the action of polyphosphoric acid [138–140]:



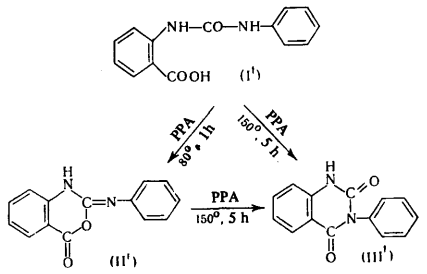
New syntheses in polyphosphoric acid of 2-phenyl-4*H*-3,1-benzoxazin-4-one (I) 2,2′-diphenyl-(6,6′-bi-4*H*-3,1-benzoxazyl)-4,4′-dione (II), 2,2′-di-*p*-tolyl-(6,6′-bi-4*H*-benzoxazyl)-4,4′-dione (III), [141,142] and a seven-membered cyclic compound (IV) containing nitrogen and oxygen as heteroatoms [143] have been developed:



Compound (I) was obtained from benzoylanthranilic acid and compounds (II) and (III) from benzidinedicarboxylic acid and benzoyl chloride or *p*-toluoyl chloride.

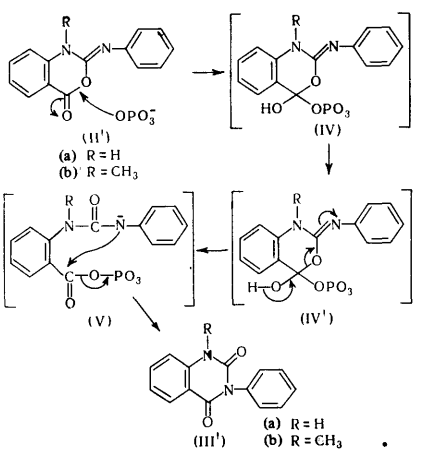
The formation of the heterocycles (III′) is accompanied by an intramolecular rearrangement [141]. Thus, when *N*-phenylcarbamoylanthranilic acid (I′) is heated for 1 h at 80–100°C, 1,2-dihydro-2-phenylimino-4*H*-3,1-benzoxazin-4-one (II′) is formed (yield 95%, m.p. 193°C). Heat

treatment of this acid at 150°C for 5 h leads to 3-phenyl-2,4-(1*H*)-quinazolinedione (III′) (quantitative yield, m.p. 280°C):



When compound (II′) is treated with polyphosphoric acid at 150°C, compound (III′) is formed in 70% yield, which can only be accounted for by the migration of the ureide group.

Kurihara and Yoda [144] suggest the following mechanism for this rearrangement: on further heating of compound (II′) in polyphosphoric acid, the carbonyl group of benzoxazinone is phosphorylated with formation of an intermediate (IV and IV′); subsequent ring opening leads to a mixed anhydride of a carboxylic and phosphoric acid (V). The negatively charged ureide nitrogen attacks the carbonyl group of the mixed anhydride displacing phosphoric acid. Recyclisation gives the quinazolinedione ring (II):



IV. SYNTHESIS OF POLYHETEROARYLENES IN POLYPHOSPHORIC ACID

The synthesis of thermostable polymers which can be worked constitutes one of the most urgent problems in the modern chemistry of macromolecular compounds. Considerable advances in this field have been achieved using the polyheterocyclisation reaction, whereby it is possible to obtain aromatic polymers with alternating carbocycles and heterocycles—the so called polyheteroarylenes [145]. In recent years considerable attention has been devoted to the development of new methods for polyheterocyclisation processes, among which high temperature polycyclisation in solution occupies a special place. This method has been successfully used in the first place for the synthesis of polyheteroarylenes (for example, polyimides [146]) soluble in the reaction mixture.

Naturally in reactions of this kind the correct choice of solvent is of exceptional importance. It is most useful to employ compounds with a high solvent power and a high boiling point or decomposition temperature which catalyse the reaction and bind the side products liberated (the usual side product in polyheterocyclisation reactions is water). Polyphosphoric acid meets all these requirements to a considerable degree.

Since 1960 polyphosphoric acid has been fairly extensively employed to prepare various polyheteroarylenes [147,148]. As shown above, polyphosphoric acid is an exceptionally effective condensing and cyclising agent; among the specific features of the syntheses of polyheteroarylenes in polyphosphoric acid, we shall mention the following.

1. As a rule, polycyclisation in polyphosphoric acid yields polymers with higher molecular weights than those obtained by other methods.

2. One of the most important problems in the synthesis of polyheteroarylenes is the attainment of the highest possible degree of cyclisation, since this parameter determines to a considerable extent the thermal and other characteristics of polymers. In solid-phase polycyclisation, macromolecular chains become increasingly rigid as the reaction proceeds, which hinders to a considerable degree the completion of the polycyclisation reaction, since the activation energy for the cyclisation process rises continuously [149] and free rotation about the bonds in the ring-forming fragments becomes more difficult.

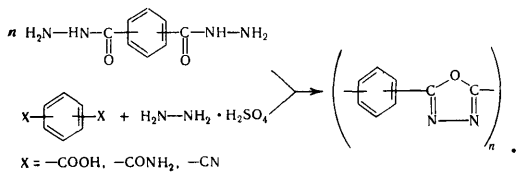
Polyphosphoric acid behaves as a plasticiser, which is responsible to a considerable degree for the possibility of attaining a higher extent of cyclisation compared with other methods.

3. In many cases the polymers obtained in polyphosphoric acid differ significantly in their properties from polymers with similar structures prepared by other procedures. Thus poly-(1,3,4-oxadiazole-2,5-diyl-1,4-phenyleneoxy-1,4-phenylene) obtained in polyphosphoric acid [150] is more soluble than the similar polymer synthesised by a multistage process [151], which may be attributed both to only a weak development in polyphosphoric acid of intermolecular "cross-linking" reactions and to the difference in the phase states of these polymers. This finding has attracted particular interest, since the synthesis of soluble and hence workable polyheteroarylenes in one stage is technologically and economically more convenient compared with a two-stage process.

4. The use of polyphosphoric acid solves to a considerable degree the problems associated with the raw material base for the synthesis of polyheteroarylenes. For example, in the synthesis of various polybenzazoles polyfunctional nucleophilic agents are employed—bis-(*o*-phenylenediamines), bis-(*o*-aminophenols), bis-(*o*-aminothiophenols), etc., which are extremely unstable in the form of free bases and are readily oxidised. When the reaction is carried out in polyphosphoric acid, these compounds may be introduced in the form of much more stable salts—hydrochlorides, sulphates, phosphates, etc. Moreover, instead of employing the halides or anhydrides of the acids as the acid component of the reaction, it is possible to employ the more readily available free polycarboxylic acids.

