# Synthesis of *meso*-phenyl-substituted porphyrins as starting compounds for the preparation of porphyrin-containing polymers

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Data on the synthesis of symmetrical and unsymmetrical *meso*-phenyl-substituted porphyrins, which are building blocks for porphyrin-based polymers of different structure, are analyzed. Methods for the porphyrin ring construction and modification by active functional groups for further immobilization onto a polymer or preparation of porphyrin monomers are considered.

**Key words:** porphyrins, porphyrin polymers, polymers, pyrroles, aldehydes.

Among the enormous number of physiologically active compounds in natural systems, tetrapyrrole macrocycles occupy a special place. They participate in most important vital processes in the Earth such as plant and bacterial photosynthesis, breathing, enzymatic catalysis, sulfite and nitro reduction, methanogenesis, and so on.

At early stages of development of life, sea phytoplankton, bacteria, and blue-green algae served as the main sources of organic carbon, whereas nowadays organic carbon comes from various higher living organisms that live or vegetate in the Earth biosphere. An enormous number of tetrapyrrole pigments represented by various forms of porphyrins and chlorins are present in various biosphere layers. Natural tetrapyrroles include the well-known porphyrin derivatives: chlorophylls and bacteriochlorophylls, which accomplish plant and bacterial photosynthesis; hemes ensuring the electron transport and molecular oxygen storage; corrinoids whose functions are related to the transfer of methyl groups and isomerizations; siroheme ensuring sulfite and nitrite reduction; nickel-containing tetrapyrrole, factor F430, a methyl reductase system component functioning at the final stage of methanogenesis, *i.e.*, methane formation by methane forming bacteria, *etc.*[1—5]

Apart from chlorophyll and hemin structures, some animal organisms produce uro-, copro-, proto-, deutero-, and pemtoporphyrins, which differ from one another by the presence of various peripheral groups in the macrocycle.[6,7] Bioporphyrins encountered in the Earth are derivatives of these tetrapyrroles.

In all biologically important photosynthesis and breathing systems, porphyrin does not exist as an isolated unit but functions only within sophisticated complexes with monomeric or polymeric compounds. A strictly definite combination of the metal ion, macroheterocyclic ligand, and a specific environment of the biopolymer is the crucial factor for exhibiting the biological activity and selectivity of these compounds in living organisms.

The main function of porphyrin and its analogs in biological systems is to involve the metal into the macrocycle coordination site where it serves as the center of biochemical processes. Minor changes in the central metal atom, the porphyrin structure, or the macromolecular environment induce various biochemical reactions.[7]

Therefore, preparation of models of natural super- and supramolecular porphyrin-containing systems resembling natural ones is of enormous interest. Today science is far from fully reproducing biological processes but the use of ideas implemented in native processes opens up broad prospects for the design of model systems based on synthetic analogs of natural tetrapyrroles. The strive to prepare highly efficient and selective catalyst systems operating under as mild conditions as biocatalysts resulted in a vigorous growth of the number of publications devoted to the preparation of porphyrins and their analogs linked in different ways to surrounding polymer macromolecules.

Fixing of porphyrin on a polymer support offers a number of advantages over the use of free porphyrins. These include cooperative interactions in polymer chains, separation of the active sites, the possibility of specific binding of different substrates to active sites, an increase in the stability of the tetrapyrrole pigment, decrease in its toxicity with respect to biological media, and

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the appearance of solubility in a specified functioning medium.

Combination of the specific properties of polymers and porphyrins gives rise to a series of absolutely new trends in the use of these compounds. These are of obvious interest for solving many problems of biotechnology, biology, pharmacology, and medicine. New materials based on polymer-bonded porphyrins and their metal complexes can exhibit quite unusual properties, in particular, owing to introduction of the metal into the polymer macromolecule, which obviously will open up new prospects for their use.

The synthesis and study of various groups of polymer-bound porphyrins should appreciably affect the development of technology and medicine of the future and contribute to solution of the eternal mystery concerning the origin of living matter from nonliving matter.

Synthetic models of natural porphyrin-containing polymers can be formed by different types of bonding of porphyrin to the polymer support macromolecule, namely, covalent, ionic, or coordination bonding. In natural polymeric complexes, only one bonding type is usually present. Therefore, the mode of binding between the tetrapyrrole macrocycles and the polymer support is the most reasonable key classification feature for the systems formed by polymers and porphyrins. The main principle that underlies the synthesis of these compounds is restriction of porphyrin mobility upon linking to the polymeric matrix. In terms of this feature, one can distinguish two large groups of polymer-bonded systems: physically secured and chemically bonded porphyrins. Since the inevitable loss of porphyrin from the support surface during operation is an essential drawback of the former group, chemically bonded porphyrin polymers are of most interest. Classification of porphyrins linked to a polymer support by chemical bonds is given in Table 1.

From the standpoint of stability of polymer systems, specificity of their properties, and diversity of their applications, of most interest are porphyrins chemically bound to a polymer.[8] These systems can be divided into three fundamentally different groups:

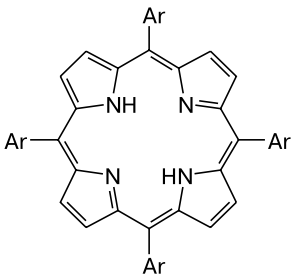
(I) polyporphyrins containing a tetrapyrrole fragment incorporated in the polymer backbone; the porphyrins or their analogs are connected through a comonomer or a linker;

(II) immobilized porphyrins having a porphyrin ligand in the polymer side chain connected to the support macromolecule through ionic or covalent bond and separated from the backbone by a particular spacer;

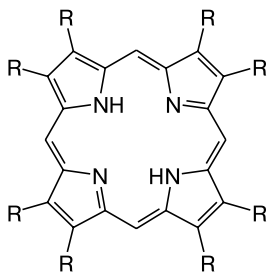
(III) coordination porphyrin polymers, which are formed only by metal porphyrins; they are connected into a polymer chain or to the polymer macromolecule through the coordination bond formed by the metal with a comonomer or polymer side groups possessing π-donor properties.

The advances in the preparative chemistry of macrocycles[9,10] have opened up synthetic routes to practically unlimited set of polymer-bonded porphyrins, as the enormous group of known porphyrins and their analogs is supplemented by the countless number of polymers with different composition, structure, and functional substitution. Currently, linear and cross-linked organic polymers and inorganic supports, in particular, silica gel and molecular sieves are widely used to bind porphyrins. Macrocyclic compounds, thus becoming a part of the polymer chain, a cross-linking fragment, or end groups, impart specific properties to the polymer. All three types of reactions used to produce polymers (polymerization, polycondensation, and polymer analogous transformations) can be successfully accomplished for the design of porphyrin polymers. The structure and properties of the resulting compound depend on the particular reaction that underlies the synthesis.

The extensive use of porphyrins in technology, engineering, and medicine is held up by poor availability of most porphyrins many of which are formed in very low yields. Therefore, of particular interest and topicality are the problems of chemistry of synthetic porphyrins. In this respect, porphyrins containing *meso*-aryl substituents, which can be subjected to various chemical transformations are especially attractive. Currently, the properties of natural porphyrins are mainly mimicked using their synthetic analogs, namely, *meso*-tetraphenylporphyrins **1**, which are easily obtained by condensation of commercially available pyrrole with benzaldehydes. However, in some cases, they are not appropriate, as, unlike natural porphyrins, they are devoid of alkyl or pseudoalkyl substituents in the β-positions of the porphyrin ring but, conversely, contain substituents in the *meso*-positions. Meanwhile, rather easily available octaalkylporphyrins **2** are also not always appropriate, as they contain no reactive groups that can be modified in order to impart specified physicochemical properties to them. Therefore, attention is attracted to porphyrins that combine the advantages of these two classes, *e.g.*, 5,15-diaryloctaalkylporphyrins **3** and 5-aryloctaalkylporphyrins **4**. These porphyrins are usually prepared by condensation of α-unsubstituted linear pyrrole derivatives with benzaldehydes.

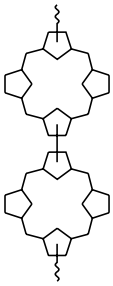
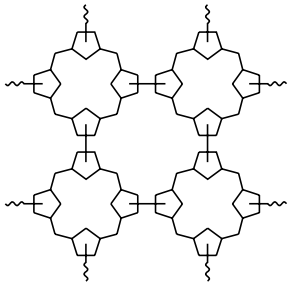
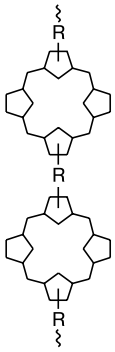
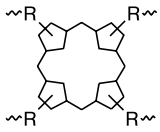


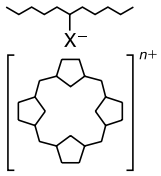
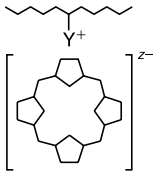
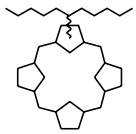
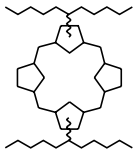
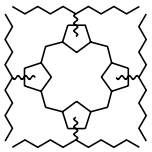

**1**

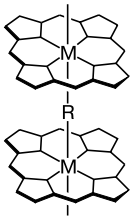
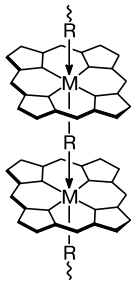
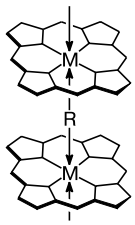
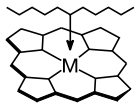
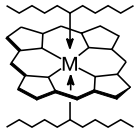


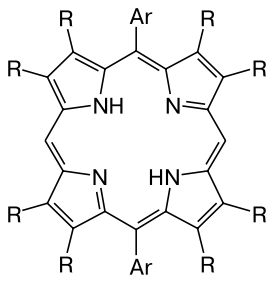

**2**

**Table 1.** Structural types of chemically bonded porphyrin polymers

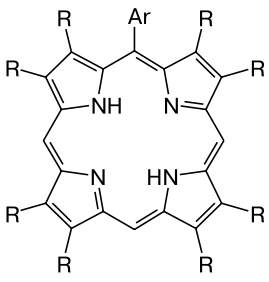
| **Polyporphyrins** | | | |
|---|---|---|---|
| Homopolymers | | Copolymers | |
| Linear | Network | Linear | Branched |
|  |  |  |  |

| **Immobilized porphyrins** | | | | |
|---|---|---|---|---|
| Ionic | | Covalently bonded | | |
| Cationic | Anionic | Linear | Cross-linked | Network |
|  |  |  |  |  |

| **Coordination polymers** | | | | |
|---|---|---|---|---|
| Covalently bonded | Covalently coordinatively bonded | Coordinated | Coordinatively added | Coordinatively cross-linked |
|  |  |  |  |  |



**3**



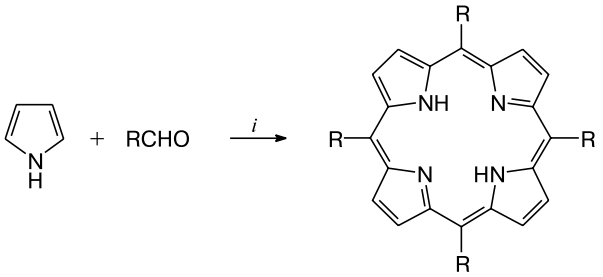
**4**

## 1. Synthesis of *meso*(5,10,15,20)-tetrasubstituted porphyrins

*meso*-Tetrasubstituted porphyrins were first prepared by the reactions of pyrrole with aldehydes[11] (Scheme 1). The condensation of acetaldehyde with pyrrole afforded *meso*-tetramethylporphin (**5a**, R = Me) in a low yield, and condensation of pyrrole with formaldehyde gave porphin (**5b**, R = H) in a negligible yield of 0.03% (see Ref. 12). In subsequent studies,[12,13] the yield of porphyrins

was substantially increased by performing the reaction in pyridine in a sealed tube at 140—240 °C (Rothemund method). The condensation of pyrrole with benzaldehyde furnished *meso*-tetraphenylporphin (**$H_2$TPP** (**5c**), R = Ph), which was formed in rather high yield and could be easily isolated from the reaction mixture.[13]

**Scheme 1**




**5a—c**

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

*i*. 140—240 °C.

Later it was shown[14,15] that the yield of **$H_2$TPP** increases upon addition of zinc acetate to the reaction mixture. Zinc tetraphenylporphin (**ZnTPP**) thus formed is then treated with a mineral acid to be converted into free porphyrin. However, the yield of **$H_2$TPP** did not exceed 18% even under these conditions, which are optimal for condensation in pyridine.

