Russian Chemical Reviews **82** (5) 412 – 428 (2013) © 2013 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2013v082n05ABEH004317

Methods for synthesis of *meso*-substituted tetrabenzoporphyrins

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Abstract. The currently known methods for synthesis of *meso*-substituted tetrabenzoporphyrins of different structures are reviewed. Characteristic features of each method are demonstrated, and their comparative analysis is presented. The bibliography includes 104 references.

I. Introduction

The chemistry of tetrabenzoporphyrins originated from the preparation of the first representatives of this large group of compounds in the late 1930s by Helberger [1] and Linstead.[2] The constantly growing interest in these tetrapyrrole macroheterocycles is caused by a number of reasons. First of all, tetrabenzoporphyrins are synthetic analogues of natural porphyrins, which determine the existence of animal and vegetal life on Earth. They are studied as models of chlorophylls, haems, cytochromes, peroxidases, catalases and other enzymes. Second, an important factor is a possibillity of modification of the tetrabenzoporphyrin macrocycle *via* introduction of different functional groups into the molecule, in particular, at the *meso*-positions, and complexation with metals of various nature. Such a modification allows for the variation of the physicochemical properties of tetrabenzoporphyrins over wide range, which stipulates their application as fat-soluble dyes,[3] efficient catalysts,[4] semiconductors,[5] drugs for diagnosis and photodynamic therapy of cancer,[6–8] phosphorescent sensors for oxygen,[9] vacuum photoresists,[10] and photochromic filters.[11] The nonlinear-optical properties of these compounds enable the creation of optical limiters based on them.[12] The acid-base [13, 14] and electrochemical [15] characteristics of *meso*-substituted tetrabenzoporphyrins determine a possibility of their application as sensors for small molecules and ions.

The above-mentioned factors account for the topicality of investigations on *meso*-substituted tetrabenzoporphyrins both from the fundamental and practical standpoints. However, unlike porphyrins, these compounds are still poorly avaiable. To obtain *meso*-substituted tetrabenzoporphyrins of the required structures in high yields, it is necessary to develop novel methods and modify the existing ones. Although there is a plethora of works on the synthesis and properties of *meso*-substituted tetrabenzoporphyrins, the number of reviews on this topic is too small. Some papers [16, 17] deal only with *meso*-aryl derivatives; other [18] survey the syntheses of these compounds by the condensation of pyrroles, while the information on other methods is quite limited; and the most comprehensive review [19] has been recently published in the poorly accessible series of monographs *Handbook of Porphyrin Science*.

Nowadays, three main methods for the synthesis of *meso*-substituted tetrabenzoporphyrins are known. The first method is high-temperature template tetramerization of phthalic acid derivatives with nucleophilic reagents serving as sources of the *meso*-carbon atoms. The second one is based on the conventional low-temperature assembling of the porphyrin system using stable saturated analogues of isoindole and aldehydes; in this case, the macrocycle aromatization occurs at the last stages of the process. Finally, the third method consists in the introduction of substituents at the *meso*-positions of the already formed porphyrin system.

The main goals of the present review are to generalize the published and authors' own data on methods for synthesis of *meso*-substituted tetrabenzoporphyrins and to elucidate the advantages and drawbacks of each of the methods.

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Received 5 April 2012
Uspekhi Khimii **82** (5) 412 – 428 (2013); translated by D V Aleksanyan

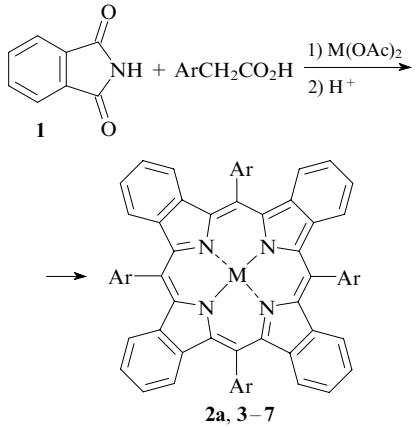
II. High-temperature template synthesis

1. *meso*-Aryl-substituted tetrabenzoporphyrins

Metal complexes should be regarded as the first representatives of *meso*-substituted tetrabenzoporphyrins. These compounds were synthesized by Luk'yanets and co-workers [20] in

1981 by heating a mixture of phthalimide (**1**) (or potassium phthalimide), arylacetic acids (or their sodium salts) and metal (zinc or cadmium) acetate to 340–380 °C for 0.25–2 h in inert gas flow. *meso*-Tetraphenyltetrabenzoporphyrin (**2a**) was obtained by passing hydrogen chloride through a chloroform solution of complex **3** (yield 40%). Metal porphyrins **3**–**7** were isolated in 3.6%–17% yields (Scheme 1).

Scheme 1



Ar = Ph: M = 2 H (**2a**, 40%), Zn (**3**, 17%), Cd (**4**, 5%);
M = Zn: Ar = 4-MeC_6H_4 (**5**, 13.5%), 4-$MeOC_6H_4$ (**6**, 4.2%), Naph (**7**, 3.6%); Naph is naphthyl

Later, it was found [21] that the application of zinc acetate leads to the formation of porphyrins having one to four aryl fragments at the *meso*-psoitions, since acetate ion serves as a source of methylene fragments. When zinc acetate is replaced by zinc hydroxide,[22] or 3-benzylidenephthalimidine (**8**) and zinc benzoate are used as the initial compounds,[23] complex **3** is formed selectively.

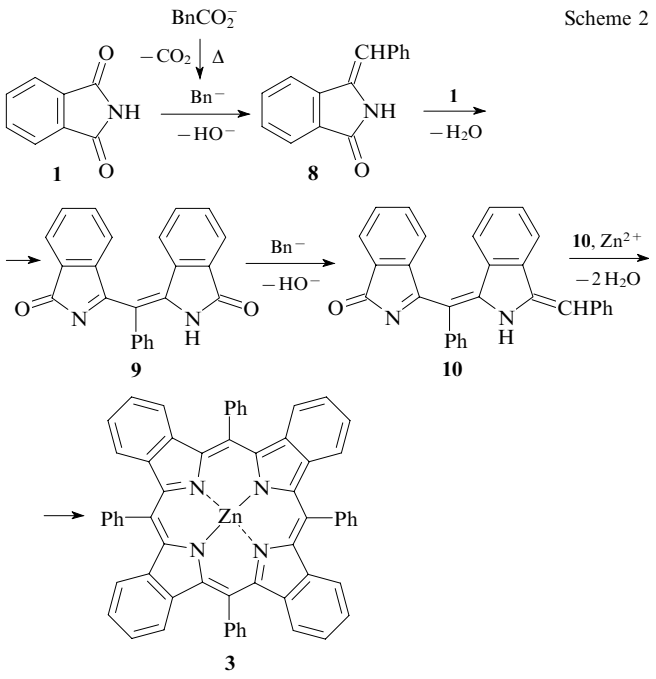
This method has long been the main one for the synthesis of metal complexes of *meso*-aryl-substituted tetrabenzoporphyrins. It was used to obtain a wide range of porphyrins with different central cations and *meso*-substituents and porphyrins having different substituents in the isoindole moieties, in particular, complexes of *meso*-tetra(1-naphthyl)tetrabenzoporphyrins with a series of lanthanides (Dy, Ho, Er, Tm, Yb, and Lu) [24] and cobalt.[25]

The interaction of phenylacetic acid with imide **1** and zinc oxide was studied at different temperatures.[26] Based on the analysis of the isolated inetrmediates **8**–**10**, the authors [27] suggested a scheme of formation of complex **3** (Scheme 2).

The first stage of the reaction is the formation of a reactive nucleophilic reagent. This is likely to be benzyl anion, which results from the thermal decarboxylation of phenylacetate anion. The benzyl anion reacts with molecule **1**, giving rise to 3-benzylidenephthalimidine (**8**). Compound **8** is a enamide capable of reacting with the second molecule of phthalimide, affording the dimeric product, 3-[(*E*)-(3-oxo-2,3-dihydro-1*H*-isoindol-1-ylidene)phenylmethyl]-1*H*-isoindol-1-one (**9**). The interaction of dimer **9** with the carbanion leads to 3-{(*E*)-[(3*Z*)-3-benzylidene-2,3-dihydro-1*H*-isoindol-1-ylidene]phenylmethyl}-1*H*-isoindol-1-one (**10**), two molecules of which are coordinated by the metal cation, and the condensation affords complex **3**.