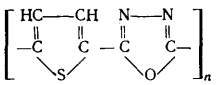
The above advantages of the synthesis of polyheteroarylenes in polyphosphoric acid led to the wide employment of the polyheterocyclisation reaction for the synthesis of a wide variety of different classes of polymers. The principal classes of polyheteroarylenes containing five-membered heterocycles are polyazoles and polybenzazoles. The characteristics of the synthesis of polyazoles in polyphosphoric acid have been investigated in greatest detail

for poly-1,3,4-oxadiazoles. Aromatic poly-1,3,4-oxadiazoles were obtained for the first time by Iwakura et al.[152] in a reaction of hydrazine sulphate with aromatic dicarboxylic acids, their amides, and nitriles, and also in the homocondensation of the dihydrazides of aromatic dicarboxylic acids:



Together with poly-1,3,4-oxadiazoles, the same investigators synthesised on the basis of isophthalic and terephthalic acids polymers containing alternating 1,3,4-oxadiazole and pyridine rings by the homocondensation of the dihydrazides of isomeric pyridinedicarboxylic acids—isocinchomeronic, dinicotinic, 2,6-dimethyldinicotinic, and dipicolinic[153].

Yet another type of polymer, containing only heterocycles—poly[2,3-thienylene-1,3,4-oxadiazole]—corresponding to the structural formula



was obtained by Manecke and coworkers[154] on heating the polyhydrazide of thiophendicarboxylic acid in polyphosphoric acid at 150°C for 5 h.

All the polymers synthesised exhibited high thermal stability and poly-1,3,4-oxadiazoles based on isophthalic and terephthalic acids also had high molecular weights: however, these polymers are soluble only in concentrated sulphuric acid and it is difficult to work them.

In order to obtain soluble polymers, Iwakura and coworkers[155] attempted to synthesise poly-1,3,4-oxadiazoles from the dihydrazides of aliphatic acids with the general formula

$$H_2NHNCO(CH_2)_mCONHNH_2,$$

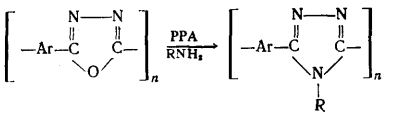
where $m = 0$, 1–10, 12, 15, and 20,[155] and alicyclic dicarboxylic acids[156]; poly-1,3,4-oxadiazole containing cyclohexane, cyclopropane, and spiro[3,4]heptane rings were obtained in the latter case[208].

In a number of cases the polymers were soluble in organic solvents but their thermal stability and resistance to heat were considerably inferior to those of aromatic poly-1,3,4-oxadiazoles.

A successful combination of useful thermal properties with solubility was achieved for poly-1,3,4-oxadiazoles by Korshak and coworkers, who synthesised these polymers on the basis of derivatives of di-(4-carboxyphenyl) ether[150] and diphenylphthalide-4′,4″-dicarboxylic acid[157,158].

The study of certain characteristics of the polyheterocyclisation reaction in polyphosphoric acid by Korshak, Krongauz, and coworkers[159] showed that the following factors favour the formation of high molecular-weight poly-1,3,4-oxadiazoles: (1) the absence of sulphuric acid from the reaction medium, which can be conveniently achieved by using hydrazinium phosphate instead of hydrazinium sulphate; (2) the binding of the water evolved in the condensation process by adding to the reaction mixture an additional amount of P_2O_5; (3) a high reaction temperature and short duration of the process.

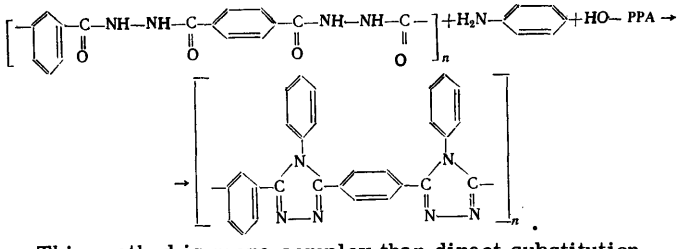
The relative ease of the opening of the 1,3,4-oxadiazole ring in polyphosphoric acid under the influence of different reagents permitted a series of polymer-analogue conversions of poly-1,3,4-oxadiazoles into other polyazole systems. Thus in a reaction of poly-1,3,4-oxadiazoles with various amines in polyphosphoric acid, Korshak and coworkers obtained a series of poly-(4-substituted)-1,2,4-triazoles[102,160–163]:



The amines employed were aniline, α-naphthylamine, cyclohexylamine, etc. Amines form stable complexes with polyphosphoric acid[164]. The reaction involving substitution of the oxygen in the oxadiazole ring by the N–R residue occurs only when the reaction medium contains a free amine, formed as a result of the dissociation of the amine–PPA complex at the reaction temperature. Therefore the successful occurrence of the substitution reaction depends on the basicity of the amines, which determines, on the one hand, the ease of dissociation of the amine–PPA complex and, on the other, the ease of substitution[162].

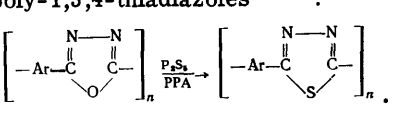
Poly(4-aryl)-1,2,4-triazoles contain bulky aryl substituents which weaken the interaction between the macromolecules; consequently these polymers are readily soluble in strong organic and inorganic acids. For this reason, the conversion of the insoluble aromatic poly-1,3,4-oxadiazoles into soluble poly(4-aryl)-1,2,4-triazoles, which can be carried out in a single reaction system without isolating the intermediate poly-1,3,4-oxadiazole[165], is of definite practical interest.

Holsten and Lilyquist showed[166,167] that analogous polymers may be obtained by heating polyhydrazides with aromatic amines in polyphosphoric acid:

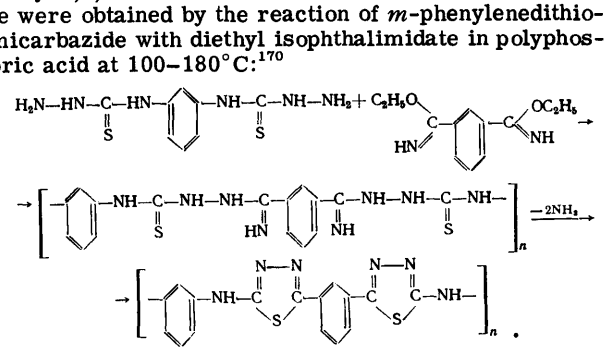


This method is more complex than direct substitution of oxygen in the 1,3,4-oxadiazole ring, but it yields products with higher molecular weights.

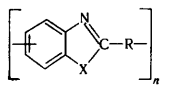
When P_2S_5 in polyphosphoric acid acts on poly-1,3,4-oxadiazoles, the latter undergo a polymer-analogue conversion into poly-1,3,4-thiadiazoles[168,169]:



Poly-1,3,4-thiadiazole with a somewhat different structure were obtained by the reaction of *m*-phenylenedithiosemicarbazide with diethyl isophthalimidate in polyphosphoric acid at 100–180°C:[170]

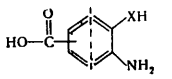


Another class of polyheteroarylenes in the synthesis of which polyphosphoric acid is widely employed are polybenzazoles. The principal representatives of this class of polyheteroarylenes are polybenzimidazoles, polybenzoxazoles, and polybenzothiazoles, corresponding to the general formula

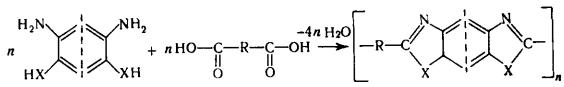


where X = NH, O, or S.