Currently, 2,4,6-trimethylpyridine (collidine)[16,17] and quinoline having higher boiling points (171 and 237 °C) than pyridine (115 °C) are also used as the reaction media. As a result, the reaction can be carried out under atmospheric pressure and on contact with atmospheric oxygen as the oxidant.

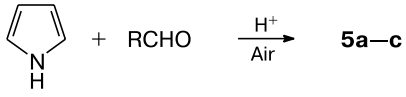
According to the Rothemund method, the reaction is carried out at high reactant concentrations (more than 1 mol $L^{-1}$), but the relatively low yield of *meso*-substituted porphyrins restricts the scope of its application. The high-temperature synthesis methods have now been modified, which in some cases allows one to avoid the use of a solvent. Thus heating of a mixture of pyrrole with benzaldehyde in the presence of a metal salt in a sealed tube at 150—250 °C without a solvent affords **$H_2$TPP** in a yield higher than 50% (see Ref. 18). Microwave irradiation of a mixture of pyrrole, benzaldehyde, and silica gel or zeolite followed by chromatographic separation gives rise to **$H_2$TPP** in a yield reaching 9% (see Refs 19—21). The injection of pyrrole into a tube containing aldehyde in the gas phase (200—250 °C) under air gives some *meso*-substituted porphyrins in a yield of up to 23% (see Ref. 22).

Recently it has been reported[23] that tetraphenylporphins are formed in yields of more than 20% when the condensation is carried out in boiling 2,4,6-trichlorophenol under air at reactant concentrations of about 0.6 mol $kg^{-1}$. In addition, manganese complexes of many (even di-*ortho*-substituted) tetraphenylporphyrins are produced in a yield more than 50%, which implies a template effect on the manganese(II) ion.

It is noteworthy that the synthesis of *meso*-substituted porphyrins in basic media, which has been undeservingly neglected in recent years due to the prevalence of acid catalysis, has its own specific applications. In particular, this is unexpendable for the synthesis of compounds containing acid-labile groups or heterocyclic residues (*e.g.*, furan or pyrrole ones).

Long-term refluxing of a mixture of pyrrole with benzaldehyde in a methanol—pyridine solvent resulted[13,24] in **$H_2$TPP** in a moderate yield. Study of the effect of various substituents has shown[25,26] that the condensation is catalyzed more efficiently by acids than by bases. Upon refluxing of reactants in acid-containing aerated organic solvents, the yield of **$H_2$TPP** estimated by spectrophotometry reaches 40% (see Ref. 25). Now the pyrrole condensation with aldehydes (Scheme 2) in acid media on contact with air is a key method for the synthesis of *meso*-substituted porphyrins (Adler method). The acidic solvents used most often include acetic acid,[25,27] propionic acid,[28,29] and mixed solvents including pyridine—acetic acid,[26] benzene—chloroacetic acid,[25] toluene—*p*-toluenesulfonic acid,[30] xylene—chloroacetic acid,[31—33] and some other. The process is usually carried out at the boiling point of the solvent, in some cases, with air being passed through the reaction mixture.[26] It was shown[34] that the yield of porphyrins depends on the temperature of the reaction medium, the highest yields being observed at ~140 °C. At lower temperatures, the rate of porphyrin formation is low, while at higher temperatures, the rate of oxidation of the porphyrins formed is too high. The optimal concentration of the reactants in the mixture is about 0.2—0.4 mol $L^{-1}$.

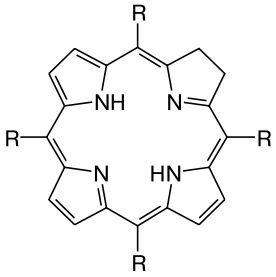
**Scheme 2**




In modern versions of the Adler method, the synthesis is carried out in the DMF—$AlCl_3$ or DMSO—$AlCl_3$ system (the yield of **$H_2$TPP** is 30%)[35] or in propionic acid under microwave irradiation (the yield of *meso*-tetraarylporphyrins is 20—43%).[36] The reaction of 4-methoxybenzaldehyde with pyrrole in propionic acid containing 30% nitrobenzene as an oxidant at 120 °C furnishes the corresponding porphyrin in 45% yield.[37] In the case of

other aromatic aldehydes, the product yields were 5—20% (see Refs 37, 38).

It should be noted that together with porphyrins, the acid-induced condensation yields the corresponding chlorins **6**, which in some cases become the major reaction products.[39] Nevertheless, they can be readily converted into the corresponding porphyrins by treatment with benzoquinone derivatives: *p*-chloranil or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[40—43]



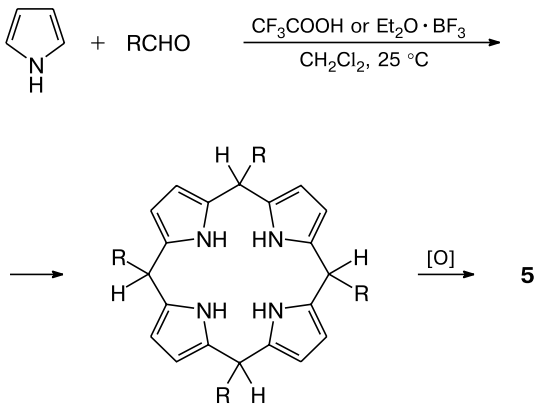

**6**

The use of a valeric acid—nitrobenzene system at 160 °C for the condensation of pyrrole with benzaldehydes allows a pronounced increase in the yield of porphyrins free of chlorins.[44]

The Adler method has proved itself excellent for the synthesis of porphyrins on a preparative scale from relatively stable aldehydes. The possibility of easy and fast preparation of porphyrins in ~20% yield at reactant concentrations of up to 0.4 mol $L^{-1}$ makes the Adler method fairly convenient. The use of the Adler method is limited in the synthesis of *meso*-substituted porphyrins from aldehydes containing substituents unstable in the presence of acids at high temperatures and many 2,6-disubstituted benzaldehydes and aliphatic aldehydes.

Quite recently, a new method for the synthesis of *meso*-substituted porphyrins under mild conditions has been proposed;[45,46] the method consists in condensation of pyrrole with aldehydes in chloroform or dichloromethane in the presence of trifluoroacetic acid (TFA), or boron trifluoride etherate under inert atmosphere at room temperature (Scheme 3). Porphyrinogens **7** formed initially are further oxidized (without isolation) with a stoichiometric amount of DDQ or *p*-chloranil[45,46] or with hydrogen peroxide in acetic acid.[47] *meso*-Alkyl-substituted porphyrinogens, which are more resistant against oxidation, can be converted into porphyrins by photochemical methods.[37]

**Scheme 3**




**7**

It was found that[45] the reaction is sensitive to the reactant concentration. The highest yields of **$H_2$TPP** (35—40%) are formed upon the reaction of 10 *mM* benzaldehyde and 10 *mM* pyrrole, and the yield is approximately halved when the reactant concentrations are 100 mmol $L^{-1}$ and 1 mmol $L^{-1}$. The loss caused by higher reactant concentrations can be partly counterbalanced by increasing the amount of acid catalyst. For example, with benzaldehyde and pyrrole concentrations of 100 mmol $L^{-1}$ and in the presence of 1, 3.2, and 10 *mM* $BF_3$ etherate as the catalyst, the yields of **$H_2$TPP** were 23, 30, and 29%, respectively. These values are still lower than the yield of 35—40% obtained with concentrations of each reactant equal to 10 mmol $L^{-1}$ in $CH_2Cl_2$ and with $BF_3$ etherate or TFA as the catalyst.[48] The reaction is also sensitive to the nature of the acid catalyst: when the concentration of each reactant is 10 *mM*, boron trifluoride etherare is efficient in 1 *mM* concentration, while TFA is required in a higher concentration (20—50 mmol $L^{-1}$).[45] It was shown that sodium or ammonium chloride additives significantly increase the yield of porphyrins.[49,50]

Using tetra(mesityl)porphin (**$H_2$TMP (5d)**, R is 2,4,6-trimethylphenyl) as an example,[51—53] it was shown that the synthesis of tetraphenylporphyrins containing electron-donating substituents in both *ortho*-positions of the phenyl ring requires the use of $BF_3$ etherate as the catalyst and ethanol (0.75%) as the co-catalyst. This method is suitable for the preparation of **$H_2$TMP** in multigram scale.[54,55] Apart from ethanol, ethylene glycol, 2-methoxyethanol,[53] or methanol[56] can be used as co-catalysts for the synthesis of **$H_2$TMP** and related porphyrins. No co-catalysts are needed for the synthesis of tetraphenylporphyrins containing electron-withdrawing groups in both *ortho*-positions of the phenyl rings. The use of 2,2-dimethoxypropane as the dehydrating agent also increases the yield of **$H_2$TMP.**[56]

The method was further developed by using air oxygen as the oxidant for porphyrinogen and iron phthalocyanine and *p*-chloranil as the catalysts.[49] In this case, the synthesis can be carried out at high reactant concentrations, which makes it suitable for large-scale syntheses,[57] despite moderate yields of products.

Mild reaction conditions employed in the condensation and oxidation stages make the Lindsey method applicable for a broad range of aldehydes and for the synthesis of sterically hindered porphyrins[52,55,58] and *meso*-alkylporphyrins,[59,60] which are poorly accessible by other methods. The yield of porphyrins can reach 50% depending on the aldehyde nature. Currently this method is used most often for the preparation of *meso*-substituted porphyrins.

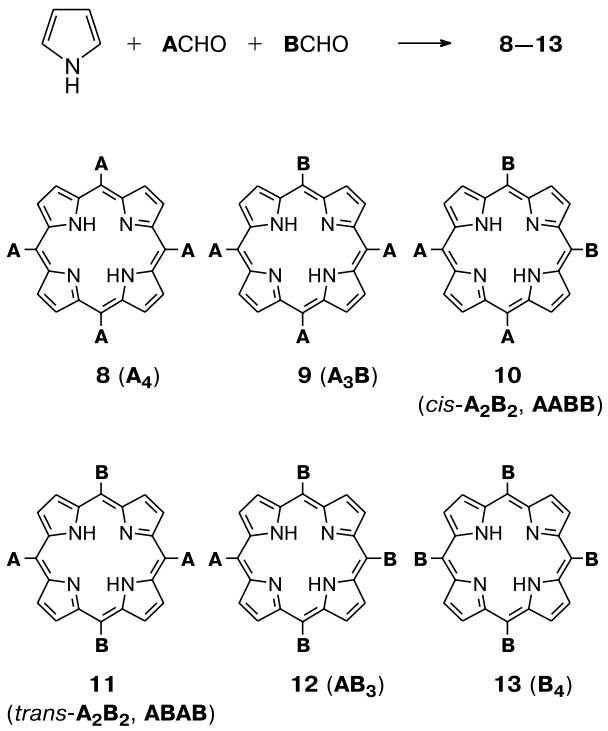
There exist a number of modifications of this method, in particular, the use of montmorillonite and related clays as the condensation catalysts.[20,21,61,62] The activity of clays is attributable to their porosity rather than acidity and their efficiency as condensation catalysts is interpreted as being due to stabilization of porphyrinogens in clay nanotubes.[21,63] For the synthesis of porphyrins with polar groups, which are formed in low yields by the Lindsey method,[45,64] a micellar synthesis was proposed[65] according to which condensation is carried out in a HCl(aq) containing dodecyl sulfate serving as a surfactant and then the reaction mixture is oxidized with a solution of *p*-chloranil in THF. This procedure is suitable for preparing tetraphenylporphins containing carboxy, hydroxy, acetamido, ether, and ester groups in phenyl rings.

The Lindsey method implies fairly mild reaction conditions. The yields are, most often, higher than in the Adler method, although the reaction at a reactant concentration of 0.01—0.1 mol $L^{-1}$ requires the removal of a large amount of the solvent at the product isolation stage and, in addition, a large amount of an expensive oxidant is required. The method is most applicable to aldehydes containing acid-sensitive substituents, 2,6-disubstituted benzaldehydes, aliphatic aldehydes, and poorly accessible expensive aldehydes (when high yields are significant).