An important conclusion made by Galanin *et al.*[26] upon analysis of Scheme 2 is that CH-acids, *e.g.*, 2-methylquinoline (**11**), can also be used as nucleophiles in the reaction. Indeed, heating of imide **1** with an excess of compound **11** and zinc oxide at 245 °C for 12 h leads to zinc *meso*-tetra(2-quinolyl)tetrabenzoporphyrin (**12**) in ~15% yield (Scheme 3). Besides complex **12**, intermediates **13** and **14** were also isolated from the reaction mixture, which confirms the mechanism presented.

Scheme 2



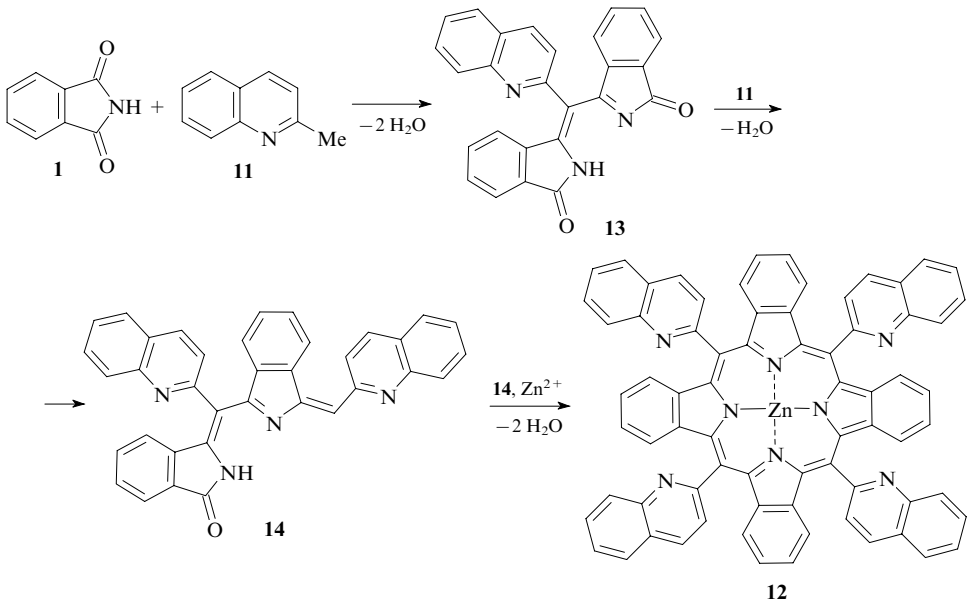
Subsequently, it was established [28] that as the reaction time increases to 36 h, the yield of complex **12** reduces to 3%. The column chromatographic purification of the reaction mixture provided, along with compound **12**, zinc complexes of *meso*-tri(2-quinolyl)- (**15**), *meso*-di(2-quinolyl)- (**16**), and *meso*-(2-quinolyl)tetrabenzoporphyrins (**17**). The formation of these compounds is explained by the thermal decomposition of complex **12**, accompanied by the elimination of the *meso*-substituents (Scheme 4).

The same was observed during investigation of the processes of thermal destruction of metal complexes of *meso*-tetraphenyltetrabenzoporphyrin. It was found [18] that heating of the metal complex results in a decrease in the sample weight that corresponds to the sequential elimination of the *meso*-phenyl substituents.

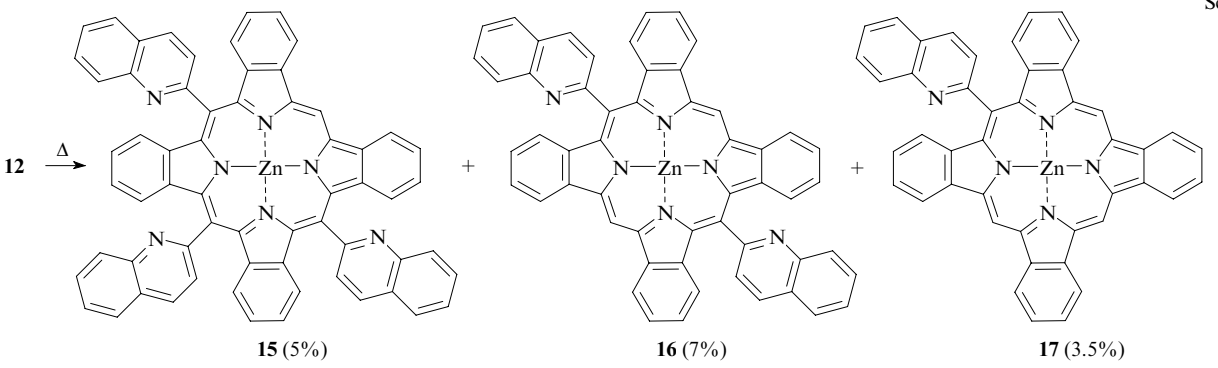
The analysis of Scheme 2 suggests that low-symmetry *meso*-aryl-substituted tetrabenzoporphyirins can also be synthesized using intermediate products, *e.g.*, compound **9**. Indeed, the reaction of dimer **9** with 1-naphthylacetic acid and zinc oxide afforded [29] low-symmetry zinc 5,15-diphenyl-10,20-di(1-naphthyl)tetrabenzoporphyrin (**18**), while replacement of 1-naphthylacetic acid by 2-methylquinoline (**11**) yielded zinc 5,15-diphenyl-10,20-di(2-quinolyl)tetrabenzoporphyrin (**19**) [30] (Scheme 5).

The high-temperature template condensation of isoindole derivatives with arylacetic acids is also suitable, with certain limitations, for the synthesis of tetrabenzoporphyrins bearing functional groups in the isoindole moieties and in the *meso*-substituents. The existing restrictions are associated both with the low availability of substituted phthalimides and instability of many of them at high temperatures. For example, an attempt was made [31]

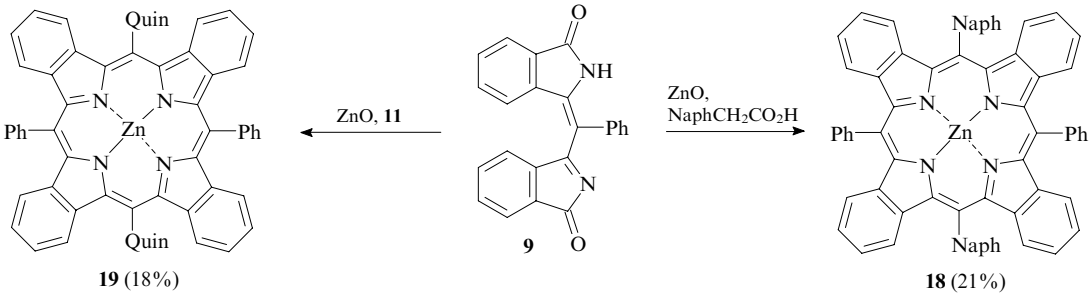
Scheme 3



Scheme 4



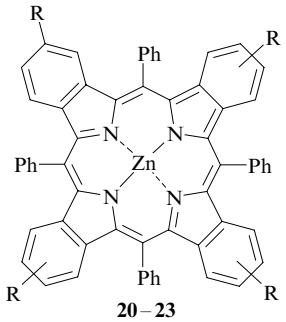
Scheme 5



Quin is quinolyl

to synthesize tetrahalo-substituted derivatives of *meso*-tetraphenylbenzoporphyrins by the condensation of 4-chloro- and 4-bromophthalimides with phenylacetic acid in the presence of zinc acetate, but only compounds contaning, on the average, two halogen atoms per porphyrin molecule were obtained.