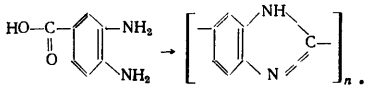
These polymers were obtained by the homocondensation of compounds with the general formula



or by the polycondensation of tetrafunctional nucleophilic agents with dicarboxylic acids or their derivatives:



Polybenzimidazoles have been investigated in greatest detail among polybenzazoles; this is probably because the majority of them dissolve in strong acid and certain amide solvents, even when the degree of cyclisation is high, and therefore by carrying out the process in one stage in polyphosphoric acid one does not preclude the formation of a workable polymer. Iwakura and coworkers [171,172] synthesised in polyphosphoric acid aromatic polybenzimidazoles by the homocondensation of 3,4-diaminobenzoic acid, its hydrochloride, sulphate, phosphate, and the potassium salt at 160°C, for 1–5 h:

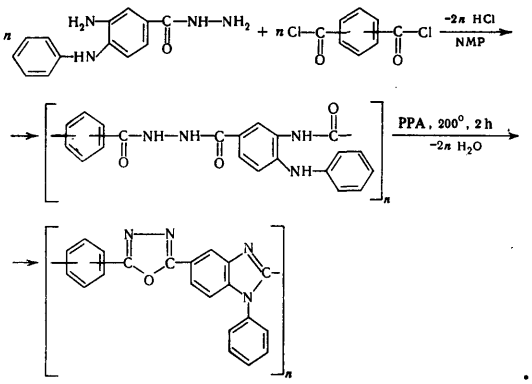


Apart from 3,4-diaminobenzoic acid, 3,4-diamino-3′-carboxybiphenyl, 3,4-diamino-4′-carboxybiphenyl, and 2,3-diamino-6-carboxynaphthalene have been employed as starting materials [171].

The same workers [173–177] synthesised polybenzimidazoles from the tetrachloride of 3,3′-diaminobenzidine and isophthalic, terephthalic, fumaric, and certain saturated aliphatic and alicyclic dicarboxylic acids. Both the acids themselves and their chlorides, nitriles, hydrazides, and esters were introduced into the reaction.

Koton and coworkers [178] employed di-(4-carboxyphenyl) ether and di(4-carboxyphenyl) sulphone as the acid components. In almost all cases high-molecular-weight polymers were obtained (ηlog† = 0.8–2.6), the syntheses of aromatic polybenzimidazoles being carried out under fairly severe conditions.

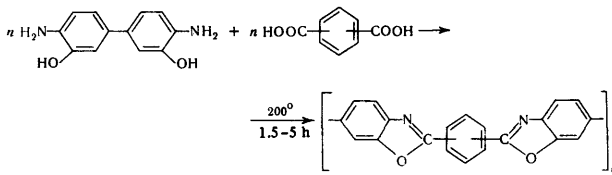
At the present time there are very few literature data on the application of polyphosphoric acid in the syntheses of poly-(*N*-aryl)benzimidazoles—polymers distinguished by enhanced solubility and resistance to thermo-oxidative degradation, compared with unsubstituted polybenzimidazoles [179]. We may note the work of Culbertson and Dietz [180], where polyaminohydrazides—the products of the low-temperature polycondensation of the hydrazide of 3-amino-4-anilinobenzoic acid with the dichlorides of isophthalic and terephthalic acid in *N*-methylpyrrolidinone—were subjected to cyclodehydration in polyphosphoric acid:



The poly-[2-(*mp*-phenylene)-5-(1,3,4-oxadiazolyl)-1-phenylbenzimidazoles] obtained in this way began to decompose only above 440°C both in nitrogen and air.

Considerable attention has been devoted to the synthesis in polyphosphoric acid of polybenzoxazoles and polybenzothiazoles. Aromatic polybenzoxazoles were obtained by the homocondensation at 160–200°C of isomeric aminohydroxybenzoic acids: 4-amino-3-hydroxybenzoic and 3-amino-4-hydroxybenzoic acids or their hydrochlorides [172]; the polymers had ηlog = 0.7–2.2.

Aromatic polybenzoxazones with a somewhat different structure were synthesised by the reaction of bis-(*o*-aminophenols) or their hydrochlorides with aromatic dicarboxylic acids [181]; 3,3′-dihydroxybenzidine has been most often employed as the bis-(*o*-aminophenol):



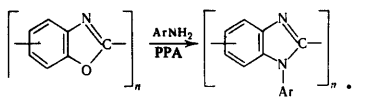
Aromatic polybenzoxazoles are obtained under very severe conditions; when the reaction is carried out at 200°C and lasts 1.5–5 h, their molecular weights reach high values (ηlog = 1.36–2.1).

The reaction of bis-(*o*-aminophenols) with aliphatic dicarboxylic acids takes place, as in the synthesis of polybenzimidazoles [176], under milder conditions—at 100 to 120°C. [181]

The study of the thermal stability of polybenzoxazoles showed that the aromatic polymers decompose in air at about 450°C and those containing aliphatic units at about 300°C.

Polybenzoxazoles based on alicyclic dicarboxylic acids have also been synthesised [177].

Although the benzoxazole ring exhibits higher thermal and chemical stability compared with the 1,3,4-oxadiazole ring, under the action of primary aromatic amines in polyphosphoric acid, polybenzoxazoles are converted into the corresponding poly-(*N*-aryl)benzimidazoles [182]:

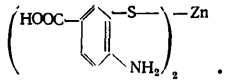


Like polybenzimidazoles and polybenzoxazoles, polybenzothiazoles may be synthesised in polyphosphoric acid both by the homocondensation of compounds containing

†Inherent viscosity or logarithmic viscosity number (Ed. of Translation).

nucleophilic and carboxy-groups and by the reaction of polyfunctional nucleophilic agents with dicarboxylic acids or their derivatives.

Iwakura and coworkers [172] synthesised aromatic polybenzothiazoles by the homocondensation of 4-amino-3-mercaptobenzoic acid as the hydrochloride and as the zinc thiophenoxide derivative:

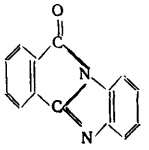


At a reaction temperature of 160–200°C for a process duration of 4 h, polymers with high molecular weights were obtained (η_{log} = 0.43–2.03). Later investigations [183] showed that 4-amino-3-mercaptobenzoic and 3-amino-4-mercaptobenzoic acids, 3-amino-4-mercaptobenzamide, and 2,2-dimethylbenzothiazole-5-carboxamide may be employed as the initial compounds. The polycondensation was carried out at 250°C for 3 h; the molecular weights of the polymers thus obtained (η_{log} = 0.91–1.33) greatly exceeded those of analogous polymers obtained in the melt and in solution in *m*-cresol and dimethylacetamide.

The syntheses of polybenzothiazoles in polyphosphoric acid on the basis of the dihydrochloride of 3,3′-dimercaptobenzidine were carried out at 200°C for 5–10 h in the case of isophthalic and terephthalic acids and at 120°C for 2 h in the case of sebacic acid [181]. The polymers had fairly high molecular weights (η_{log} = 0.31–1.02).