The condensation of aldehyde with pyrrole gives porphyrin having four identical *meso*-substituents. However, the synthesis of polymer porphyrins often requires the presence of different substituents in the *meso*-positions of the porphyrin ring. A simple approach to this goal is so-called mixed-aldehyde condensation (Scheme 4). The reaction of pyrrole with a mixture of two aldehydes affords a mixture of six porphyrins **8—13**, which can be separated by thin layer chromatography[66] or, in the case where one aldehyde contains a polar group, column chromatography.[67]

The expected ratio of porphyrins formed upon mixed-aldehyde condensation is specified by binomial distribution. For 1 : 1 aldehyde ratio, the distribution is as follows: $\mathbf{A_4}$, 6.25%; $\mathbf{A_3B}$, 25%; *cis*-$\mathbf{A_2B_2}$, 25%; *trans*-$\mathbf{A_2B_2}$, 12.5%; $\mathbf{AB_3}$, 25%; $\mathbf{B_4}$, 6.25%. This outcome implies equal reactivity of both aldehydes at any stage of porphyrin formation. The porphyrins $\mathbf{A_3B}$ are prepared most often by mixed-aldehyde condensation. The highest yield of the porphyrin $\mathbf{A_3B}$ is obtained for the initial aldehyde ratio **A** : **B** = 3 : 1, namely, $\mathbf{A_4}$, 31.64%; $\mathbf{A_3B}$, 42.19%; *cis*-$\mathbf{A_2B_2}$, 14.06%; *trans*-$\mathbf{A_2B_2}$, 7.03%; $\mathbf{AB_3}$, 4.69%; $\mathbf{B_4}$, 0.39%. A higher content of aldehyde **A** increases the yield of porphyrin $\mathbf{A_4}$ with decreasing absolute quantity of porphyrin $\mathbf{A_3B}$. However, the aldehyde ratio providing the highest isolated yield of porphyrin $\mathbf{A_3B}$ depends on the actual reactivities of these aldehydes and on the ease of separation of the porphyrin mixture.[68] If a mixture of highly polar, poorly accessible aldehyde and a low-polarity cheap aldehyde is used for the preparation of porphyrins $\mathbf{AB_3}$, it is expedient to take a large excess of the latter aldehyde in order to ensure a fuller conversion of the former one. This mainly yields symmetrically substituted porphyrin $\mathbf{B_4}$, which, however, can be readily separated from porphyrin $\mathbf{AB_3}$ by chromatography.[69—71] Using this method, a number of dimeric porphyrins connected by various spacers through *meso*-positions have been prepared.[71—76]

**Scheme 4**




The reactivities of aldehydes in mixed-aldehyde condensation are, most often, sharply different. Therefore, best suited for these syntheses is the Lindsey method or the modified Adler method in which the first stage is carried out in the absence of air oxygen, in order to avoid the oxidation of porphyrinogen formed by more reactive aldehyde and to attain equilibrium between porphyrinogens, which is specified by the ratio of initial aldehydes.

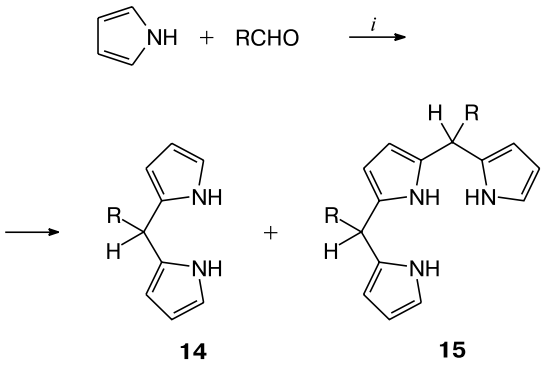
In some cases, the reaction is carried out with two aldehydes of similar reactivities or with aldehydes stable under the reaction conditions and, subsequently, the substituents are modified to attain the desired polarity or structure.[20,77,78]

Aldehydes that do not form themselves *meso*-tetrasubstituted porphyrins often serve as components of mixed-aldehyde condensation.[79—81]

A more promising method for the synthesis of asymmetrical *meso*-tetrasubstituted porphyrins implies the use of pre-synthesized *meso*-substituted dipyrrolylmethanes **14**. The condensation of unsubstituted pyrrole with aldehydes results in a mixture of various products:

dipyrrolylmethanes **14**, tripyrranes **15**, bilanes, cyclic porphyrinogens **7**, and higher linear and cyclic oligomers. However, the use of a substantial excess of pyrrole allows the reaction to be terminated after the formation of *meso*-substituted dipyrrolylmethanes **14** (Scheme 5). A large number of methods was proposed for direct condensation leading to dipyrrolylmethanes.[82—94] As the condensation catalyst, TFA or $BF_3$ etherate is used most often; the reaction is carried out at room temperature in solution or without a solvent. The removal of excess pyrrole *in vacuo* gives dipyrrolylmethane, which is purified by recrystallization,[87] chromatography,[87] or sublimation.[86,95] The isolation of the corresponding tripyrrane **15** from crude dipyrrolylmethane was also reported.[95]

**Scheme 5**




*i*. TFA or $Et_2O \cdot BF_3$.

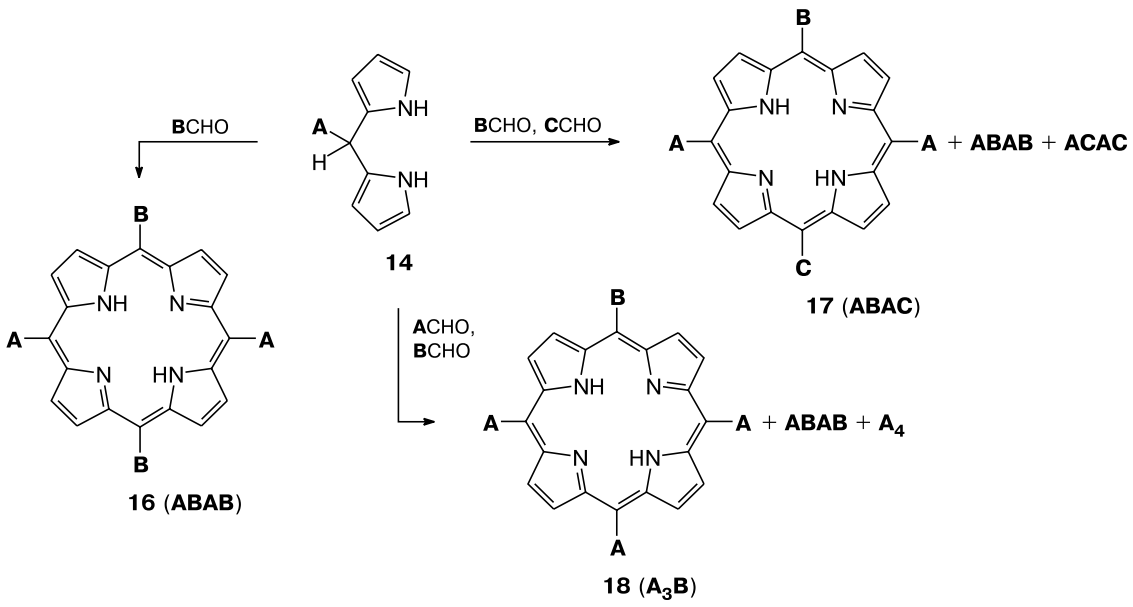
The condensation of *meso*-substituted dipyrrolylmethane **14** with aldehydes results in *meso*-tetrasubstituted porphyrins *trans*-**ABAB 16** (see Refs 96—98). Using two different aldehydes in the condensation, one can obtain porphyrin **ABAC 17**; however, in this case, **ABAB** and **ACAC** are also formed as by-products (see Refs 89,99—101). If one of the aldehydes has a substituent identical to the dipyrrolylmethane substituent, porphyrin $\mathbf{A_3B}$ **18** is mainly formed (see Refs 102—104) (Scheme 6).

The condensation of a mixture of two different *meso*-substituted dipyrrolylmethanes with an aldehyde similar to one of the *meso*-substituents of dipyrrolylmethane affords mainly porphyrin $\mathbf{A_3B}$ **18**, while condensation of an aldehyde with a different substituent gives porphyrin **ACBC 19** (Scheme 7). In both cases, other porphyrins are also formed; they can be separated by chromatography if substituents contain polar groups.

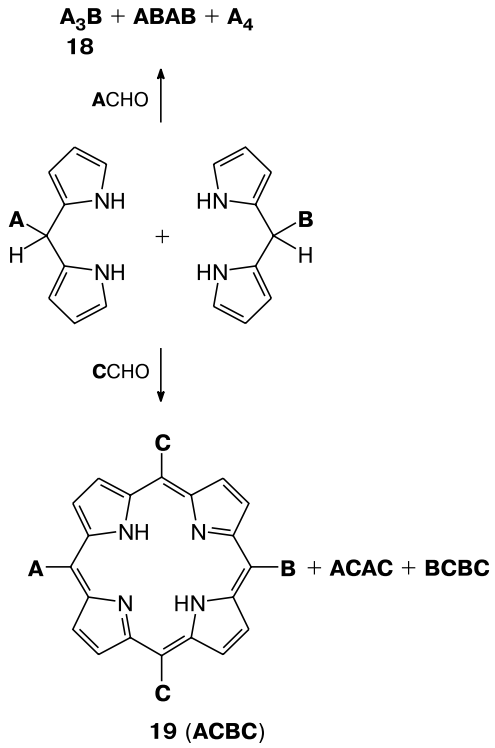
It is noteworthy that only the low-temperature Lindsey method is suitable for syntheses of this type, because heating of *meso*-substituted dipyrrolylmethanes in acid media induces rearrangements and, hence, the subsequent oxidation yields complex product mixtures (Scheme 8).

However, it was shown[105] that condensation carried out in propionic acid in the presence of zinc acetate affords individual *trans*-porphyrin **16**, which may be due to oxidation taking place before ring closure. This reaction carried out by the two-stage Lindsey method gives a mixture of porphyrin isomers, although in a high yield.[102,105]

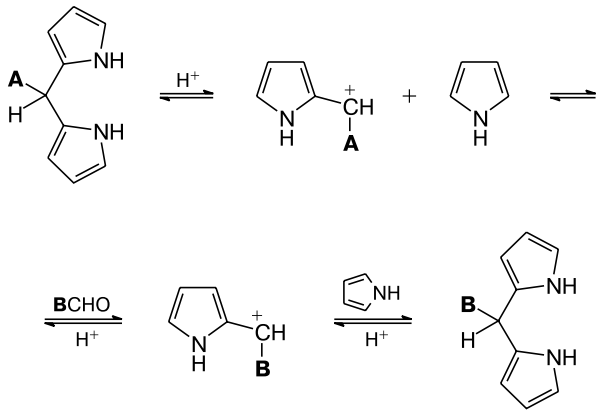
**Scheme 6**



**Scheme 7**




**Scheme 8**

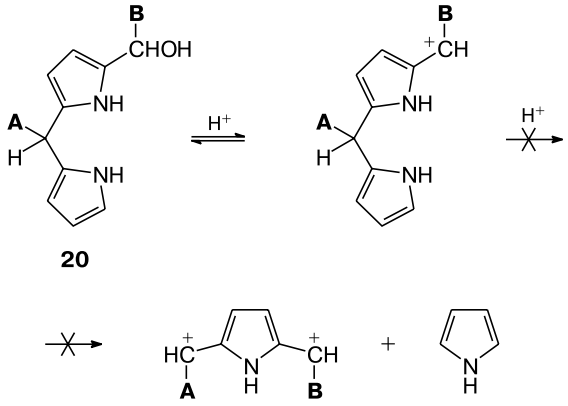



Dipyrrolylmethanes having sterically hindered or perfluoroalkyl substituenrts in *meso*-positions are most stable against acidolysis.[106,107]

Acidolysis can be avoided by using *meso*-substituted 2-hydroxymethyl-5-(pyrrolylmethyl)pyrroles **20** (instead of an aldehyde and dipyrrolylmethane mixture), because in this case, no unstabilized dicarbocation is formed (Scheme 9).

Scheme 10 shows some possible routes for using substituted 2-hydroxymethyl-5-(2-pyrrolylmethyl)pyrroles **20** and analogous diols **21** for the synthesis of unsymmetrical

**Scheme 9**




*meso*-tetrasubstituted porphyrins of various types. Of particular interest is the last route, which may afford fully unsymmetrical *meso*-tetrasubstituted porphyrins **22** (see Refs 106—108).