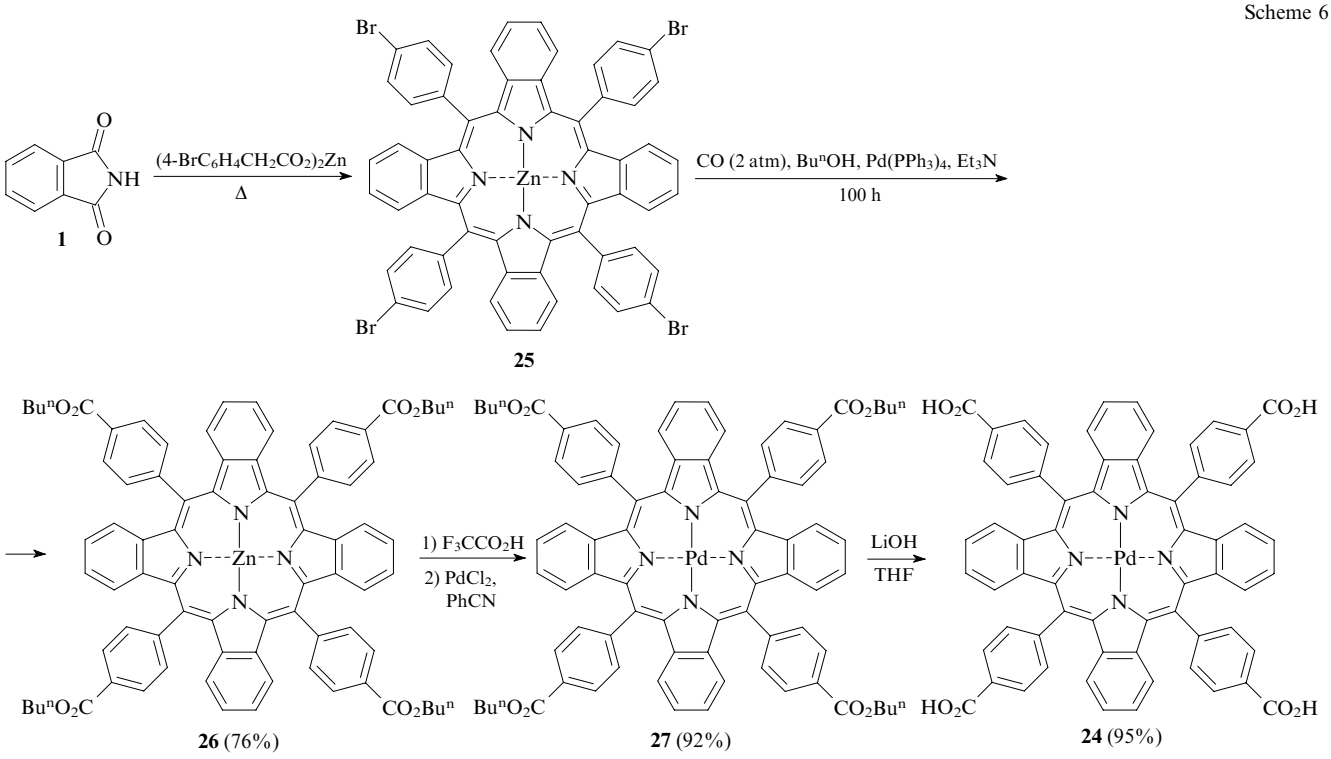
The synthesis of metal complexes of *meso*-substituted tetra(4-phenylbenzo)- (**20**), tetra(4-nitrobenzo)- (**21**), tetra(4-aminobenzo)- (**22**), and tetra(4-phenoxybenzo)porphyrins (**23**) was reported.[32, 33] Compounds **20**, **21** and **23** are formed upon heating of the corresponding phthalimides with phenylacetic acid in the presence of zinc oxide or acetate.



20–**23**

R = Ph (**20**), NO_2 (**21**), NH_2 (**22**), OPh (**23**)

Scheme 6

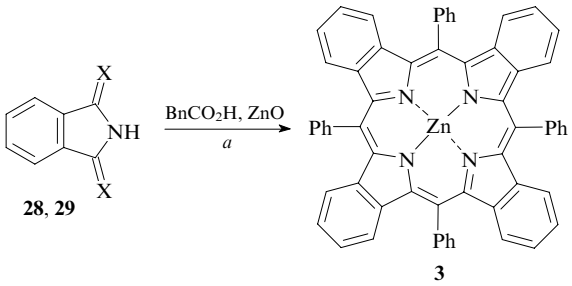


Porphyrin **22** was obtained by the reduction of complex **21** with tin(II) chloride in concentrated hydrochloric acid. It should be emphasized that the nitro groups present in the molecule of porphyrin **21** initiate its oxidative decomposition at the synthesis temperature. Therefore, unlike unsubstituted *meso*-aryltetrabenzoporphyrins or their aryl and aryloxy derivatives, in this case, no even traces of compound **21** were formed in the reaction carried out in air. Even under argon, the yield of **21** did not exceed 5%–6%, which is almost three times lower than the yields of phenyl- (**20**) and phenoxy-substituted (**23**) porphyrins upon their synthesis in air.

Substituted phenylacetic acids can be used for the synthesis of *meso*-tetraarylbenzoporphyrins having functional groups as parts of *meso*-substituents, *e.g.*, palladium complex of 5,10,15,20-tetrakis(4-carboxyphenyl)tetrabenzoporphyrin (**24**)[34] (Scheme 6). Heating of a mixture of imide **1** with an excess of zinc 4-bromo-phenylacetate to 380–390 °C under inert atmosphere leads to zinc 5,10,15,20-tetrakis(4-bromophenyl)tetrabenzoporphyrin (**25**) in a low yield (<1%). The reaction of complex **25** with carbon(II) oxide in the presence of $Pd(PPh_3)_4$ and Et_3N in n-butanol at 90 °C under pressure of 2 atm for 100 h according to a literature procedure[35] affords zinc complex of tetrabenzoporphyrin **26**. This complex is demetallated by treatment with trifluoroacetic acid, and the corresponding free liagnd is heated with $PdCl_2$ in benzonitrile. Under action of LiOH in THF, palladium complex **27** is transformed into porphyrin **24**, which serves as a precursor for the synthesis of porphyrin-containing dendrimers based on polyethylene glycols or polyglutamates.[34]

All the above methods of template synthesis of *meso*-aryl-substituted tetrabenzoporphyrins are characetrized by low yields of the target products, no higher than 20%. To increase the yield of porphyrins, it was suggested to harness more active reagents than imide **1**, namely, dithiophthalimide (**28**)[36] and 1,3-diiminoisoindoline (**29**).[37] The reaction of these compounds with phenylactic acid and zinc oxide for 1 h affords porphyrin **3** (Scheme 7).

Scheme 7



X = S (**28**), NH (**29**); (*a*) 290 °C (X = S) or 270 °C (X = NH)

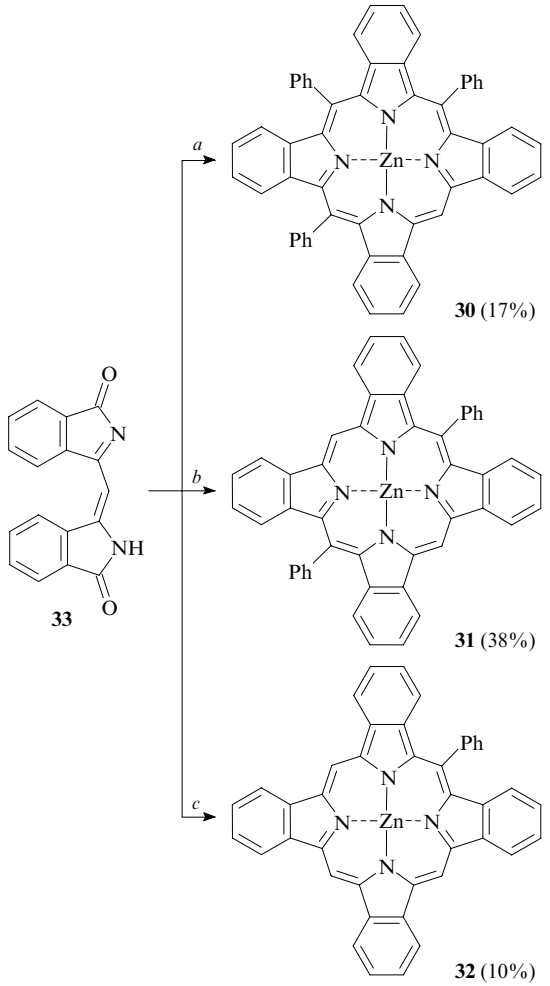
The product yield in the case of imide **28** is 27% and that for imide **29** is 43%. Moreover, in the case of porphyrinogens **28**, **29**, the reaction temperature can be reduced by 60–80 °C, which allows one to avoid the formation of by-products from the decomposition of the target metal complex.