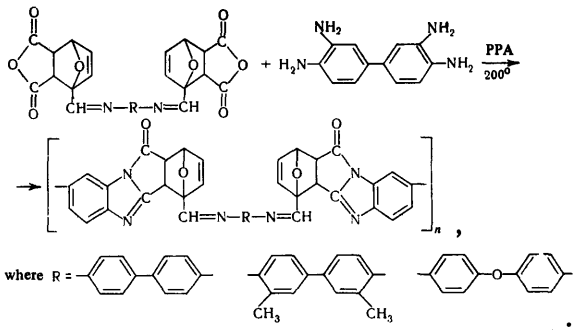
Hergenrother and coworkers [184] synthesised polybenzothiazoles from the dihydrochloride of 3,3′-dimercaptobenzidine and the following acid components: isophthalic acid, the diamide of isophthalic acid, di-(4-carboxyphenyl) ether, and the dimethyl ester of 4,4′-dicarboxybenzophenone. They succeeded in obtaining products with even higher molecular weights (η_{log} = 0.36–1.51).

Yet another class of polybenzazoles which were synthesised in polyphosphoric acid is polybenzoylenebenzimidazoles containing 1,2-benzoylenebenzimidazole as the characteristic structural fragment of the condensed system:



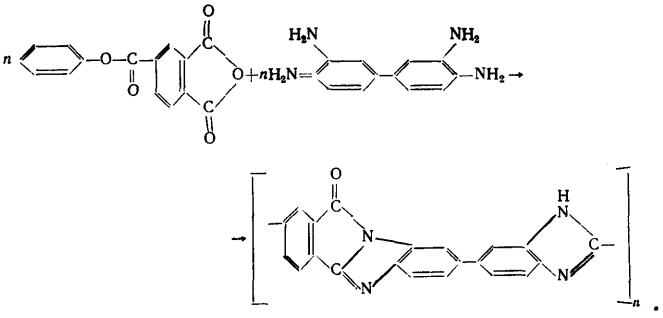
Polybenzoylenebenzimidazoles have been recently attracting particularly close attention of investigators in connection with the search for new types of so called "ladder" and "block-ladder" polymers, which, according to Tessler's theoretical postulates [185], should exhibit higher thermal stability and heat resistance than the usual polyheteroarylenes.

Dawans and Marvel [186] synthesised polybenzoylenebenzimidazoles in polyphosphoric acid from pyromellitic dianhydride and the tetrahydrochlorides of 1,2,4,5-tetraaminobenzene, 3,3′-diaminobenzidine, and di-(3,4-diaminophenyl) ether. The polycyclisation reactions were carried out at 200–220°C and yielded polybenzoylenebenzimidazoles with η_{log} = 1.91–1.81‡. Berlin and coworkers [187] obtained polybenzoylenebenzimidazoles by the reaction in polyphosphoric acid of the dianhydrides of tetracarboxylic acids obtained as the bisadducts of the Diels–Alders reaction of furans and maleic anhydride derivatives with 3,3′-diaminobenzidine at 200°C for 8 h:

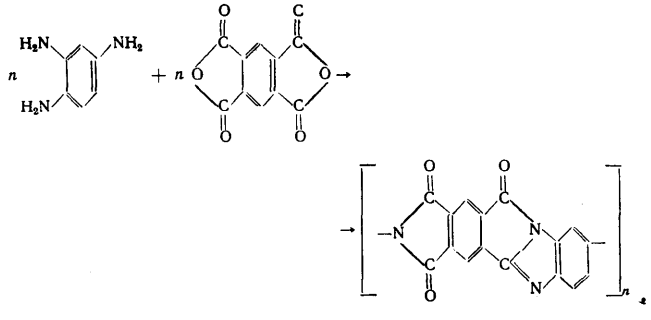


The polymers proved to be stable in air up to 350 to 450°C and dissolved in polyphosphoric acid and sulphuric acid; the reduced viscosity of their 1% solutions in concentrated sulphuric acid did not exceed 0.25.

Culbertson and Murphy [188], who carried out the reaction of the anhydride of 4-phenyltrimellitate with the tetrahydrochloride of 3,3′-diaminobenzidine in polyphosphoric acid at 200–210°C for 2 h, obtained an aromatic polymer containing alternating benzimidazole and benzolyenebenzimidazole rings and soluble in concentrated sulphuric acid only (η_{log} = 0.22):



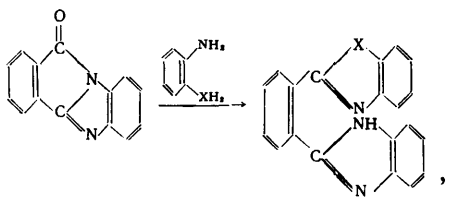
The polymer exhibited high thermal stability—intense decomposition in nitrogen and in air began at 550°C; in nitrogen the polymer retained 70 wt.% of its weight at 1000°C. A polymer with an analogous structure but a higher molecular weight (η_{log} = 0.513) was obtained by the reaction of trimellitic anhydride with 3,3′-diaminobenzidine [189]. In addition the reaction of 1,2,4-triaminobenzene with pyromellitic dianhydride gave poly(imidobenzoylenebenzimidazole) with η_{log} = 0.63:[189]



All the polymers containing benzoylenebenzimidazole rings and obtained in polyphosphoric acid are very insoluble. This may be a consequence both of the nature of the macromolecules themselves, and the presence of

‡Intrinsic viscosity = 1.1–1.8 according to the original paper (Ed. of Translation).

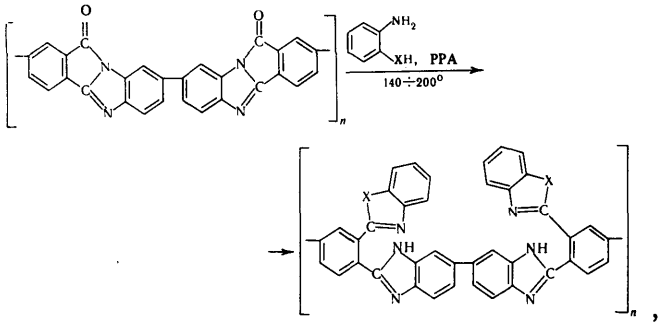
"cross-links" between them. "Cross-linked" structures may be formed as a result of the reaction of 1,2-benzoylenebenzimidazole with aromatic nucleophilic agents in polyphosphoric acid, analogous to the reaction of these compounds in nitrobenzene [190]:



where X = NH, O, or S.

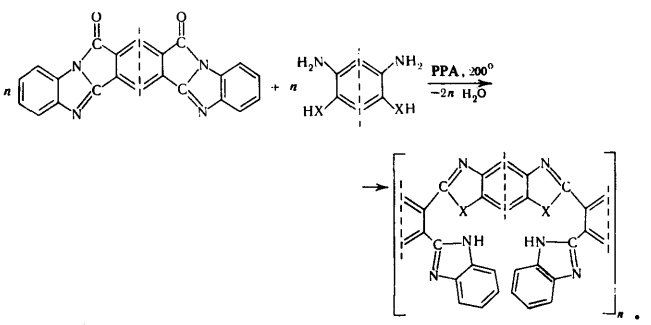
According to this reaction, one may expect that the terminal *o*-phenylenediamine groups of these macromolecules may react with the benzoylenebenzimidazole rings in their centre giving rise to "branching" of the bibenzimidazole type, which subsequently leads to "cross-linking". This reaction of the benzoylenebenzimidazole ring has been used to prepare various polybenzazoles containing attached benzazole groups.