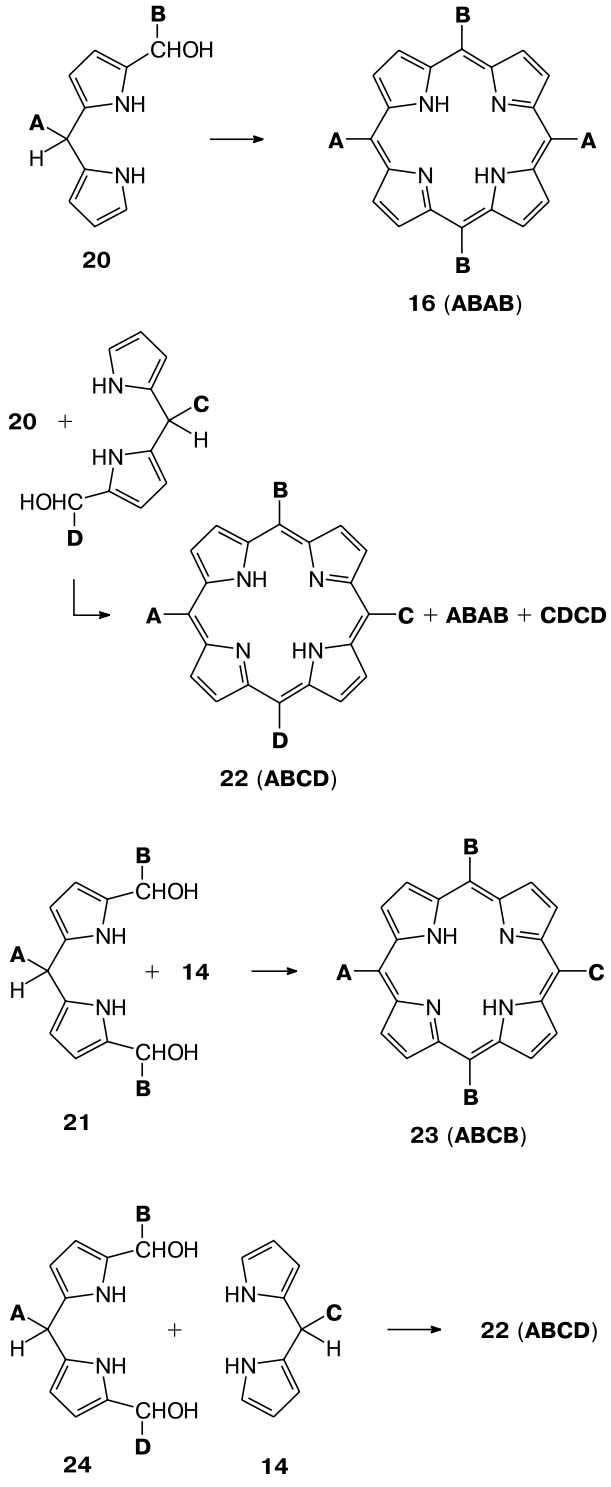
Apart from pyrrole, 3,4-disubstituted pyrrole derivatives can condense with aldehydes to give, after oxidation, *meso*-tetra-β-octasubstituted porphyrins containing a distorted porphyrin ring due to steric interaction of the substituents in the neighboring *meso*- and β-positions[109,110] (Scheme 11).

Currently, numerous data demonstrate that the porphyrin macrocycle is rather flexible and can exist in nonplanar conformations.[111—113] These properties of porphyrin molecules are under extensive research, because distortion of the porphyrin ring can play a significant role in biological photosynthetic and redox systems;[114—116] in addition, the conformational distortions of the porphyrin chromophore can serve as a tool for fine tuning of its physicochemical properties.

Note the difference between hindered and distorted porphyrins. A specific feature of the former is that the central cavity of the porphyrin molecule is shielded by bulky substituents from attacks by reagents. This steric hindrance markedly affects the reactivity of porphyrins but has little influence on their physical properties. Unlike these compounds, distorted porphyrins have a nonplanar, deformed macrocycle, which changes significantly their chemical and physical properties.

The methods for synthesis of dodecasubstituted porphyrins **25** differ little from those for tetraphenylporphins (see Scheme 11). These are mainly two known modifications of the method: pyrrole condensation with aldehyde in a boiling solvent containing an organic acid on contact with atmospheric oxygen (Adler method)[27,117,118] or condensation catalyzed by an acid or $BF_3$ etherate under mild conditions to give porphyrinogen, which is subsequently oxidized without isolation (or with isolation) to porphyrin with benzoquinone derivatives (Lindsey method).[119—125] Owing to high stability against oxidation, porphyrinogens

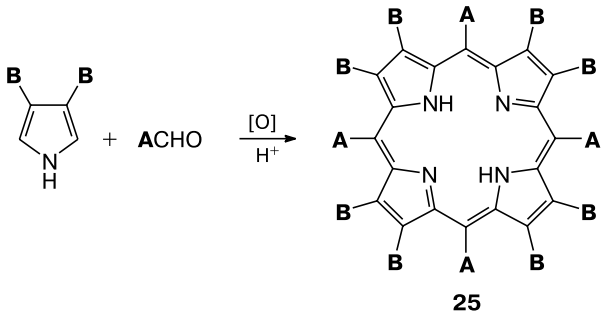
**Scheme 10**




can be isolated in a pure state and then oxidized to porphyrins.

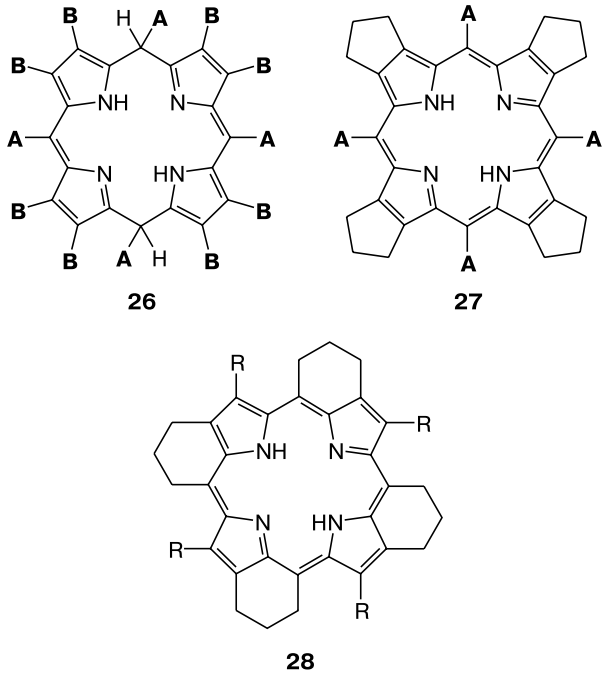
It was found[126–128] that a pronounced distortion of the porphyrin ring can be induced, in particular, by the presence of bulky substituents such as *tert*-butyl or adamantyl groups in the *meso*-positions in the absence of β-substituents in the ring.

**Scheme 11**




Distorted β-alkyl-substituted porphyrins **25** (**B** = Alk) are better formed upon condensation in acidified alcohol solvents followed by isolation of porphyrinogens and their subsequent oxidation with DDQ in THF. For the synthesis of β-arylporphyrins **25** (**B** = Ar), the condensation should be carried out in boiling acetic acid and porphyrinogen should either be oxidized without isolation by refluxing with DDQ or should be isolated and then oxidized also with DDQ in boiling toluene. The use of the Lindsey method[125,129] is justified for the synthesis of porphyrins **25** with *o*,*o*′-disubstituted phenyl groups in the *meso*-positions.

The condensation of 3,4-dialkylpyrrole with aliphatic aldehydes and the subsequent oxidation of the reaction




**A**, **B** = Alk

mixture with benzoquinone derivatives does not give distorted dodecaalkylporphyrins but stops after the formation of porphodimethenes **26** (see Ref. 124). In this case, distortion of the macrocyclic core is so pronounced that the oxidation potential of the oxidants used does not suffice for aromatization. Conversely, almost nondistorted porphyrins **27** and **28** are formed in high yields.[124,130]

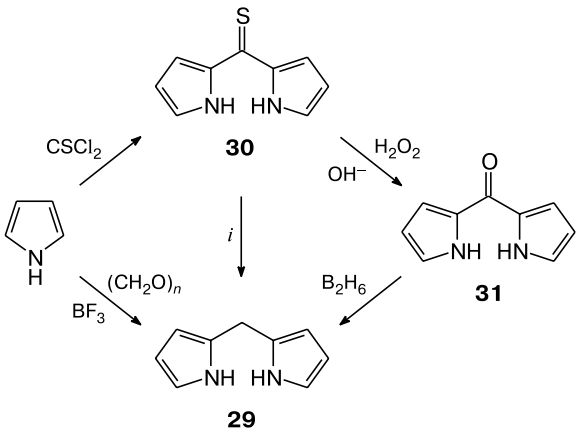
### 2. Synthesis of *meso*(5,15)-disubstituted porphyrins

5,15-Diphenylporphyrin and its β-alkyl-substituted analogs are of interest by the fact that they combine structural features of 5,10,15,20-tetraphenylporphyrin and porphin (or, correspondingly, β-alkylporphyrins). Note that these porphyrins are not as poorly accessible as the fully unsubstituted initial porphin.

Symmetrical octaalkylsubstituted 5,15-diphenylporphyrins **3** (*trans*) have been rather long known, while their β-unsubstituted analogs were described only recently when unsubstituted dipyrrolylmethane **29** (see Refs 26, 83, 131, 132) and *meso*-phenyldipyrrolylmethanes **14** (see Ref. 87, 131, 133) had become available.

Dipyrrolylmethane **29** containing neither *meso*- nor β-substituents is prepared in three stages from pyrrole and thiophosgene *via* thioketone **30**, which is treated with hydrogen peroxide in an alkaline medium to be converted into ketone **31**,[134] which is reduced to **29** with diborane in an overall yield of about 40% (see Ref. 132, 135) (Scheme 12).

**Scheme 12**

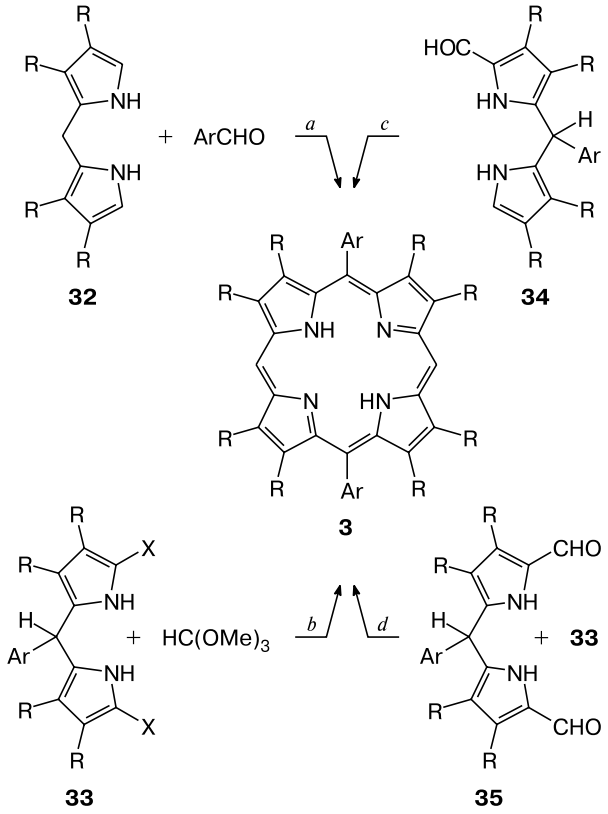



*i*. Ni or $NaBH_4$.

Recently, it was found that compound **29** can be prepared by direct desulfurization of thioketone **30** with Raney nickel or sodium borohydride.[131] In addition, condensation of paraformaldehyde with excess pyrrole in the presence of $BF_3$ etherate or TFA, resulting in dipyrrolylmethane **29** in a 40% yield in one stage, was accomplished on a moderate scale (see Refs 136, 137).

Considering structural features of *meso*(5,15)-disubstituted porphyrins, several possible pathways for their synthesis can be proposed (Scheme 13). All these methods have been tested for the synthesis of *trans*-substituted porphyrins but pathways *a* and *b* (see Scheme 13) are most applicable, as pathways *c* and *d* require an additional stage to prepare formyldipyrrolylmethanes. However, pathway *d* allows the synthesis of porphyrins unsymmetrically substituted in the phenyl rings without formation of other porphyrin by-products.