As it was mentioned above,[21] the interaction of imide **1** with arylacetic acids in the presence of metal acetates affords the products of incomplete *meso*-substitution in tetrabenzoporphyrin. These compounds are not only of theoretical but also of practical interest, since they possess unique electrooptical properties. It was established,[6] *e.g.*, that complex **3** is characterized by an intensity of fluorescence, induced by the absorption of two photons, four times higher than zinc tetraphenylporphyrin, and the symmetry violation in the molecule of **3** with a reduction in the number of *meso*-phenyl substituents to three additionally enhances this value by a factor of three. These properties of *meso*-tri-, di- and monoaryl-substituted tetrabenzoporphyr-

ins required the development of more rational methods for their synthesis, since the application of metal acetates as template agents[21] or the prolonged heating of *meso*-tetraaryl-substituted tetrabenzoporphyrins[28] affords the target products in low yields (2%–5%) and as parts of complex multicomponent mixtures.

More selective methods for synthesis of zinc complexes of 5,10,15-triphenyltetrabenzoporphyrin (**30**),[38] 5,15-diphenyltetrabenzoporphyrin (**31**)[39] and 5-phenyltetrabenzoporphyrin (**32**)[40] are based on the construction of the macrocycle (Scheme 8). An analogue of compound **9**, 3-[(*E*)-3-oxo-2,3-dihydro-1*H*-isoindol-1-ylidenemethyl]-1*H*-isoindol-1-one (**33**), is used as the initial compound; it can be obtained by the reaction of imide **1** with an excess of nickel acetate at 240 °C for 30 min (yield 25%).[39] The conditions for preparation of complexes **30**–**32** are shown in Scheme 8.

Scheme 8

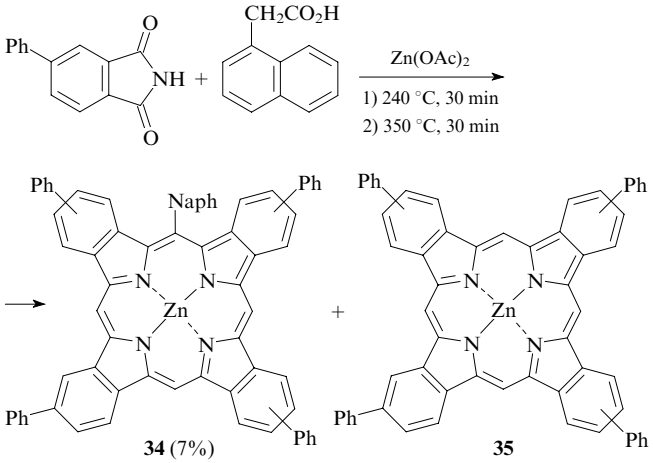


(*a*) $BnCO_2H$, **1**, ZnO, 350 °C, 15 min;
(*b*) $BnCO_2H$, ZnO, 350 °C, 15 min;
(*c*) $BnCO_2H$, $Zn(OAc)_2$, 350 °C, 25 min

Although the synthesis of porphyrins **30** and **32** results in a mixture of *meso*-substituted tetrabenzoporphyrins, the content of the target metal complexes comprises 60%–70%, which considerably faciliatates their chromatographic separation. In the case of complex **31**, the amount of porphyrins with a different number of *meso*-substituents is insignificant.

The selective synthesis of *meso*-aryl-substituted tetrabenzoporphyrins can be carried out, besides the stepwise condensation, *via* the reaction of arylacetic acids having bulky aryl residues with sterically hindered phthalimides. Thus, it was found[41] that the interaction of 4-phenylphthalimide with 1-naphthylacetic acid in the presence of zinc acetate gives rise to a mixture of zinc 5-(1-naphthyl)tetra(4-phenylbenzo)porphyrin (**34**) and zinc tetra(4-phenylbenzo)-porphyrin (**35**) (Scheme 9).

Scheme 9



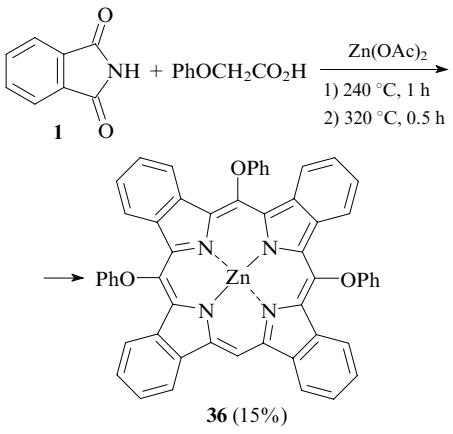
Mass spectral analysis of the reaction mixture showed that porphyrin **34** is the only *meso*-substituted product; porphyrins with higher number of *meso*-substituents are not formed in this case due to the essential steric hindrances.

2. *meso*-Aryloxy-substituted tetrabenzoporphyrins

The variation of the number and nature of *meso*-aryl substituents in the molecules of tetrabenzoporphyrins can serve for targeted modification of the properties of these compounds. It is also of particular interest to study the effect of aryl substituents in the molecule of tetrabenzoporphyrin connected with the macrocyle through spacers. These spacers can be, *e.g.*, an oxygen atom or CH_2O group.

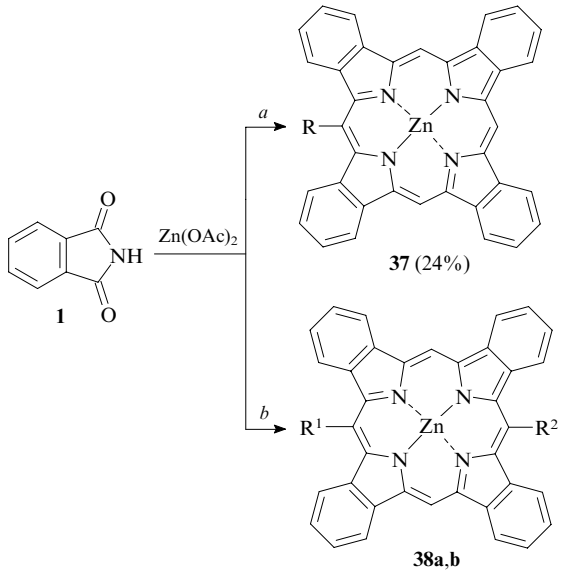
The condensation of phenoxyacetic acid with imide **1** in the presence of nickel acetate afforded zinc 5,10,15-triphenoxytetrabenzoporphyrin (**36**) (Scheme 10).[42] The use of zinc oxide instead of zinc acetate provided no reaction.

Scheme 10



The interaction of compound **1** with 4-(triphenylmethyl)phenoxyacetic or -propionic acid in the presence of zinc acetate leads to tetrabenzoporphyrins[43] containing substituents with bulky triphenylmethyl groups at the *meso*-positions (Scheme 11).