Thus, by treating polybenzoylenebenzimidazoles with *o*-phenylenediamine, *o*-aminophenol, and *o*-aminothiophenol in polyphosphoric acid at 140–200°C, polybenzimidazoles were obtained with attached benzimidazole, benzoxazole, and benzothiazole groups in the *o*-position relative to the benzimidazole rings of the main macromolecular chains [191,192]:



where X = O, S, or NH.

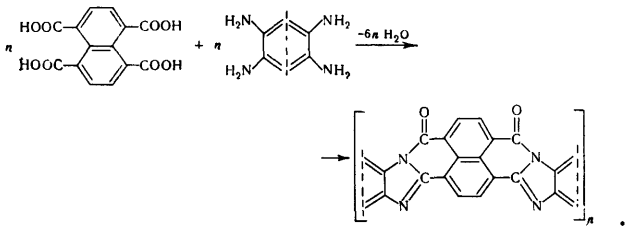
When this reaction was extended to bisbenzoylenebenzimidazoles, which are the products of the reaction of aromatic tetracarboxylic acids or their anhydrides with *o*-phenylenediamine, various polybenzazoles containing attached benzimidazole groups were obtained [193,194]:



Polymers of this kind show a combination of high thermal stability with high solubility in polar solvents.

Polyphosphoric acid has been used successfully in syntheses of polymers containing five- and six-membered condensed heterocycles, typical representatives of these polymers being polynaphthoylenebenzimidazoles—the products of the reaction of naphthalene-1,4,5,8-tetracarboxylic acid or its derivatives with bis-(*o*-phenylenediamines).

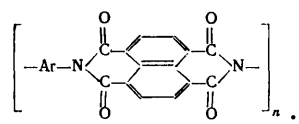
Van Deusen and coworkers [195,196] carried out the reaction of naphthalene-1,4,5,8-tetracarboxylic acid with 1,2,4,5-tetra-aminobenzene tetrahydrochloride and 3,3′-diaminobenzidine in polyphosphoric acid at 180–190°C for 20–24 h:



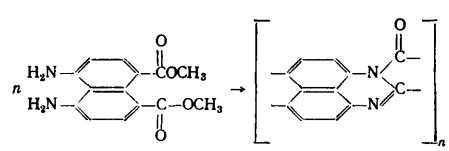
In the first case the product was a polymer entirely of the "ladder" type and in the second a polymer containing "ladder" blocks comprising eight condensed rings. The polymers dissolved in polyphosphoric and sulphuric acids had a high viscosity ($\eta\log$ =0.9–1.5).

Berlin and coworkers [197,198] synthesised polymers of a similar structure from the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid and 3,3′-diaminobenzidine. The same investigators obtained polynaphthoylenebenzimidazoles based on di-(3,4-diaminophenyl)methane and di-(3,4-diaminophenyl) ether [199,200]. When the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid was replaced by the dianhydride of perylene-3,4,9,10-tetracarboxylic acid, the polymers had a relatively low molecular weight but exhibited high thermal stability [200,201].

When aromatic diamines (benzidine and others) were introduced into these reactions instead of bis-(*o*-phenylene diamines), polymers containing six-membered imide rings were obtained [198,200]:



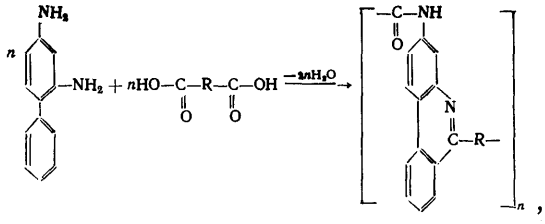
Van Deusen and coworkers [202] showed that the homypolycondensation of dimethyl 4,5-diaminonaphthalene-1,8-dicarboxylate and the anhydride of 4,5-diaminonaphthalene-1,8-dicarboxylic acid in polyphosphoric acid at 100 to 250°C results in the formation of a polymer with a "ladder" structure–poly(perimidine-6,7 : 1,2-tetrayl-1-carbonyl):



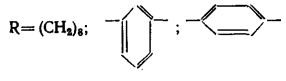
Polymers of this type are distinguished by high thermal stability: they are stable in air up to 450°C and in argon up to 600°C.

A number of studies have been made on the synthesis in polyphosphoric acid of other polyheteroarylenes incorporating six-membered nitrogen-containing heterocycles.

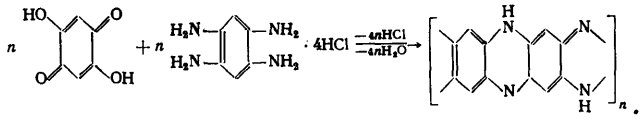
Thus Kolesnikov and coworkers [203] synthesised polyphenanthridinylamides from 2,4-diaminobiphenyl and aliphatic and aromatic dicarboxylic acids:



where

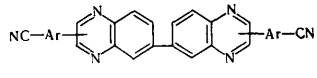


Stille and coworkers [204-207] employed polyphosphoric acid as a reaction medium in the synthesis of "ladder-type" polyquinoxalines. Thus, in the polycondensation of 2,5-dihydroxy-*p*-benzoquinone with 1,2,4,5-tetra-aminobenzene tetrahydrochloride in polyphosphoric acid at 150°C for 6–12 h, a hydrogenated aromatic "ladder-type" polyquinoxaline soluble in hexamethylphosphoramide and having $\eta_{log} = 1.4$ was obtained [204,206,207]:



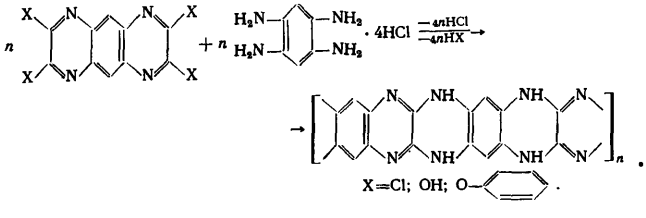
At an elevated temperature the polymer was dehydrogenated and acquired a stable fully aromatic structure. Other starting materials employed were 1,2,6,7-tetraoxopyrene and 1,2,5,6-tetraoxoanthracene [205,207] and also 2,3,6,7-tetra-aminodibenzo-*p*-dioxin and 3,3'-diaminobenzidine [207].

Copolymers containing in the main chain quinoxaline and benzimidazole rings were obtained by the reaction of phenoxycarbonylphenylglyoxals with bis-(*o*-phenylene diamines) [208]. The same polymers were also formed by the reaction of biscyanoarylquinoxalines having the general formula

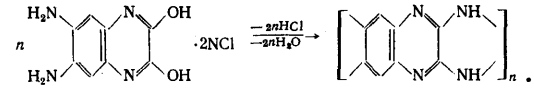


with 3,3'-diaminobenzidine tetrahydrochloride in polyphosphoric acid.