**Scheme 13**

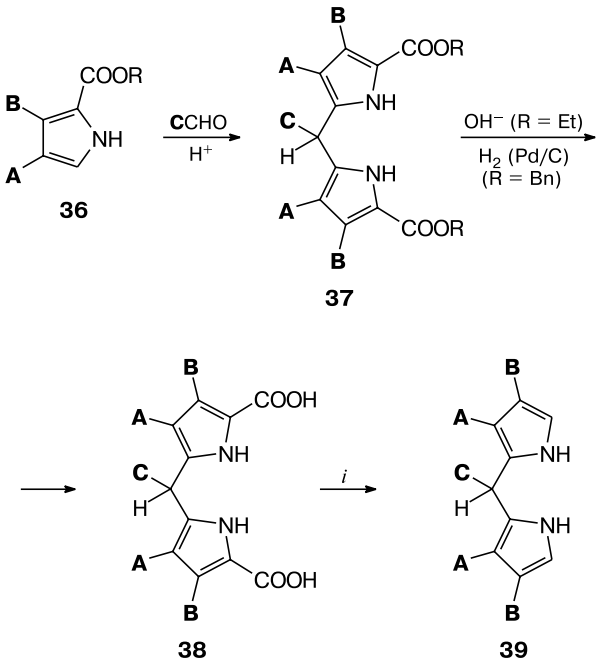



It is noteworthy that β-substituted dipyrrolylmethanes used for the preparation of 5,15-substituted porphyrins along pathways *a*, *b*, and *d* should have a symmetrical substitution pattern with respect to the *meso*-carbon atom; otherwise, two isomeric porphyrins are formed.

β-Substituted dipyrrolylmethanes **39** symmetrical relative to the *meso*-carbon atom are prepared by acid-catalyzed condensation of aldehydes with pyrroles **36** in which one α-position bears a good leaving group (usually, ethoxy- or benzyloxycarbonyl group)[105,138,139] (Scheme 14). This is followed by the removal of protect-

ing groups by either alkaline hydrolysis of **37** (R = Et) or hydrogenolysis of **37** (R = Bn)[132] with subsequent decarboxylation of diacids **38** by heating in high-boiling solvents such as ethylene glycol,[105] ethanolamine, DMF,[132] or diethylformamide.[140,141] In the case of ethyl esters **37** (R = Et), the protecting group can be removed in one stage by heating the compound in an alkaline aqueous solution in a sealed tube at 180 °C (see Ref. 142) or by refluxing in alkaline ethyene glycol under inert atmosphere.[143]

**Scheme 14**

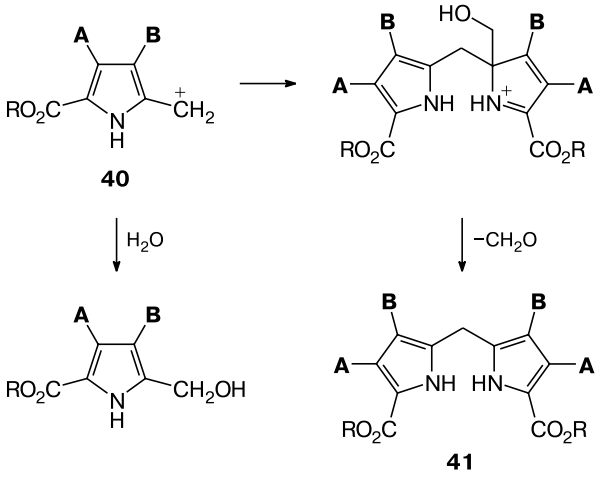



*i*. Heating or refluxing.

Symmetrical *meso*-unsubstituted dipyrrolylmethanes **41** are prepared by self-condensation of pyrrolylmethyl cations **40** in binary solvents containing water for the removal of formaldehyde[66,144,145] (Scheme 15). The products are formed in a nearly quantitative yield.

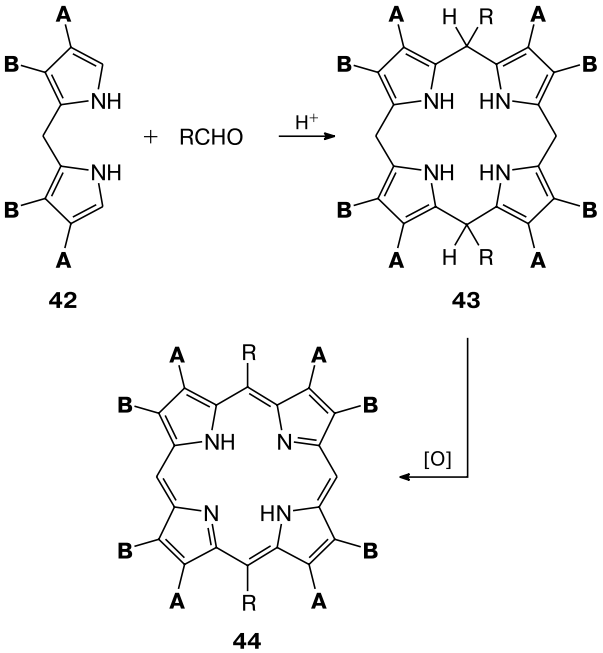
The method used most widely for the synthesis of 5,15-diphenylporphyrins **3** is based on condensation of α,α′-unsubstituted dipyrrolylmethanes **32** with aldehydes in the presence of an acid (see Scheme 13, pathway *a*) and is similar to the method of synthesis of *meso*-tetraphenylporphins. The condensation of dipyrrolylmethane **32** (R = Et) with aromatic aldehydes in benzene containing a catalytic amount of TFA and oxidation by air oxygen gave *trans*-substituted porphyrins **3** in 30—40% yield and traces of monoarylporphyrins **4**. Conversely, refluxing of these reactants in propionic acid in the presence of zinc acetate resulted in only monoarylporphyrins **4** in 15—25% yield.[146]

**Scheme 15**




Originally, the synthesis was carried out under conditions similar to those used in the one-stage synthesis of tetraphenylporphins in acidified solvents;[26] however, later it was shown[147] that the best results are attained by using the two-stage method with isolation of the intermediate porphyrinogen **43** followed by its oxidation to porphyrin **44** with benzoquinone derivatives (Scheme 16).

**Scheme 16**



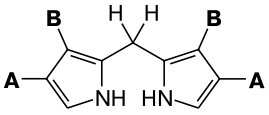

Thus 5,15-diarylporphyrins **44** were prepared in up to 60% yields starting from tetraalkyldipyrrolylmethanes **42** (**A**, **B** = Me, Et) and benzaldehydes.[147—151]

A study of the conditions of this reaction in methanol with organic acid additives[150] showed that the yield of

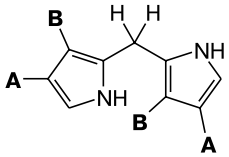
diphenylporphyrins hardly depends on the nature of the acid used ($CF_3COOH$ or $CCl_3COOH$); however, the rate of the process markedly decreases on moving from trifluoroacetic to benzoic acid.

The condensation and oxidation stages can be carried out in dichloromethane or chloroform, similarly to the Lindsey method for *meso*-tetraphenylporphins, without isolation of intermediate porphyrinogens. In this case, it is possible to use rather high reactant concentrations (as opposed to the Lindsey method). Studies have shown that the reaction should better be carried out in chloroform with the addition of chloro- or trichloroacetic acid followed by oxidation of the reaction mixture with *o*-chloranil, *p*-chloranil, or DDQ.[152]

The effect of the length of the alkyl substituent in the starting dipyrrolylmethanes **42** on the yield of 5,15-diphenyloctaalkylporphyrins **44** has been investigated.[143] The presence of small substituents in positions 3, 3′ of dipyrrolylmethane (**B** = H, Me, Et; **A** = H, Me) affects only slightly the porphyrin yield but the presence of more bulky groups (**B** = Pr, Bu, *n*-$C_5H_{11}$, *n*-$C_6H_{13}$, and especially Bn; **A** = Me) substantially reduces the yield. These facts indicate that bulky 3, 3′-substituents in dipyrrolylmethanes prevent the substrate molecule from acquiring the proper conformation **42a**. In this case, the molecules mainly exist in the energetically more favorable transoid conformation **42b**.




**42a**



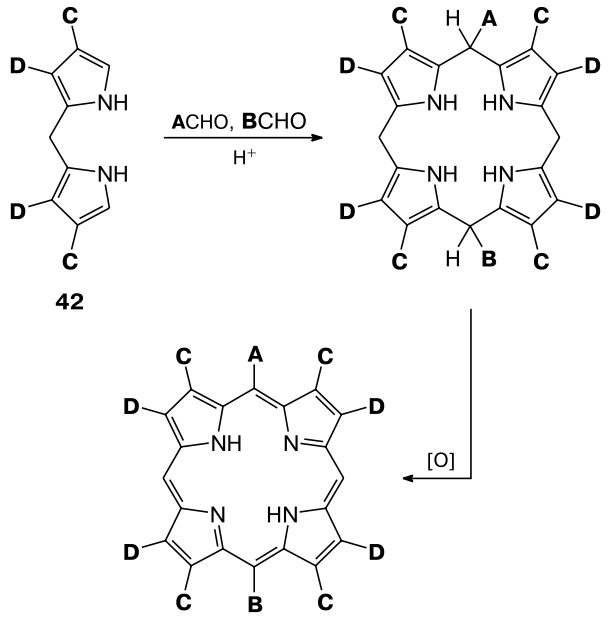

**42b**

The introduction of a methyl group in positions 4 and 4′ of dipyrrolylmethane **42** (**A** = Me) has little influence on the yield of porphyrin **44** (the yield even somewhat increases); however, in the case of the ethyl group (**A** = Et), steric restrictions result in a lower yield.

On going from formaldehyde to acetaldehyde, the yield of porphyrins **44** significantly increases. Transition to benzaldehyde has little influence on the yield. The electronic nature and the positions of substituents also have little influence on the yield of porphyrins **44**, except for the case where two substituents occur in both *ortho*-positions of the phenyl ring, which results in a pronounced reduction of the yield.[143]

The condensation of a mixture of two aldehydes affords three porphyrins (Scheme 17); from statistical considerations, the theoretical yield of the unsymmetrical product **45** is 50%. This mixture can be separated much more easily than the mixture of six porphyrins formed upon the condensation of two aldehydes and pyrrole (see Scheme 4), which accounts for the wide use of this method.[153—159] It is noteworthy that in some cases, it is expedient to take a large excess of one, more readily accessible aldehyde in order to utilize more fully the other aldehyde.[160,161]

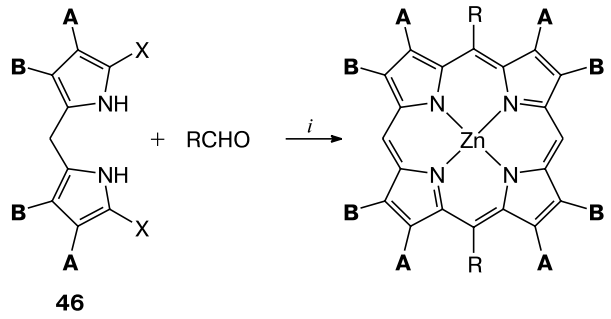
**Scheme 17**




As noted above, the reaction (see Scheme 13, pathway *a*) is complicated by yielding monophenylporphyrin by-products due to partial rearrangement of dipyrrolylmethanes or intermediate tetrapyrroles in an acid medium.[147] In some cases, monophenylporphyrins become the major or even the only reaction products, especially at high temperature.[143,146,147]

For eliminating the undesirable rearrangements, of considerable interest is the use of a method similar to the Rothemund method for the synthesis of diphenylporphyrins **44**. The method includes condensation of dipyrrolylmethanes **46** with aldehydes in high-boiling heterocyclic solvents (pyridine, quinoline, collidine) in the presence of coordinating agents (zinc acetate) (Scheme 18).[162] When pyridine is used, the process is carried out at 180 °C under a pressure with nitrobenzene as the oxidant; with higher-boiling quinoline, it is possible to perform the reaction under reflux on contact with air. The yields of phenyl-substituted porphyrins in this process are 10—20%; however, this method rules out the acid-induced rearrangements and allows the use of more oxidation-resistant and readily accessible α,α′-dicarboxydipyrrolylmethanes **46** (X = COOH), and, in addition, this method is of interest for performing condensations of acid-sensitive aldehydes.

**Scheme 18**

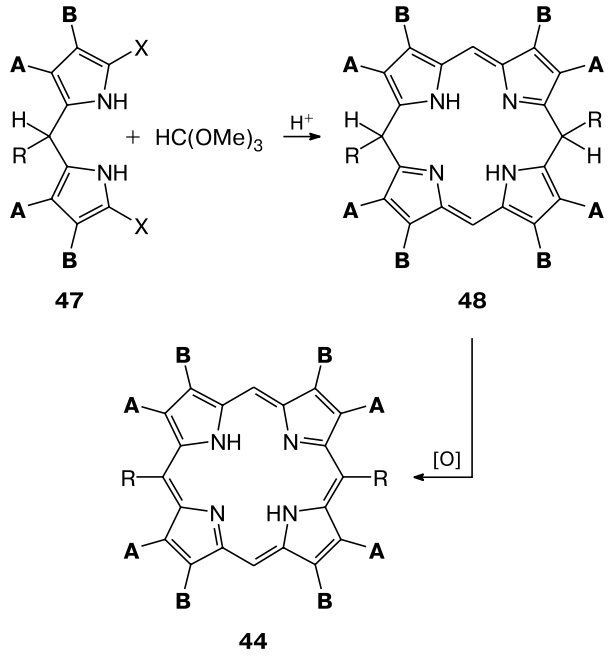



*i*. $Zn(OAc)_2$, pyridine, $PhNO_2$.