Scheme 11



(*a*) 4-$Ph_3CC_6H_4OCH_2CO_2H$, 310 °C, 50 min;
(*b*) 4-$Ph_3CC_6H_4OCH_2CH_2CO_2H$, 320 °C, 1 h;
R = 4-$Ph_3CC_6H_4O$ (**37**); R^1 = 4-$Ph_3CC_6H_4OCH_2$: R^2 = H (**38a**, 10%), 4-$Ph_3CC_6H_4OCH_2$ (**38b**, 11%)

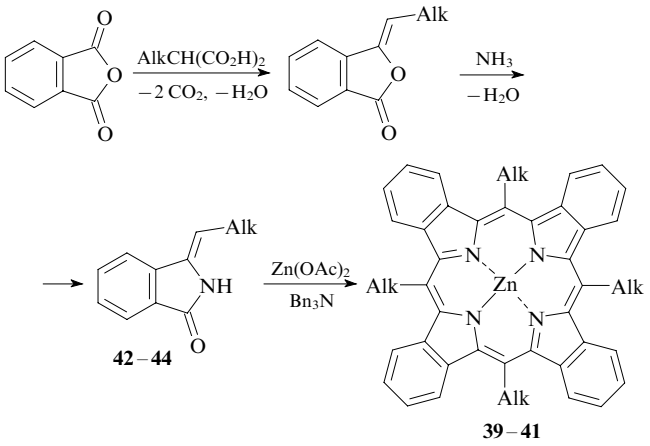
It was found[43] that the reactions afford only *meso*-monosubstituted (**37**, **38a**) and *meso*-disubstituted (**38b**) tetrabenzoporphyrins. Considerable steric hindrances hamper the formation of porphyrins with a higher number of *meso*-substituents.

Heating of imide **1** with [3-(heptyloxy)phenoxy]acetic acid and zinc acetate also yields[44] only two *meso*-substituted tetrabenzoporphyrins, zinc 5-[(3-heptyloxy)phenoxy]-tetrabenzoporphyrin (yield 10%) and zinc 5,15-bis[(3-heptyloxy)phenoxy]tetrabenzoporphyrin (yield 6%). Hence, the application of aryloxyacetic acids with bulky substituents in the synthesis of *meso*-substituted tetrabenzoporphyrins also increases the selectivity of formation of low-symmetry porphyrins.

3. *meso*-Alkyl- and meso-alkoxy-substituted tetrabenzoporphyrins

Unlike well studied *meso*-aryl-[45–48] and *meso*-alkylporphyrins,[49,50] the corresponding *meso*-alkyl derivatives of their tetrabenzo analogues have been studied to a considerably lesser degree. The first work[51] dealing with the synthesis and properties of these compounds reported the preparation of zinc *meso*-tetramethyl-, *meso*-tetraethyl-, and *meso*-tetrapropyltetrabenzoporphyrin complexes (**39**–**41**). These complexes were obtained through the reaction of 3-alkylidene-2,3-dihydro-1*H*-isoindol-1-ones **42**–**44** with zinc acetate in the presence of tribenzylamine at 340–360 °C under helium atmosphere. Starting compounds **42**–**44** were derived from the reaction of phthalic acid anhydride with the corresponding alkylmalonic acids followed by the amination (Scheme 12).

Scheme 12

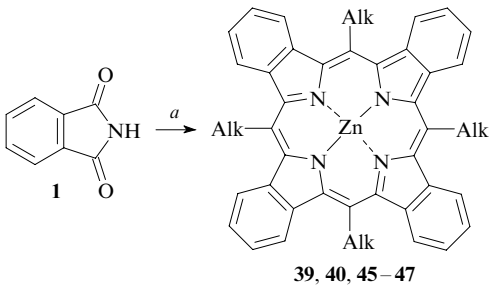


Alk = Me (**39**, **42**), Et (**40**, **43**), Pr^n (**41**, **44**)

The process consists of three stages; furthermore, the synthesis utilizes poorly accessible alkylmalonic acids. The yields of porphyrin metal complexes **39**–**41** at the last stage did not exceed 14%, and those calculated relative to the initial phthalic acid anhydride comprise 2%–4%. The difficulty of realization and low yields of the target products make this method ineffective.

The synthesis of zinc *meso*-tetraalkyltetrabenzoporphyrins *via* the reaction of imide **1** with an excess of zinc salts of palmitic, stearic and other higher aliphatic carboxylic acids was described.[52–54] According to authors' data, the yields of zinc porphyrins reached 62%, which raises serious doubts. The attempts to reproduce the suggested procedures appeared to be unsuccessful.[55,56] In the case of zinc salts of lower, propionic and butyric, acids, the yields of porphyrins did not exceed 22%, and the application of caprylic, capric, and stearic acid salts afforded only the trace amounts of the complexes, since the authors were unable to achieve high temperatures (320–350 °C) necessary for the reaction completion. The boiling points of the reaction mixtures were 250–270 °C, and the prolonged heating at these temperatures led to the decomposition of complexes. The problem was solved using a 50% excess of imide **1**, which allowed increasing the temperature of the reaction mixture to the required level. Hence, a series[56] of *meso*-tetraalkyl-substituted zinc tetrabenzoporphyrins **39**, **40**, **45**–**47** were obtained (Scheme 13).

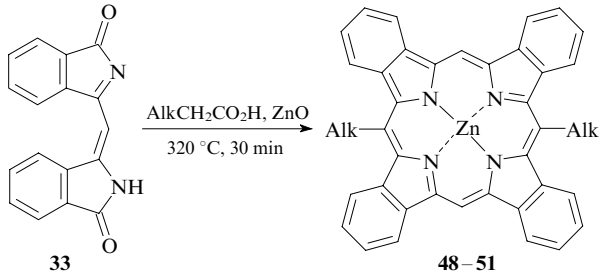
Scheme 13



(*a*) $(AlkCH_2CO_2)_2Zn$ (1/3 equiv.), 320 °C, 1.5–6 h;
Alk = Me (**39**, 1.5 h, 22%), Et (**40**, 1.5 h, 20%), n-C_6H_{13} (**45**, 6 h, 15%), n-C_8H_{17} (**46**, 6 h, 14%), n-$C_{16}H_{33}$ (**47**, 6 h, 17%)

The introduction of compound **33** into the reaction with carboxylic acids and zinc oxide yielded zinc 5,15-dialkyl-substituted tetrabenzoporphyrins **48**–**51**[55,57] (Scheme 14).

Scheme 14

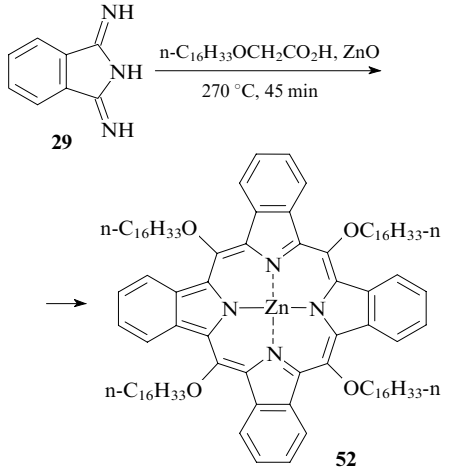


33 **48–51**

Alk = Me (**48**, 34%), n-C_6H_{13} (**49**, 35%), n-C_8H_{17} (**50**, 33%), n-$C_{16}H_{33}$ (**51**, 33%)

The attempts to synthesize zinc complex of 5,10,15,20-tetrakis(hexadecyloxy)tetrabenzoporphyrin (**52**) by heating of hexadecyloxyacetic acid with imide **1** and zinc oxide at 350 °C at different reactant ratios were unsuccessful.[58] A reason is the low stability of acid and the products of its condensation with imide **1** at high temperatures. Therefore, the synthesis of complex **52** was performed starting from compound **29** (Scheme 15), which allowed the researchers to lower the process temperature to 270 °C. The yield of complex **52** did not exceed 2%, and the main porphyrin-type products in this case were *meso*-alkoxy-substituted tetrabenzoazaporphyrins.[58]

Scheme 15



29 **52**

4. meso-Amino-substituted tetrabenzoporphyrins

As it was already mentioned, the template method for synthesis of tetrabenzoporphyrins has an essential drawback, the lability of many substituted acetic acids at high temperatures. Among these acids is glycine, which already starts to decompose at 240 °C (see Ref. 59, p. 299) with the primary amino group serving as the oxidation centre. To protect it from the oxidation, acylation is often used, and depending on the nature of the acylating agent, both secondary and tertiary amides are formed. The latter are more stable to heating, therefore, in another study,[60] phthalic acid anhydride was used as the acylating agent; its reaction with glycine in DMF led to *N*-carboxymethylphthalimide. On heating with imide **1**, its zinc salt **53** yielded zinc 5,10,15,20-tetrakis(*N*-phthalimido)tetrabenzoporphyrin (**54**), which was treated with hydrazine hydrate in pyridine to afford zinc 5,10,15,20-tetraminotetrabenzoporphyrin (**55**) (Scheme 16).[60]

At present, this approach is the only method allowing for direct introduction of the amino group at the *meso*-positions of tetrabenzoporphyrin *via* the template synthesis.