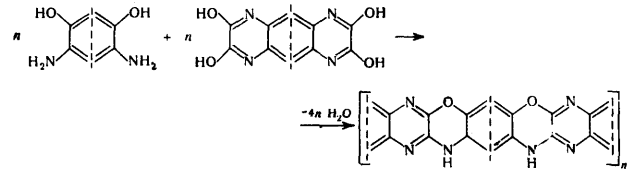
Marvel and coworkers [112,209-211] condensed substituted derivatives of quinoxaline with bis-(*o*-phenylenediamines), bis-(*o*-aminophenols), and bis-(*o*-aminothiophenols) to synthesise quinoxaline-containing polymers. Thus the reaction of tetra-aza-anthracene derivatives with 1,2,4,5-tetra-aminobenzene tetrahydrochloride in polyphosphoric acid at 250°C for 24 h gave "ladder-type" polymers containing quinoxaline and diazine rings [209]:



A polymer with a similar structure was obtained in the homopolycondensation of a diaminodihydroxy-compound containing a quinoxaline ring [209]:

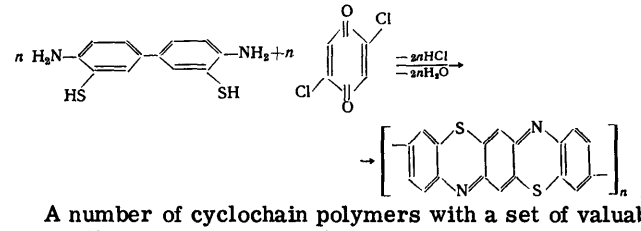


The reaction of diaminodihydroxy-compounds (2,5-diamino-1,4-dihydroxybenzene and 3,3'-dihydroxybenzidine) with tetrasubstituted quinoxalines [2,3,7,8-tetrahydroxy-1,4,6,9-tetra-aza-anthracene, 2,2',3,3'-tetrahydroxy-6,6'-bisquinoxaline, and bis-(2,3-dihydroxy-6-quinoxalyl) ether] in polyphosphoric acid at 230–250°C for 24 h resulted in the formation of polymers containing quinoxaline and oxazine rings, which were partially soluble in concentrated sulphuric and methanesulphonic acids [210,211]:

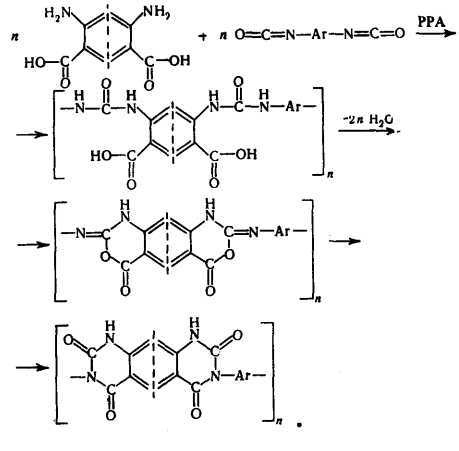


Tetrachloro-substituted quinoxalines have also been employed as the quinoxaline component [211].

Polytriphenodithiazine was obtained similarly by the reaction of 3,3'-dimercaptobenzidine with 2,5-dichloro-*p*-benzoquinone in polyphosphoric acid [212]:



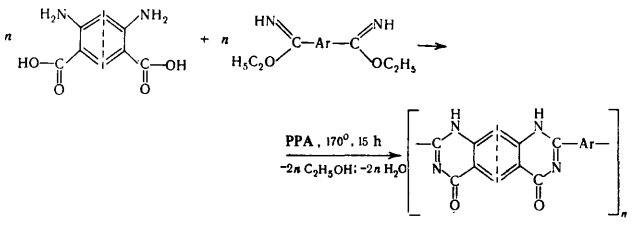
A number of cyclochain polymers with a set of valuable properties were synthesised on the basis of certain diaminodicarboxylic acids. In particular, a detailed study was made of the products of the bisanthranilic interaction in polyphosphoric acid of bisanthranilic acids [4,4'-diamino-3,3'-biphenylenedicarboxylic acids (Ed. of Translation)] with di-isocyanates—the so called polyquinazolinediones [141,142,213,214]:



3,3'-Dicarboxybenzidine is the most widely employed bisanthranilic acid. [Inorganic] isocyanate, 3,3'-dimethyl-4,4'-diphenylene di-isocyanate, 3,3'-dimethoxy-4,4'-phenylmethane, etc. have been employed together with this

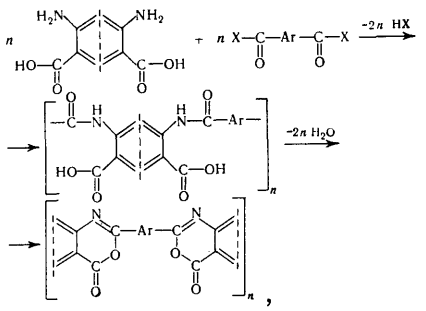
compound. *p*-Phenylene di-isocyanate, *p,p'*-diphenylmethylene di-isocyanate, 1,5-naphthylene di-isocyanate, 3,3'-dimethyl-4,4'-diphenylene di-isocyanate, 3,3'-dimethoxy-4,4'-diphenylene di-isocyanate, 2,4-toluylene di-isocyanate, etc. have been used as the di-isocyanate component.

Eda and coworkers synthesised polyquinazolones by the reaction of bisanthranilic acids with bisimino ethers[215]:



The polyquinazalones had a comparatively low molecular weight—the characteristic§ viscosities of 0.5% solutions of these polymers in sulphuric acid did not exceed 0.15.

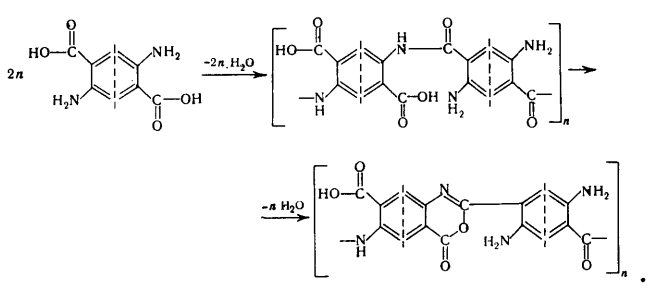
Products with much higher molecular weights were obtained by the reaction of bisanthranilic acids with aromatic dicarboxylic acids and their derivatives[216-220]. Here the first stage involves the formation of poly-*o*-carboxyamides, which on further increase of temperature are cyclised to the corresponding polybenzoxazinones:



where X = COOH, COCl, COBr, $CONH_2$, CN, or $COOCH_3$.

Polybenzoxazinones as well as polyquinazolinediones are very insoluble—they dissolve only in sulphuric and nitric acids; therefore it is desirable to convert them into finished products at the stage of poly-*o*-carboxyamides, which are soluble in organic solvents. The temperature of the onset of the decomposition of the fully aromatic polymers reaches 550°C.

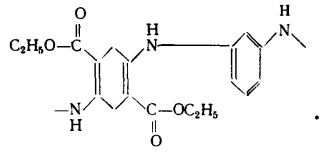
Polymers containing benzoxazine fragments were obtained by the homopolycondensation of bisanthranilic acids (2,5-diaminoterephthalic, benzidine-3,3'-dicarboxylic, and others) in polyphosphoric acid[221,222]:



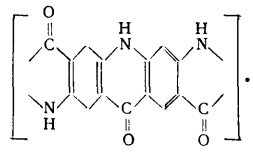
§Probably inherent (Ed. of Translation).