X = H, COOH

Yet another, most well-known method for the preparation of 5,15-diphenylporphyrins **44**, first used by Baldwin,[163] includes condensation of α,α′-unsubstituted or α,α′-dicarboxy-*meso*-substituted dipyrrolylmethanes **47** with trialkylorthoformates in the presence of trichloroacetic or trifluoroacetic acid in chloroform or dichloromethane[92,131,162–167] (Scheme 19, *cf.* Scheme 13, pathway *b*). The oxidation of the intermediate porphodimethene **48** can be accomplished by air oxygen or 1,4-benzoquinone[162,166,167] or DDQ[92] added at the end of the synthesis. The reaction proceeds *via* formylation of compound **47**, condensation of formyldipyrrolylmethenes to porphodimethene **48**, and oxidation of **48** to porphyrin **44**, thus being a simplified version of pathways *c* or *d* (see Scheme 13).

**Scheme 19**

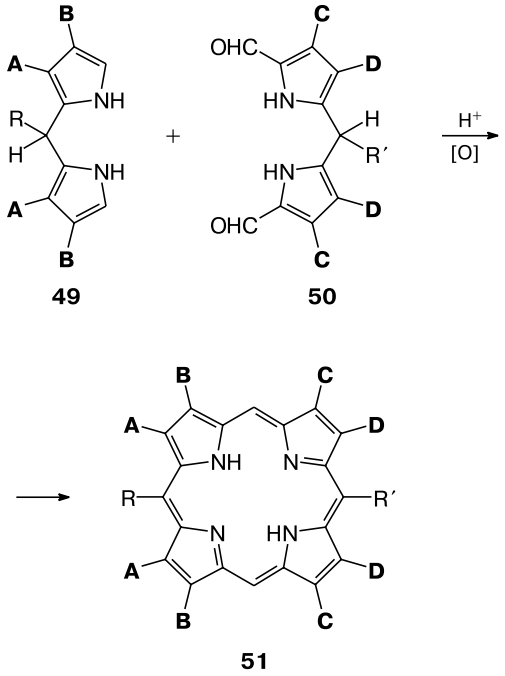



X = H, COOH

It has been shown[166] that the yield of porphyrin **44** depends appreciably on the presence of traces of water in the initial dipyrrolylmethane-α,α′-dicarboxylic acid, whereas in the case of α,α′-unsubstituted dipyrrolylmethane, the reaction is less dependent on the reaction conditions. The use of the benzoquinone oxidant at the last stage increases the yield of porphyrins with respect to that achieved with air oxidation.

Pathway *d* (see Scheme 13) allows one to obtain *trans*-disubstituted porphyrins **51** containing different *meso*-substituents; however, it can be implemented only with two different dipyrrolylmethanes **49** and **50**, each being unable to undergo self-condensation[168] (Scheme 20).

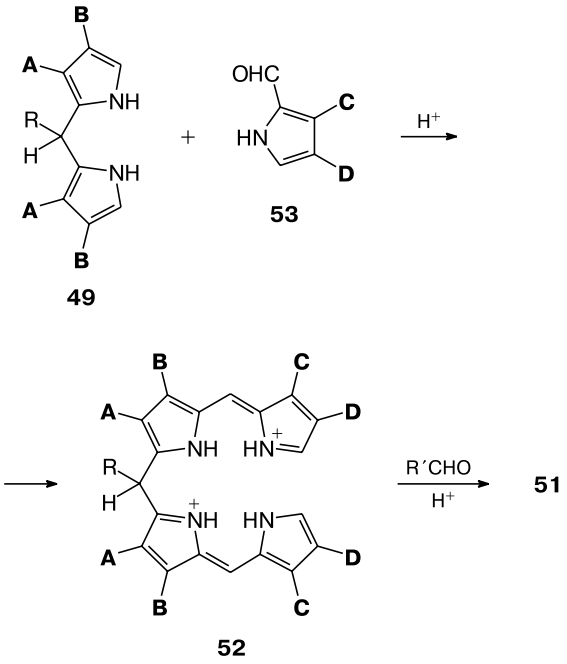
**Scheme 20**




In addition, unsymmetrically substituted diphenylporphyrins **51** can be prepared by condensation of 1,19-unsubstituted 10-substituted biladienes **52** with aldehydes. An example of this type of synthesis is shown in Scheme 21 (see Ref. 169). Biladienes **52** can be obtained by condensation of *meso*-substituted dipyrrolylmethanes **49** with 2-formylpyrroles **53**.

The thus prepared diarylporphyrins containing reactive functional groups in the phenyl rings can serve as the starting monomers for the preparation of linear porphyrin-containing polymers. The porphyrin fragments usually alternate in their molecules with elementary units formed from other co-monomers. These polymers are

**Scheme 21**



prepared by the classical polycondensation of monomeric diarylporphyrins with bi- or polyfunctional monomers of a nonporphyrin nature. The use of symmetrical tetrasubstituted macrocyclic ligands gives a network polymer in which porphyrin serves as the network node.[170] From the preparative chemistry standpoint, bifunctional monomers are preferred for the synthesis of polycondensed polyporphyrins, as this markedly facilitates the isolation and the subsequent analysis of the polymer.

Linear polymer **54** with molecular mass of ~$10^5$ containing a tetrapyrrole macrocycle in the polymer backbone was prepared by polycondensation of 5,15-di(aminophenyl)tetramethyltetrapropylporphin with sebacic acid dichloride and hexamethylenediamine (Scheme 22) in anhydrous chloroform. The obtained powdered polymer is readily soluble in *m*-cresol and has an enhanced thermal stability compared to analogous polyamides containing no porphyrin in the polymer macromolecule.[171]

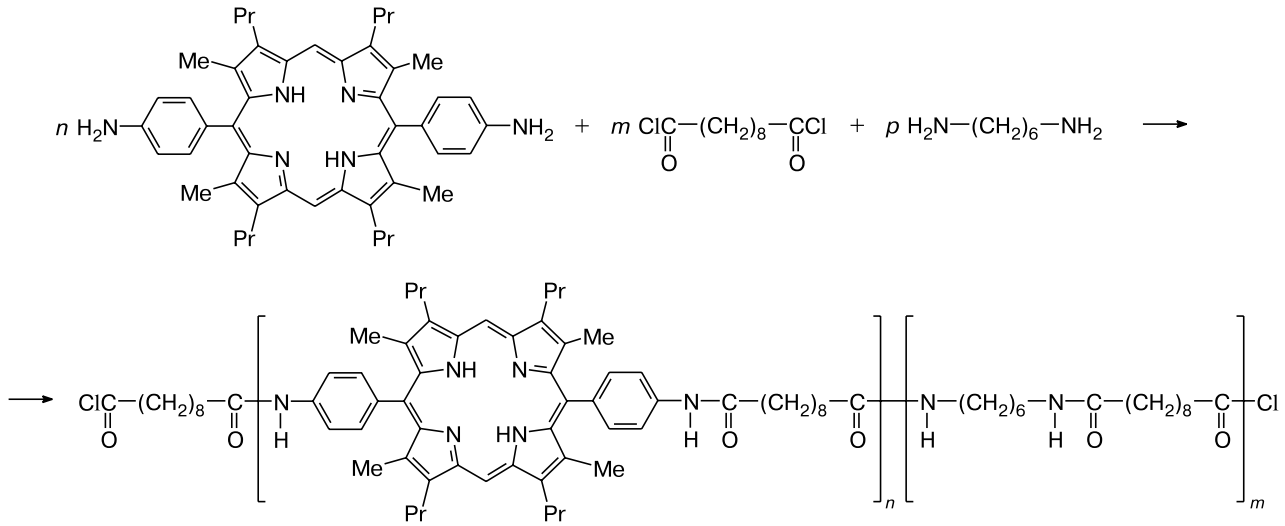
Thus, the use of multiporphyrin systems in the design of molecular devices and materials is now a novel and promising trend. Cooperative interaction between the porphyrin macrocycles is unambiguously manifested in oligomeric and polymeric systems based on porphyrins and their analogs in which energy and electron transfer takes place from one porphyrin center to another. By varying the spacer, the central metal atom, and the peripheral substituents in macroheterocycles, one can design chromophore systems with prespecified properties

### 3. Synthesis of *meso*-(5)-phenyl-β-octaalkylporphyrins

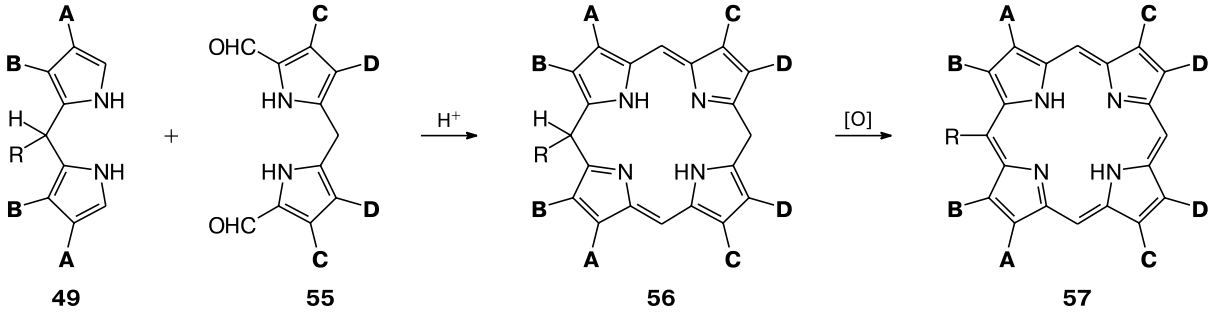
There exist several methods for the synthesis of 5-phenyloctaalkylporphyrins **4**. Previously, it was shown[146,147] that monophenylporphyrins are formed upon rearrangements in the acid medium (see Scheme 16) as by-products of the condensation of α-unsubstituted dipyrrolylmethanes with aldehydes; in some cases, they are major reaction products.

The method for the synthesis of 5-substituted porphyrins **57** used most extensively involves the condensation of *meso*-substituted α-unsubstituted dipyrrolylmethanes **49** with 5,5′-diformyldipyrrolylmethanes **55**

**Scheme 22**



**Scheme 23**

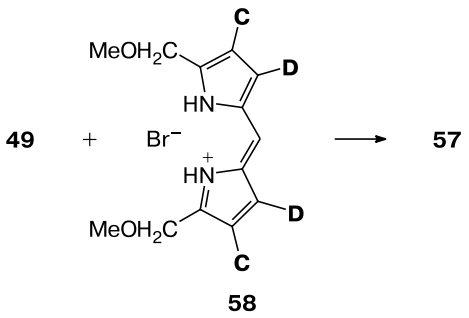



in alcohols or dichloromethane induced by strong acids (hydroiodic, perchloric, or *p*-toluenesulfonic acid) (Scheme 23).[153,166,172—182] Air oxygen or benzoquinone derivatives serve as oxidants for the intermediate porphodimethene **56**.