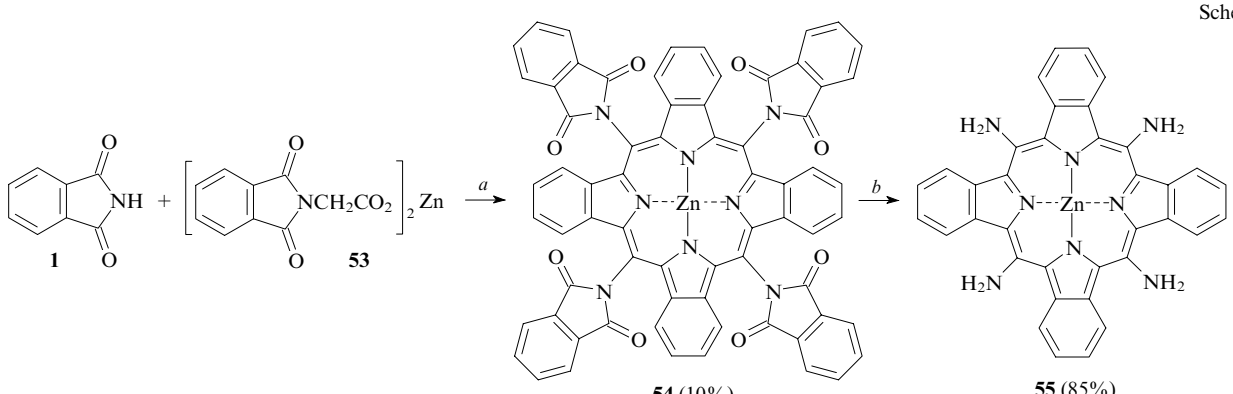
Hence, the high-temperature template method for synthesis of *meso*-substituted tetrabenzoporphyrins has essential drawbacks. They are associated, first of all, with the instability of the initial compounds at high temperatures, which makes impossible the synthesis of many tetrabenzoporphyrins having nitro- and carboxy groups, halogen atoms, and other functional substituents *via* this method. Second, the yields of target compounds usually do not exceed 20%. Finally, the synthesis of tetrabenzoporphyrins by the template method gives metal complexes, and transformation of these products into free bases requires the stage of demetallation. At the same time, this method features high simplicity and economy, which determines its intensive development at present.

III. Low-temperature condensation of saturated isoindole analogues with aromatic aldehydes

The demand for *meso*-substituted tetrabenzoporphyrins bearing different functional groups promoted the development of novel synthetic methods that feature considerably milder conditions than the template method. By analogy with the methods for synthesis of *meso*-substituted porphyrins devised by Rothemund,[61,62] Adler's and Longo's[63–65] and Lindsey's groups,[66,67] these methods are based on the reaction of isoindole with aldehydes.

Indeed, complex **3** was obtained in > 50% yield[68] by the reaction of isoindole with benzaldehyde in the presence of zinc acetate at high temperature. However, the severe conditions of synthesis, unavailability and instability of

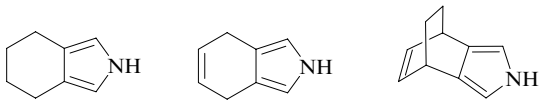
Scheme 16



1 **53** **54** (10%) **55** (85%)

(*a*) 320 °C, 2 h; (*b*) $NH_2NH_2 \cdot H_2O$, pyridine, Δ, 1.5 h

isoindole makes this method hardly suitable for preparative applications. Therefore, for the synthesis of tetrabenzoporphyrins, the saturated analogues of isoindole (pyrroles with annulated alicycles) were suggested, which are rather stable compounds. Nowadays, three groups of such compounds are known. The first one includes 4,5,6,7-tetrahydro-2*H*-isoindole derivatives (**56**), the second one comprises 4,7-dihydro-2*H*-isoindole derivatives (**57**), and the third one consists of 4,7-ethano-4,7-dihydro-2*H*-isoindole derivatives (**58**).



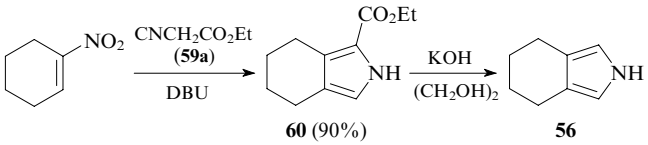
56 **57** **58**

The methods for synthesis of *meso*-substituted tetrabenzoporphyrins using pyrroles **56**–**58** started to be developed at the beginning of the 2000s. They are based on the condensation of these compounds or their derivatives with aldehydes according to the Lindsey method [66, 67] or by the MacDonald's [2 + 2] method.[69] Saturated analogues of tetrabenzoporphyrin are subjected at the last stage either to oxidative aromatization (in the case of derivatives of imines **56**, **57**), or thermal aromatization by the retro-Diels–Alder reaction (in the case of derivatives of imine **58**). The first stage of each process is the synthesis of the starting pyrroles.

1. Synthesis of saturated isoindole analogues

Compounds **56**–**58**, necessary for the preparation of tetrabenzoporphyrins, are generally synthesized by the Barton–Zard reaction.[70, 71] Thus, the interaction of 1-nitrocyclohexene with ethyl isocyanoacetate (**59a**) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded ethyl 4,5,6,7-tetrahydro-2*H*-isoindole-1-carboxylate (**60**) [72] in high yield. On treatement with potassium hydroxide in ethylene glycol, compound **60** undergoes deethoxycarbonylation, giving rise to pyrrole **56** (Scheme 17). [73]

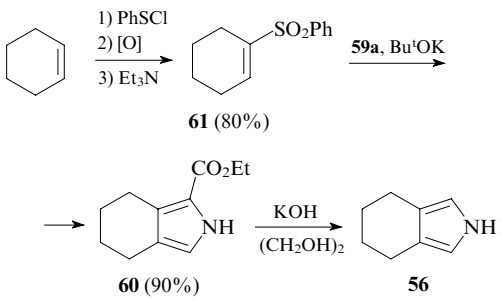
Scheme 17



60 (90%)

Later, unsubstituted cyclohexene was suggested to be used in the synthesis of compound **60**.[74] Upon the sequential treatment with phenylsulfenyl chloride, an oxidant (*m*-chloroperbenzoic acid or oxone) and triethylamine, it transforms into cyclohex-1-en-1-ylsulfonylbenzene (**61**),

Scheme 18

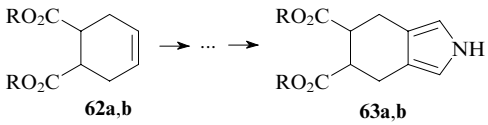


61 (80%) **60** (90%) **56**

which reacts with ethyl isocyanoacetate (**59a**) in the presence of potassium *tert*-butoxide to give pyrrole **60**. Under the action of alkali in ethylene glycol, the elimination of ester group takes place (Scheme 18).