These polymers showed somewhat lower thermal stability compared with polyquinazolinediones and polybenzoxazinones: they proved to be stable in an inert atmosphere up to 450°C and began to decompose under the conditions of thermo-oxidative degradation at 350°C.

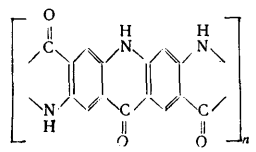
Kimura[223] developed a synthesis of polyquinolones—a new class of polyheteroarylenes. The reaction in polyphosphoric acid of diethyl succinosuccinate with aromatic diamines [m-phenylenediamine and di-(4-aminophenyl) ether] gave polyamines of the following type:



Their cyclisation in polyphosphoric acid (in an inert atmosphere) yielded insoluble polydihydroquinolones infusible up to 400°C and having a "ladder" structure:



The same polyamines may be oxidised by chloranil in dimethylformamide to aromatic polyamines, whose cyclisation in polyphosphoric acid gives infusible and insoluble polyquinolones:



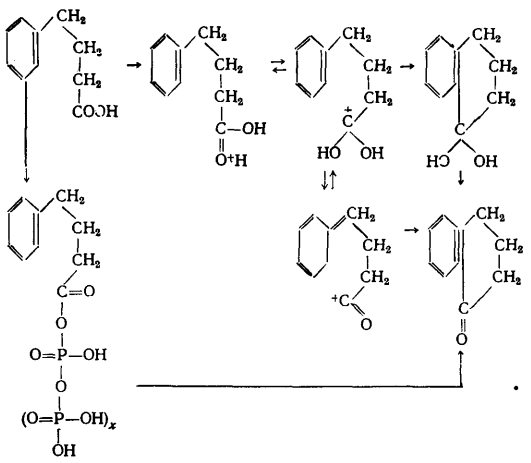
V. THE MECHANISM OF CYCLISATION REACTIONS IN POLYPHOSPHORIC ACID

The complex composition of polyphosphoric acid makes it extremely difficult to investigate the mechanism of reactions occurring in it and for this reason very little has been done in this field. The high viscosity of polyphosphoric acid, which prevents the isolation of intermediates by crystallisation, and the impossibility of employing cryoscopic methods made it very difficult to carry out the necessary kinetic measurements and therefore in the interpretation of the mechanisms there remains a considerable element of guesswork.

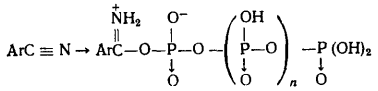
Among the reactions in polyphosphoric acid, the cyclisation of substituted aromatic acids, the conversion of γ-lactones into cyclopentanones, and the Beckmann and Lossen rearrangements have been investigated in greatest detail.

According to the literature, polyphosphoric acid functions simultaneously as a protic acid, a Lewis acid, and a phosphorylating agent[224]. Thus in the cyclisation of γ-phenylbutyric acid protonation or the formation of a

mixed anhydride is postulated as the initial stage, as shown below:



In the conversion of γ-lactones into cyclopentanones the intermediate formation of a ketocarbonium ion is suggested[225]. In the cyclisation of nitriles and also in the conversion of γ-lactones into cyclopentanones, phosphate esters may be formed and in the first case this is probably preceded by the addition of elements of polyphosphoric acid to the triple bond[5]:

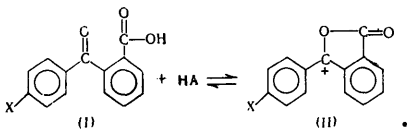


The presence of the intermediate carbonium ion has been confirmed only indirectly[226].

Since the majority of the latest communications on the applications of polyphosphoric acid are related to cyclodehydration or more specific intermolecular acylation, kinetic study of this type of reaction is of the greatest practical and theoretical interest. The elucidation of the mechanism of these reactions was preceded by a detailed study of the acid properties of polyphosphoric acid itself treated as the P_2O_5–H_2O system.

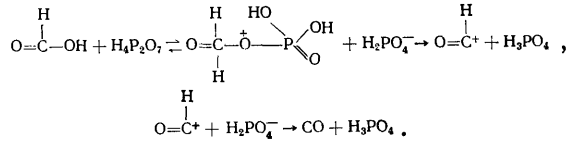
In an early investigation by Downing and Pearson[29] it was shown that the acidity of the P_2O_5–H_2O system (from 65 to 85.7 wt.% P_2O_5 at 25–27°C) increases monotonically with increasing P_2O_5 content. The data obtained by Gel'bshtein et al.[227] in a study of the acid properties of the P_2O_5–H_2O system between 2.7 and 83.5 wt.% P_2O_5 at 25°C with 2,4-dichloro-6-nitroaniline and 2-bromo-4,6-dinitroaniline as indicators also confirm the absence of an acidity maximum in the P_2O_5–H_2O system in the region corresponding to polyphosphoric acid.

In this connection it is noteworthy that, when polyphosphoric acid is employed as a catalyst in a number of reactions, its catalytic activity passes through a maximum. For example, the rate of heterolytic decomposition of formic acid is a maximum at 80 wt.% P_2O_5.[228] This was also reported by Downing and Pearson[229], who established that the rate of intermolecular acylation of *o*-benzoylbenzoic acids [*o*-benzoyl-, *o*-(*p*-chlorobenzoyl)- and *o*-(*p*-tolyl)-benzoic acids] passes through a maximum in the range of compositions corresponding to 78–83 wt.% P_2O_5. The authors found it difficult to explain this observation, since they postulated that the mechanism of the cyclisation of *o*-benzoylbenzoic acids in polyphosphoric acid is in general analogous to the mechanism proposed by Newman[230] for sulphuric acid, i.e. that the reaction takes place via an intermediate cyclic carbonium ion (II):



Thus in the above reactions there is no correspondence between the acidity of the medium and their rate. This is also reflected in the fact that for certain heterolytic reactions, a given rate is observed in polyphosphoric acid with a much lower acidity than in sulphuric acid, for example. Thus the rate constants for the reaction $HCOOH = CO + H_2O$ at 50°C in polyphosphoric acid containing 80.5 wt.% P_2O_5 and in 90% sulphuric acid are virtually identical (2.4×10^{-3} s^{-1} and 2.7×10^{-3} s^{-1} respectively). Nevertheless the acidity function of polyphosphoric acid of the above composition is $H_0 = -5.80$ at 25°C and that of 90% sulphuric acid is $H_0 = -8.44$ at 20°C.[228] Analogous relations have been observed for the Beckmann rearrangement of acetophenone oximes[231] and also for intramolecular cyclisation[229]. According to many investigators, the above findings may be explained by rejecting the hypothesis of purely proton-dependent mechanisms of the above reactions in polyphosphoric acid, adopting instead a mechanism including acid-catalysed phosphorylation. Probably polyphosphoric acid transfers to the substrate the $(H_2PO_3)^+$ ion, and not H^+, with formation of the corresponding anion, for example: $H_4P_2O_7 = [H_2PO_3]^+ + H_2PO_4^-$.