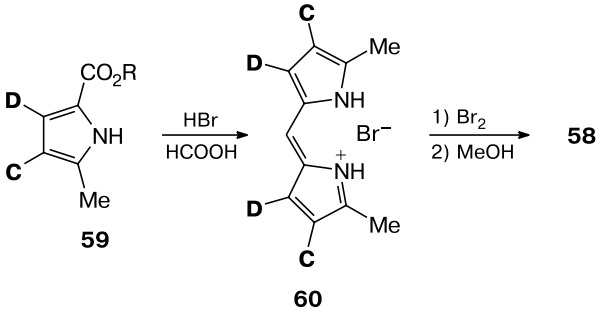
Di(5-formylpyrrol-2-yl)methanes **55** are prepared by the Vilsmeier formylation of α-unsubstituted dipyrrolylmethanes **42** with a $POCl_3$—DMF mixture[132] or with a mixture of ethyl orthoformate and trifluoroacetic acid.[183]

A related method is the condensation of α-unsubstituted *meso*-phenyldipyrrolylmethanes **49** with 5,5′-(dimethoxymethyl)dipyrrolylmethenes **58** in refluxing benzene followed by oxidation with benzoquinone derivatives[139] (Scheme 24). A lower yield of porphyrins is made up for by easy accessibility of dimethyl ethers **58** (see Refs 121, 184, 185) (Scheme 25). Diethers **58** are prepared by solvolysis of pyrrole derivatives **59** in a hot solution of hydrobromic (48%) and formic (88—90%) acids, giving rise to high yields (80—90%) of dipyrrolylmethenes **60** symmetrical relative to the *meso*-bridging carbon, which are then brominated in methanol. The method is complicated by the fact that the formation of 5-phenylporphyrins **57** is accompanied by the formation of rather large amounts of *meso*-unsubstituted octaalkylporphyrins. In order to rule out the possibility of undesirable rearrangements of β- and *meso*-substituents, the synthesis of **57** is carried out in the absence of acid catalysts.[139]

**Scheme 24**



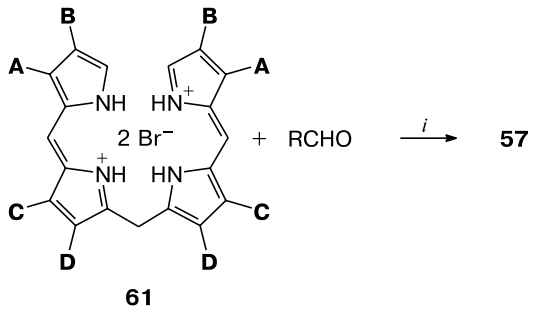

**Scheme 25**




R = H, Et, Bu$^t$

Yet another popular method for the synthesis of 5-phenylporphyrins **57** is the acid-[176,180,184] or base-catalyzed[185] condensation of benzaldehydes with 1,19-diunsubstituted biladienes **61** in alcohols (Scheme 26). This reaction implies no restrictions for the symmetry of β-substituents in the porphyrin ring, as their set is dictated by the initial biladiene. The initial biladienes are quite readily available and are produced upon acid-catalyzed reaction of dipyrrolylmethanes **46** with formylpyrroles **52** (Scheme 27). An interesting feature of this synthesis of 5-phenylporphyrins is the fact that along with the target 5-phenylporphyrin **57**, the reaction may give

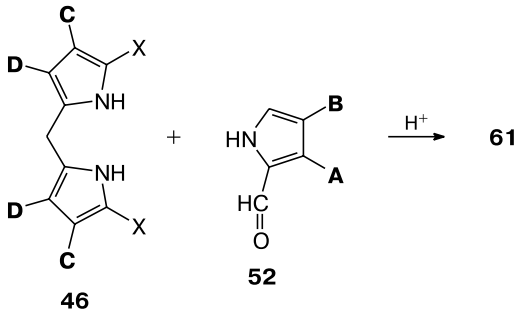
**Scheme 26**




*i*. $H^+$ or $OH^-$.

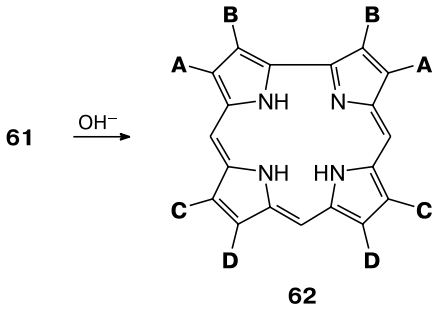
corrole **62**, its amount being determined by the rate of formation of porphyrin. Corroles **62** are the only products of cyclization of 1,19-diunsubstituted biladienes **61** in the presence of bases on treatment with mild oxidants[186] or on exposure to light[187] (Scheme 28).

**Scheme 27**




X = H, COOH

**Scheme 28**



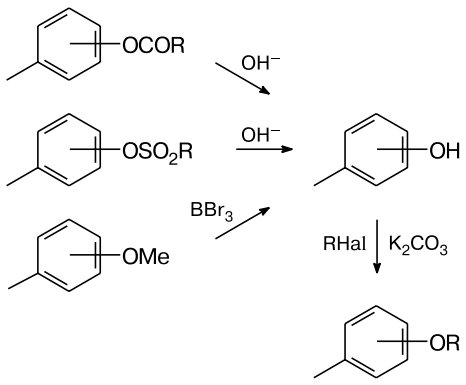

## 4. Modification of substituents in the phenyl rings of *meso*-phenyl-substituted porphyrins

Many derivatives of phenyl-substituted porphyrins can hardly be prepared by condensation of pyrrole or its linear derivatives with benzaldehydes. Therefore, it is pertinent to consider methods that make use of modification of substituents in the benzene rings of porphyrins prepared in high yields. Of considerable interest are porphyrins containing reactive substituents, *e.g.*, hydroxy or amino groups, in the phenyl rings, as they can undergo various chemical transformations. Unfortunately, direct synthesis gives these porphyrins in low yields if at all.

### 4.1. *meso*-(Hydroxyphenyl)porphyrins and their modification

*meso*-(Hydroxyphenyl)porphyrins are produced upon condensation in low yields and with large amounts of impurities that are difficult to separate. The protection of the hydroxy groups in hydroxybenzaldehydes by acylation[67] or sulfonylation[188] results in significant increase in the yields of the porphyrins, which can be converted rather easily into the required *meso*-(hydroxyphenyl)porphyrins by alkaline hydrolysis. However, O-demethylation of readily available *meso*-(methoxyphenyl)porphyrins holds more promise (Scheme 29).

**Scheme 29**




The attempts at O-demethylation of (methoxyphenyl)porphyrins with 48% hydrobromic acid demonstrated that this method has low utility due to the long time required and incomplete conversion. The use of anhydrous aluminum chloride in boiling chlorobenzene as the demethylating reagent does not lead to a satisfactory outcome either, because under these drastic conditions porphyrins are substantially destroyed.

The use of pyridine and aniline hydrochlorides under reflux as the demethylating agents proved to be advantageous.[189] This method is, however, applicable only for the synthesis of most stable *meta*- and *para*-hydroxy-substituted tetraphenylporphyrins, whereas *ortho*-substituted tetraphenylporphyrins and mono(hydroxyphenyl)- and di(hydroxyphenyl)porphyrins undergo substantial destruction.

A more appropriate demethylating agent for the synthesis of hydroxyphenylporphyrins is 60% hydrobromic acid (refluxing in an inert atmosphere); in this case, the product yield substantially increases.[189]

Currently, cleavage of anisoles is carried out using a mild demethylating agent, boron tribromide in dichloromethane at −20 °C under inert atmosphere.[190–195] However, it was shown[196,197] that the reaction can be carried out in chloroform at room temperature in air without a decrease in the yield.

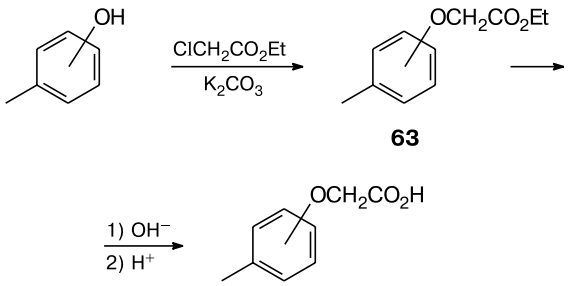
Alkylation of (hydroxyphenyl)porphyrins with haloalkanes is of interest, because porphyrins possessing diverse physicochemical properties or containing reactive groups at the periphery of the molecule can thus be pre-

pared in one stage from one precursor. These reactive groups can react with the reactive central part of the porphyrin macrocycle or serve for linking the molecule to various substrates.

Alkylation of (hydroxyphenyl)porphins is, most often, carried out in DMF in the presence of potassium carbonate.[198—200] The reaction is carried out at room temperature for labile hydroxyphenylporphyrins[198,201] or with reflux for stable tetraphenylporphin derivatives, which considerably reduces the reaction time.[200] The yields of alkoxyporphyrins are on average 80—95%. Alcohols are seldom used as solvents, since both the initial porphyrins and the reaction products are poorly soluble in alcohols.

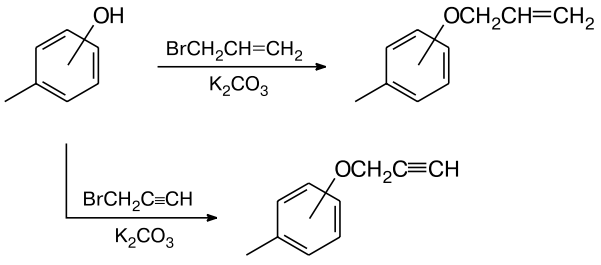
This method was used to prepare alkoxy-substituted porphyrins readily soluble in nonpolar organic solvents[200,201] and tetra(ethoxycarbonylmethoxyphenyl)porphyrins **63**, which are hydrolyzed to give tetra(carboxymethoxyphenyl)porphyrins **64** soluble in alkaline solutions (Scheme 30).[202]

**Scheme 30**




The alkylation of (hydroxyphenyl)porphyrins with allyl or propargyl bromide allows one to prepare porphyrins that can act as co-monomers in polymerization (Scheme 31).

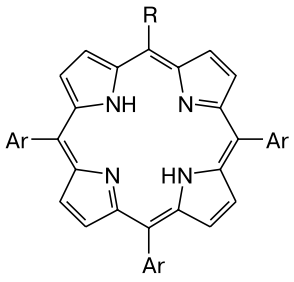
**Scheme 31**



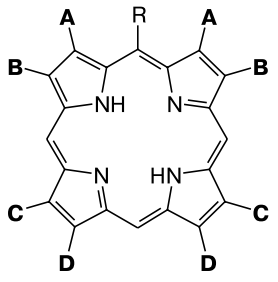

In nature, metal porphyrins function within chromoproteins whose protein groups have a strong influence on the properties of metal complexes.[203] Therefore, of considerable interest are porphyrins having, at the periphery of the molecule, reactive functional groups able to react with the central reaction site of the porphyrin macrocycle.

The synthesis of these compounds based on modification of natural porphyrins is rather complicated and includes numerous stages.[164] The bonds formed upon linking of the residues with reactive groups are nor very strong (mainly, these are amide or ester bonds).[164,204—206]

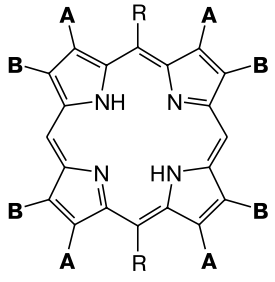
For the synthesis of such compounds, it is reasonable to use synthetic porphyrins with hydroxyphenyl groups able to form stable ether bonds. The number of reactive groups per porphyrin molecule rarely exceeds one; therefore (hydroxyphenyl)porphyrins with one or two hydroxyphenyl groups are most appropriate for this purpose, *e.g.*, (hydroxyphenyl)triarylporphyrins **65a**, which can be obtained rather easily by the condensation of pyrrole with a mixture of hydroxybenzaldehyde and benzaldehyde,[46,66,67] or *meso*-hydroxyphenyl-β-alkylporphyrins **66a**, **67a**, which resemble more closely natural porphyrins.




**65a—c**




**66a—c**



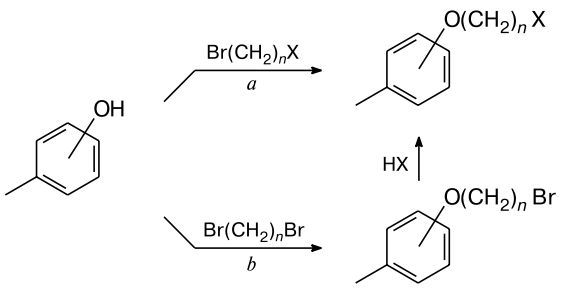

**67a—c**

R =  (**a**),  (**b**),  (**c**)

The general pattern of the synthesis of porphyrins with reactive groups by alkylation is shown in Scheme 32.

It can be seen from Scheme 32 that residues with reactive groups can be linked to porphyrin in two ways, either by alkylation of (hydroxyphenyl)porphyrin with haloalkane containing a reactive group (pathway *a*) or by preliminary alkylation of (hydroxyphenyl)porphyrin with excess α,ω-dibromoalkane and subsequent transforma-

**Scheme 32**




X is the residue with a reactive group

tion of the second halogen atom into a reactive functional group (pathway *b*).

Pathway *a* is preferred as it is shorter and gives the target product in a higher yield. However, it is not always possible to obtain the required functional haloalkane in a pure state. Therefore, pathway *b* is used most often[198,207]

### 4.2. *meso*-(Aminophenyl)porphyrins and their modification

One can hardly expect a high yield of (aminophenyl)porphyrins in the condensation of aminobenzaldehydes with pyrrole and its derivatives. Aminobenzaldehydes are known to be highly unstable, for example, 4-aminobenzaldehyde polymerizes in an acid medium and 3-aminobenzaldehyde exists only in dilute solutions or as a complex with tin dichloride.