This method was used with substituted cyclohexenes **62a**,**b** to prepare substituted pyrroles **63a**,**b** (Scheme 19).[74]

Scheme 19

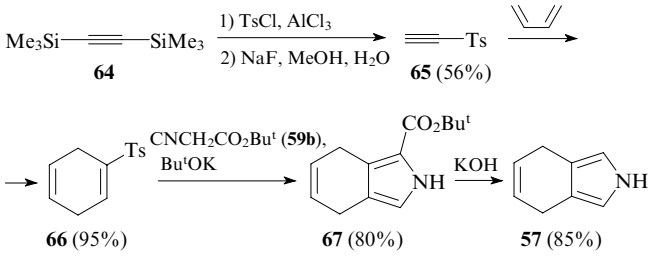


62a,**b** **63a**,**b**

R = Me (**a**), Bu^n (**b**)

Another analogue of isoindole, 4,7-dihydro-2*H*-isoindole (**57**), was synthesized [75, 76] starting from bis(trimethylsilyl)acetylene (**64**). This compound was made to react with tosyl chloride in the presence of aluminium chloride, which was followed by treatment with sodium fluoride in a methanol–water mixture, to be converted to tosylacetylene (**65**). The interaction of alkyne **65** with buta-1,3-diene leads to *p*-(cyclohexa-1,4-dien-1-ylsulfonyl)toluene (**66**), which is converted to *tert*-butyl 4,7-dihydro-2*H*-isoindole-1-carboxylate (**67**) by the Barton–Zard reaction. The treatment of compound **67** with potassium hydroxide in diethylene glycol yields pyrrole **57** (Scheme 20).

Scheme 20

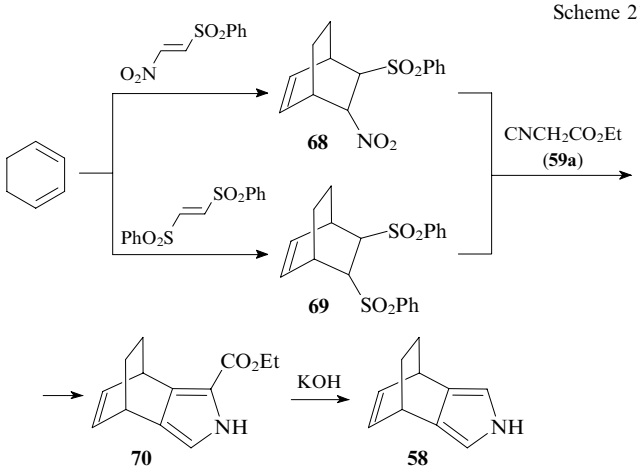


64 **65** (56%) **66** (95%) **67** (80%) **57** (85%)

Ts = 4-MeC$_6$H$_4$SO$_2$

Among the third group of pyrrole derivatives used in the synthesis of tetrabenzoporphyrins are 4,7-ethano-4,7-dihydro-2*H*-isoindole (**58**) and its derivatives. A precursor for their synthesis is cyclohexa-1,3-diene, which is introduced into the Diels–Alder reaction or is made to react with 1-(phenylsulfonyl)-2-nitroethene [77, 78] or 1,2-bis(phenylsulfonyl)ethene.[79] The resulting bicyclic derivatives **68**, **69**

Scheme 21

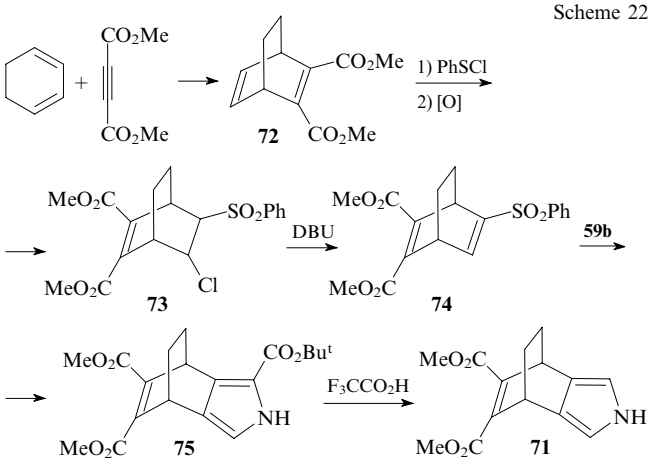


68 **69** **70** **58**

react with ethyl isocyanoacetate (**59a**) affording compound **70**, which is transformed then into product **58** (Scheme 21).

5,6-Di(methoxycarbonyl)-4,7-ethano-4,7-dihydro-2*H*-isoindole (**71**)[80] can be derived from the reaction of cyclohexa-1,3-diene with dimethyl acetylenedicarboxylate. The resulting dimethyl bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (**72**) is treated with phenylsulfenyl chloride and *m*-choloroperbenzoic acid. This gives rise to sulfolene **73**, which under the action of a base is transformed into compound **74**. Pyrrole **75** is obtained by the Barton–Zard reaction upon treatment of compound **74** with isocyano acetic acid *tert*-butyl ester (**59b**), and the subsequent reaction of triester **75** with trifluoroacetic acid gives compound **71** (Scheme 22). The yield of pyrrole **71** calculated in relation to dimethyl acetylenedicarboxylate comprises 72%.

Scheme 22



Pyrroles **56**–**58** and their derivatives **63**, **67**, **71** obtained by this method were used in the synthesis of *meso*-substituted tetrabenzoporphyrins of variable structure.

2. Synthesis of *meso*-substituted tetrabenzoporphyrins based on 4,5,6,7-tetrahydro-2*H*-isoindoles

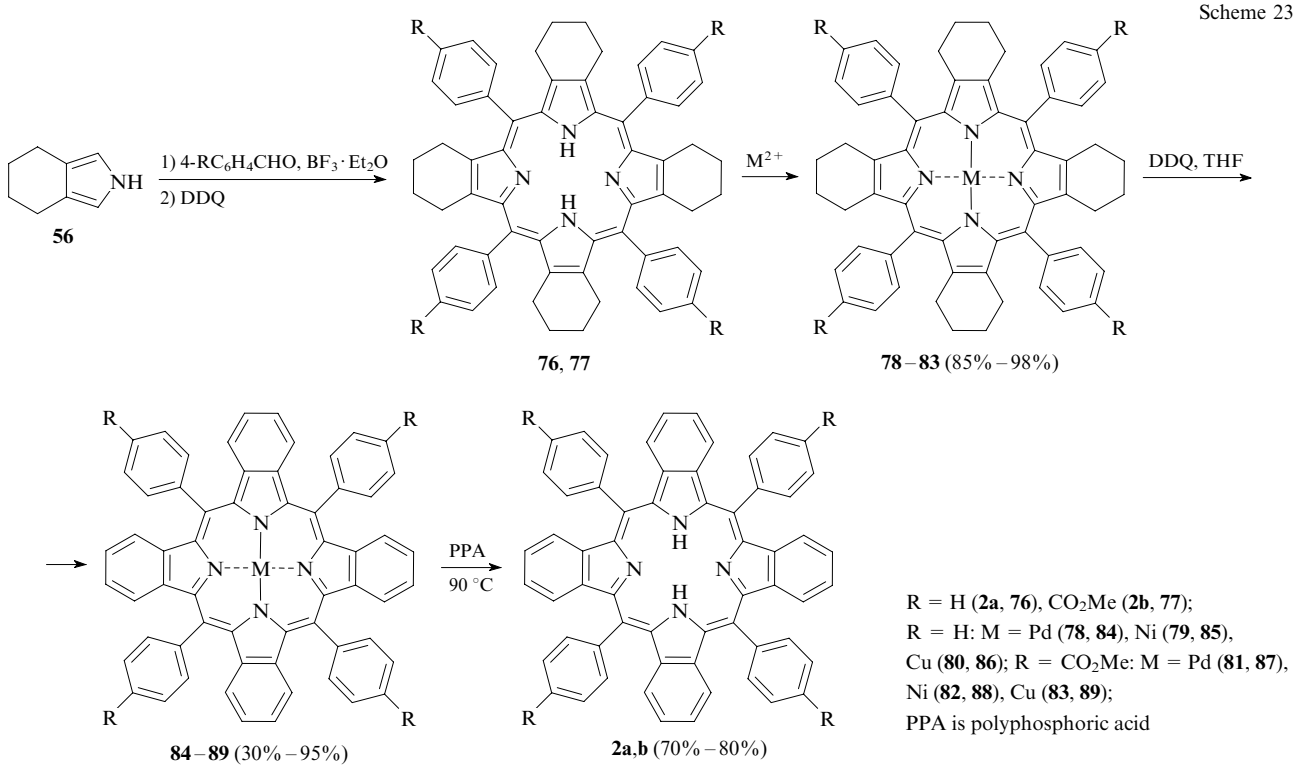
The synthesis of *meso*-aryl-substituted tetrabenzoporphyrins using compound **56** was carried out for the first time in 2001.[73] The interaction of pyrrole **56** with benzaldehyde or 4-methoxycarbonylbenzaldehyde in the presence of $BF_3 \cdot Et_2O$ as a catalyst followed by the treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) leads to porphyrins **76** and **77**[73] in 54% and 45% yields, respectively (Scheme 23).