In the decomposition of formic acid in polyphosphoric acid this will correspond to the following mechanism:

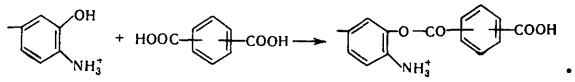


It is known that H_3PO_4 and polymeric metaphosphoric acid $(HPO_3)_n$ are incapable of phosphorylation, while acids such as $H_4P_2O_7$ and $H_5P_3O_{10}$ behave as phosphorylating agents. The content of these acids in the P_2O_5–H_2O system is a maximum in the range of P_2O_5 concentrations where there are maxima in the rates of the reactions considered. Thus the existence of reaction rate maxima in polyphosphoric acid has been explained. In media incapable of phosphorylation, the reactions take place via a proton mechanism which corresponds to a lower rate at the same acidity[227].

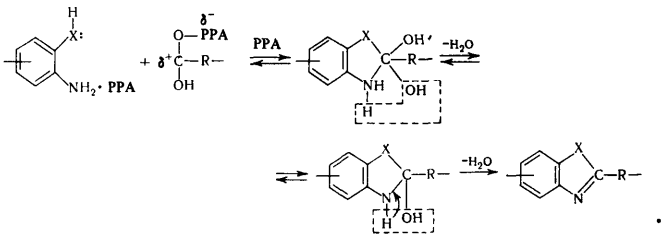
The results of kinetic studies on the ring closure of 2-carboxy-2'-deuterobiphenyl to fluorenone by Donney and Klemchuk[232] and the data of Goldberg and Wragg[233], who determined the rate constants for the cyclisation of *o*-phenoxybenzoic acid to xanthone in polyphosphoric acid containing 81.6% P_2O_5, can also be explained from this standpoint.

Problems associated with the changes in the reactivity of various compounds in polyphosphoric acid are of considerable interest[181]. It has been shown that polyphosphoric acid, which is a strong Lewis acid, increases the positive charge at the carbon atom of the carbonyl group and thereby leads to an increase of its electrophilic reactivity. It is also interesting to note that in reactions in polyphosphoric acid the basicity of the hydroxy-group is higher than that of the amino-group; therefore in the reaction of bis-(*o*-aminophenols) with dicarboxylic acids

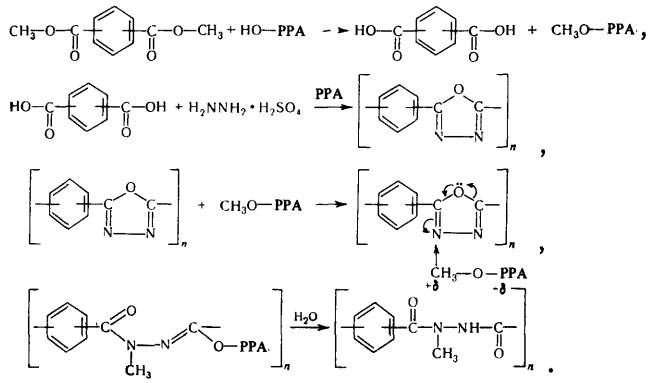
in polyphosphoric acid, there is initially selective formation of a polyester [181]:



Taking into account these facts, Iwakura and coworkers [181] proposed the following general mechanism for the formation of polybenzazoles:

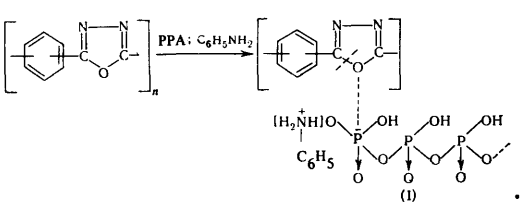


Probably the mechanism of the formation of poly-1,3,4-oxadiazoles from dicarboxylic acids and hydrazine derivatives is similar. However, in the presence of alkylating agents the 1,3,4-oxadiazole ring is opened. Thus, when dimethyl and diethyl esters of isophthalic and terephthalic acids were employed as starting materials, poly-(*N*-alkyl)-hydrazides were obtained [147]. The reaction probably takes place via the following mechanism:

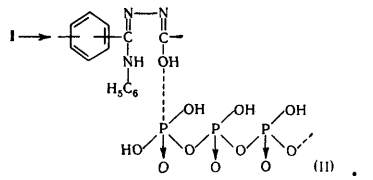


This mechanism is supported by the finding that in the interaction of poly-1,3,4-oxadiazole (obtained separately) with alkylating agents in polyphosphoric acid, the oxadiazole ring is opened with subsequent *N*-alkylation and formation of a poly-(*N*-alkyl)hydrazide.

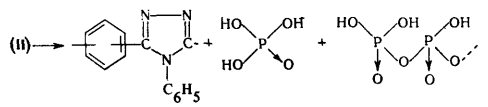
Substitution of one of the heteroatoms in the heterocycle by another also takes place with opening of the oxadiazole ring. The mechanism of the substitution reaction was examined in the synthesis of poly-(4-phenyl-1,2,4-triazoles) [161]. According to the mechanism proposed, a molecule of the polyphosphoric acid salt and a molecule of aniline add to the oxygen atom of the oxadiazole ring, forming an unstable intermediate complex (I), in which the C–O bond in the ring is weakened:



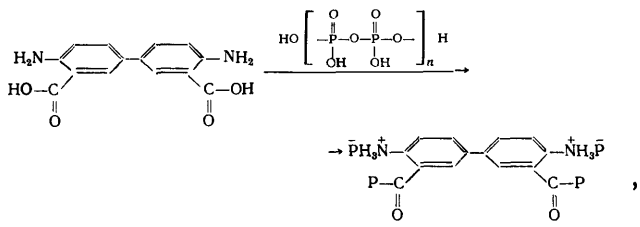
Under the influence of high temperature, the complex (I) dissociates with liberation of free aniline, which attacks the weakened C–O bond. The ring is then opened and the aniline residue adds to the carbon atom in the 5-position and the proton adds to the oxygen atom [compound (II)]:



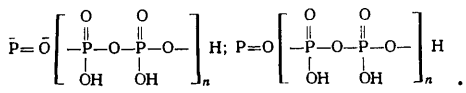
Then the polyphosphoric acid molecule is split off together with the hydroxy-group and the mobile hydrogen atom at the nitrogen acts on the O–P bond and facilitates the dissociation of an orthophosphoric acid molecule from polyphosphoric acid; at the same time the ring is closed and a polytriazole is formed:



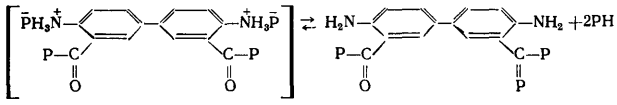
The mechanism of the homocondensation and co-condensation reactions of bisanthranilic acid in polyphosphoric acid [234,235], which takes place via the formation of a phosphorylated intermediate, was examined in somewhat greater detail:



where



When the temperature is raised, the phosphorylated product dissociates:



The products thus formed contain free amino-groups and mixed anhydride groups, which facilitates the amidation reaction and is responsible for the possibility of both the homocondensation of bisanthranilic acids and their copolycondensation with dicarboxylic acids.

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The cyclisation and polycyclisation reactions in polyphosphoric acid constitute a comparatively new and rapidly developing field, which will undoubtedly enrich organic chemistry in new valuable experimental and theoretical data in the immediate future.

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