Only direct synthesis of tetrakis(4-aminophenyl)porphin with irreproducible yield of about 1% was described in the literature.[26] Amino group protection by acylation results in a considerable (to 10%) increase in the porphyrin yield; however, other (aminophenyl)porphyrin isomers cannot be prepared in this way.

In view of the foregoing, the synthesis of aminophenylporphyrins by the reduction of nitrophenylporphyrins, which can be prepared in rather high yields by condensation of nitrobenzaldehydes with pyrrole and its derivatives, appears more promising. Currently, tin dichloride in hydrochloric acid or in polar solvents with a hydrochloric acid additive serves as the only reducing agent for this reaction.[208]

Tetra(nitrophenyl)porphyrins are reduced with a 1.5-fold excess of tin dichloride dihydrate in concentrated hydrochloric acid at 70—80 °C; this provides a nearly quantitative yield of tetra(aminophenyl)porphyrins.[209—212]

Mono- (**65b**, **66b**) and disubstituted (**67b**) nitrophenylporphyrins require milder reduction conditions; therefore, in this case, the reduction is carried out at room temperature[213,214] in methanol, which dissolves the resulting (aminophenyl)porphyrins and promotes complete reduction of the initial nitrophenylporphyrins.

Recently, a more convenient reduction method has been proposed, using hydrazine hydrate as the reducing agent, palladium on carbon as the catalyst, and a benzene—methanol mixture as the solvent; this allows one to avoid labor-consuming separation of inorganic salts from aminophenylporphyrin.[215]

(Aminophenyl)porphyrins are of interest, first of all, for immobilization onto polymer supports of various natures.

Polymer-analogous transformations represent the most convenient method for immobilization of porphyrins; this can provide covalent, ionic, or coordination binding of porphyrin or its analog with a preformed polymer support with known properties and a specified structure.

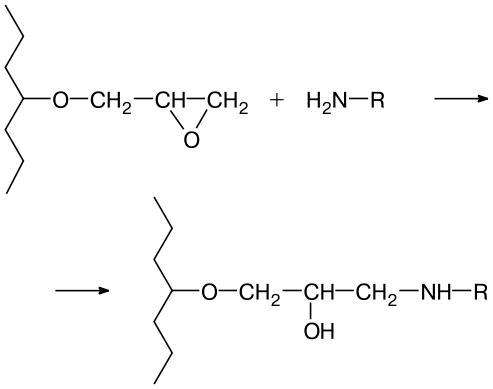
Monoamino-substituted porphyrins give linear polymers with rather mobile macrocycles accessible for reagents. Diamino-substituted porphyrins form cross-linked polymers, the degree of cross-linking and, as a consequence, the properties of the polymer depending on the porphyrin concentration. The use of symmetrical tetrasubstituted macroheterocycles gives cross-linked, usually insoluble polymers in which porphyrin is a cross-linking point. The lack of solubility of the cross-linked polymer facilitates its separation from the reaction mixture but complicates analysis of its structure.

For porphyrin immobilization, one should bear in mind that drastic reaction conditions can induce thermooxidative destruction of the polymer. Porphyrins and their metal complexes, especially natural ones, are also sensitive to external action. Therefore, the search for mild immobilization conditions that would exclude side processes is of prime importance in the development of synthetic routes to porphyrin polymers.

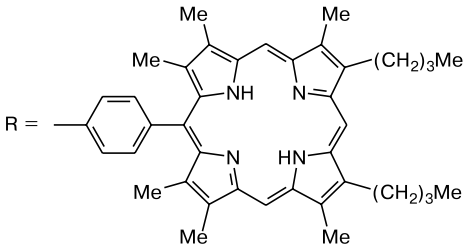
Therefore, mild conditions for immobilization of porphyrins containing an active hydrogen atom in a functional group (—OH, $NH_2$, —COOH) onto a hydroxyl-containing polymer support subjected to epoxy activation was proposed[216—219] (Scheme 33). The essence of the method is that on treatment with epichlorohydrin or another reagent having epoxy groups, the reactive hydroxy groups of the polymer are converted into highly reactive epoxidized groups that easily react with compounds containing an active hydrogen atom in a functional group. Using this method, immobilization of different porphyrins on the polymer matrix is possible. Better results in porphyrin immobilization are obtained when hydroxy groups are sparsely distributed over the polymer support macromolecule. The allyl alcohol—styrene copolymer can be used as such support; variation of the composition of this copolymer allows one to change the polymer solubility in various media and to control the amount of porphyrin in polymer **68**.

This method was used to prepare immobilizates of both free porphyrins, for example, 5-(4′-aminophenyl)-2,3,7,8,12,18-hexamethyl-13,17-dibutylporphin and

**Scheme 33**



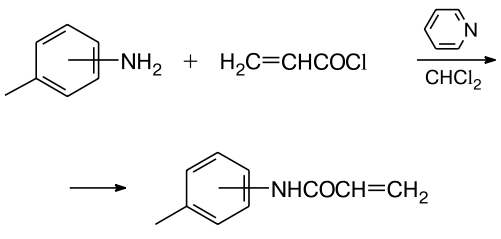
**68**



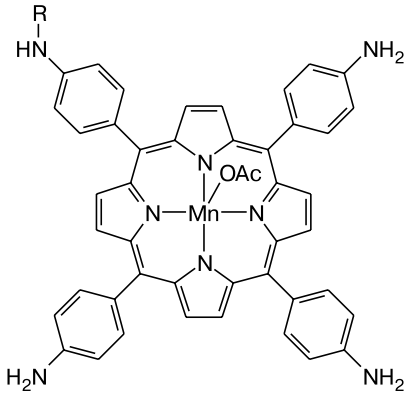
metal porphyrins on the allyl alcohol—styrene copolymer. The $Zn^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Mn^{3+}$ porphyrin complexes can be immobilized either directly as metal porphyrins or by complexation of metal-free immobilizates with metal salts in solutions. The immobilized $Co^{2+}$ and $Ni^{2+}$ complexes of aminophenyl-substituted porphins showed a high catalytic activity in the epoxidation of styrene with dioxygen in acetonitrile.[216,217]

Aminophenylporphyrins are readily acylated with acid chlorides to give acylamino derivatives. On acylation with acryloyl chloride, the resulting unsaturated derivatives can be used as co-monomers (Scheme 34), together with other traditional vinyl monomers, for the preparation of porphyrin-containing polymers with specified contents of tetrapyrrole compounds in the side chain of the macromolecule.

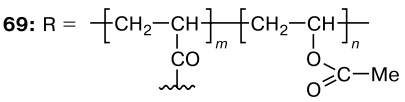
**Scheme 34**

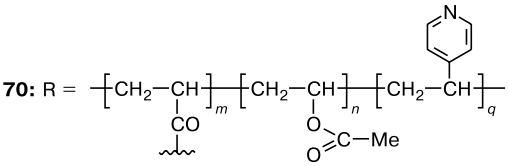


Porphyrin-containing copolymers (**69**) and terpolymers (**70**) were prepared by radical copolymerization or terpolymerization of manganese(III)-tetra(4-aminophenyl)porphyrin acetate acylated with acryloyl chloride with methacrylate or with 4-vinylpyridine and methacrylate, respectively, in a DMF solution.[220] It was shown that the catalytic activity of immobilizate **69** in cholesterol oxidation with dioxygen is much higher than that of monomeric metal porphyrin. It was noted that the introduction of bulky side groups into the polymer, such as the pyridyl residue in **70** decreases the catalytic activity of the polymeric metal porphyrin, which may be due to shielding of the reaction centers. The specific catalytic activity depends on the combination of hydrophilicity and hydrophobicity of fragments of the macromolecular catalyst and on the content of metal porphyrin in the catalyst.



**69**, **70**

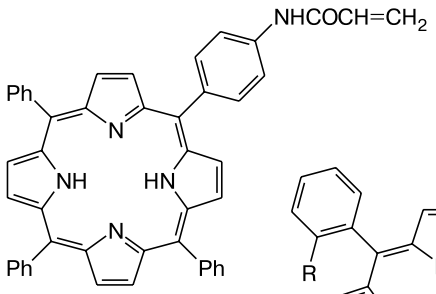




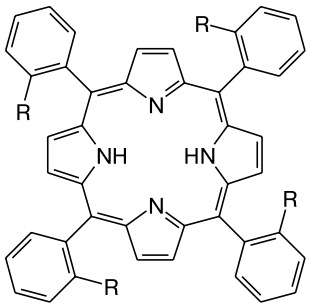
The same method was used to carry out copolymerization of $Mn^{3+}$-5,10,15,20-tetra(4′-arylamidophenyl)porphyrin with methyl methacrylate or divinylbenzene in DMF, which gave linear soluble or cross-linked insoluble copolymers, respectively.[221] These products also proved to be efficient stable catalysts in cholesterol oxidation.

Styrene copolymerization with (acrylamidophenyl)triphenylporphin **71**, tetra(2′-methacrylamidophenyl)porphin **72**, and other porphyrins was studied.[222–230] The yield of copolymers containing less than 1% free porphyrin was 20 to 40%. Due to the low porphyrin content in the macromolecular chain, no interaction of the porphyrin fragments with one another was detected.

Comparison of the copolymers prompts the conclusion that free porphyrin bases are more convenient comonomers in polymerization than metal porphyrins.

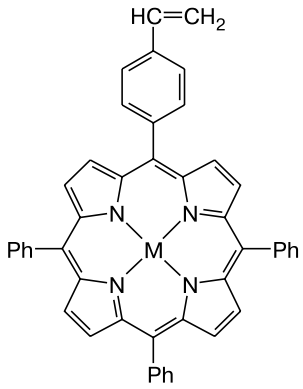



**71**



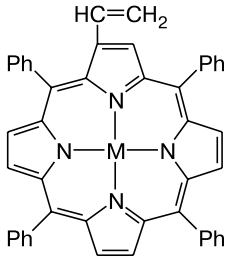

**72**

R = NHCOC(Me)=CH2




**73**

M = 2 H, $Cu^{2+}$, $Zn^{2+}$



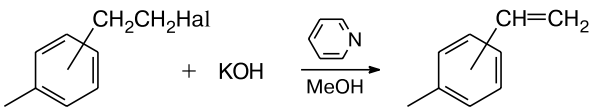

**74**

The presence of a metal in the porphyrin coordination site increases the probability of side reactions during copolymerization.

### 4.3. Synthesis of (vinylphenyl)porphyrins

Porphyrins containing vinylphenyl groups in *meso*-positions are also prepared more conveniently by the two-stage method. The intermediates produced upon condensation of haloethyl-substituted benzaldehydes with pyrrole or its linear derivatives are dehydrohalogenated and, as a result, the haloethyl groups on preformed porphyrins are converted into vinyl groups (Scheme 35).[231]

**Scheme 35**




In order to prepare a synthetic vinyl monomer based on tetraphenylporphin, the vinyl group was introduced by the Wittig reaction into both the phenyl ring and the β-position of the macrocycle. Monomers **73** and **74** and their copper and zinc complexes were subjected to radical copolymerization to give a series of copolymers with styrene or methyl methacrylate.[232—234]

The authors demonstrated that the content of porphyrin in the resulting copolymer depends on both the initial comonomer ratio and copolymerization conditions. The molecular mass ($M_W$) of the copolymers varies from 120000 to 678000; for copolymer containing monomer **73**, this value is 2—4 times higher than that for monomer **74**. The porphyrin content in the copolymer varied from 0.001 to 0.04 mole fractions and depended on the monomer ratio in the initial reaction mixture.

The use of vinyl-containing porphyrins for the synthesis of homopolymers is inexpedient because this may give only oligomers with a low degree of polymerization; in addition, high concentration of porphyrin fragments in the polymer leads inevitably to their interaction and a decrease in the activity. The preparation of copolymers based on vinyl-containing porphyrins provides the route to porphyrin polymers with different structures depending on the field of application.

Currently the porphyrin polymer systems attract increasing attention of researchers due to new fields of their application. Apart from highly selective catalysts, prospects for using these systems as materials for nonlinear optics, sensors, gas separation membranes, electronic and photoelectronic wires, drugs, and various nanosized materials have appeared.

In this connection, the problem of development of new methods for the synthesis of porphyrin polymer immobilizates remains topical. Solution of this problem opens up prospects for the design of new functional materials, including nanomaterials, for various fields of science, engineering, and medicine.

The chemistry of porphyrins and their analogs is now being vigorously developed; therefore, this review does not claim to fully cover the relevant publications. It can be recommended as a strategy for the synthesis and modification of desired *meso*-substituted porphyrins based on the synthetic routes most developed by now.

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