Porphyrins **76**, **77** were introduced into the complexation with palladium, nickel and copper salts in benzonitrile (for Pd complexes) or a dichloromethane–methanol mixture (for Ni and Cu complexes), and resulting complexes **78**–**83** were oxidized by refluxing with DDQ in THF for 0.5–3 h. The yields of products **84**–**89** varied from 30% to 95%; for porphyrins **87**–**89** having electron-withdrawing groups in the *meso*-substituents, the yields were somewhat higher. The corresponding free bases **2a**,**b** were obtained by treating complexes **84**–**89** with polyphosphoric acid under heating.

Highly substituted tetrabenzoporphyrins **90**–**94** and their metal complexes **95**–**109** were synthesized starting from pyrrole **63a** and different benzaldehydes (Scheme 24).[74]

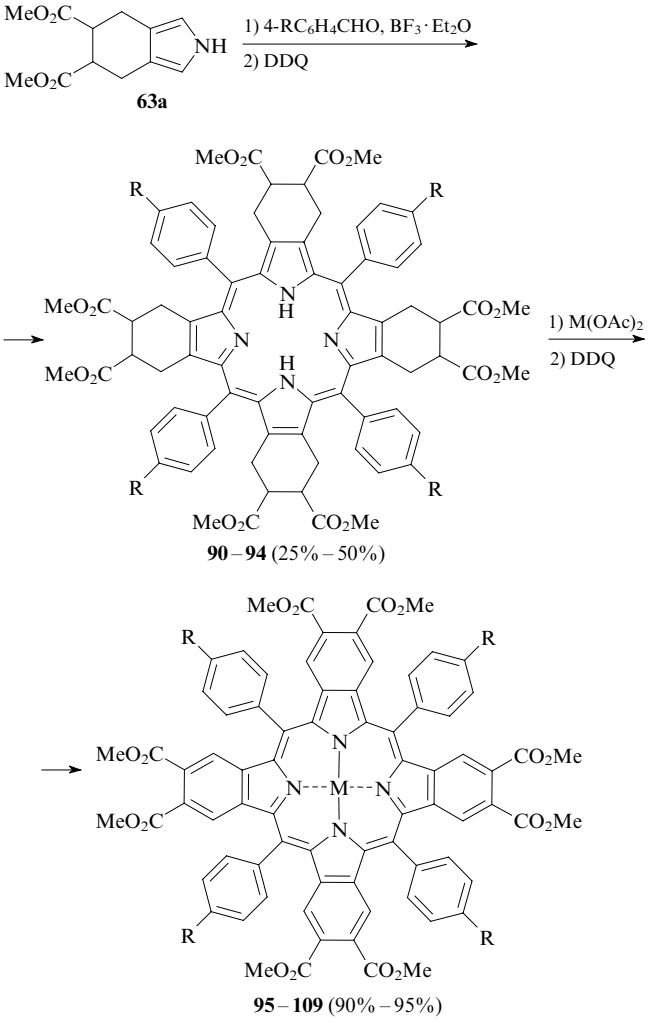
It was established[74,81] that due to the high basicity of porphyrins **76**, **77**, **90**–**94**, their synthesis by the Lindsey method (see Schemes 23, 24) affords the corresponding dications. These dications are rather stable and do not transform into the free bases even while being dissolved in basic solvents. Thus, in a dichloromethane–pyridine mixture (3 : 1), their content comprises 50%, while in neat pyridine, it is 10%. The low reactivity of dications does not allow one to perform the aromatization even under long-term treatment with DDQ, *p*-chloranil or other oxidants. It was also revealed that due to the lability of zinc

Scheme 23



R = H (**2a**, **76**), CO_2Me (**2b**, **77**);
R = H: M = Pd (**78**, **84**), Ni (**79**, **85**), Cu (**80**, **86**); R = CO_2Me: M = Pd (**81**, **87**), Ni (**82**, **88**), Cu (**83**, **89**);
PPA is polyphosphoric acid

Scheme 24



complexes, the aromatization does not proceed to the full extent; iron, cobalt, and manganese complexes decompose upon treatment with an oxidant, and the best results can be obtained by the aromatization of copper, nickel, and palladium complexes.

3. Synthesis of *meso*-substituted tetrabenzoporphyrins based on 4,7-dihydro-2*H*-isoindoles

The possibility of application of pyrrole **57** in the synthesis of *meso*-aryl-substituted porphyrins was shown for the first time in 2006.[75] The condensation with aromatic aldehydes by the Lindsey method gave 5,10,15,20-tetraaryltetracyclohexenoporphyrins **110a–d** (yields 23%–48%), which are aromatized under action of DDQ, resulting in the quantitative formation of tetrabenzoporphyrins **2a–d** (Scheme 25).[75, 76, 82]

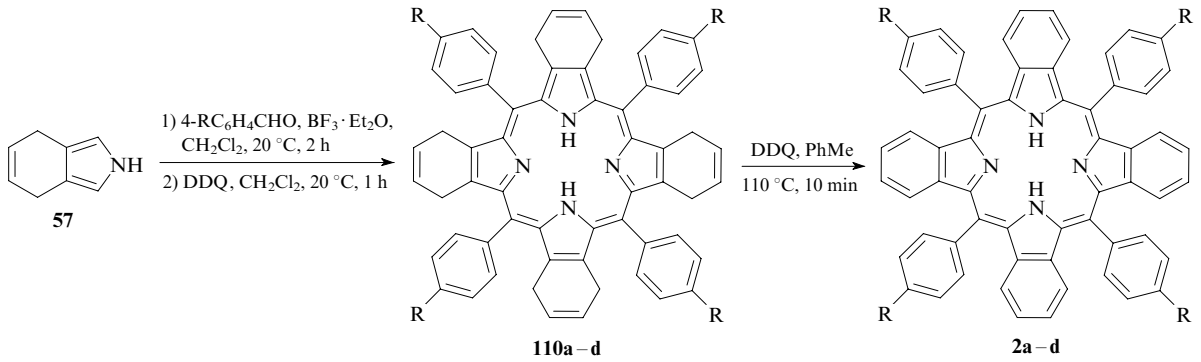
It was found[76] that the ease of aromatization of the intermediate tetracyclohexenoporphyrins allows combining two stages, namely, condensation of pyrrole **57** with aldehydes and aromatization of its products under the action of an excess of DDQ, into one process, which makes this method much more ready and economical.

Pyrrole **67** was used to obtain 5,15-diaryl-substituted tetrabenzoporphyrins.[76, 83] The synthesis of these compounds was performed by two methods: using MacDonald's [2+2] method based on the condensation of *meso*-aryldipyrrolylmethanes with analogous diformyl derivatives (Scheme 26), and *via* the condensation of *meso*-unsubstituted dipyrrolylmethane with aldehydes (Scheme 27).

It was found that the addition of anhydrous tetrabutylammonium chloride during the condensation of pyrrole **67** with aldehydes catalyzes the process, which allows increasing the yield of dipyrrolylmethane **111** from 60%–70% to 90%–100%. Compound **111** is transformed into α-unsubstituted dipyrrolylmethane **112** and into diforlmyldipyrrolylmethane **113**; combined condensation of these products leads to porphyrin **114**. The latter undergoes aromatization resulting in 5,15-diphenyltetrabenzoporphyrin **115a** in quantitative yield (see Scheme 26).

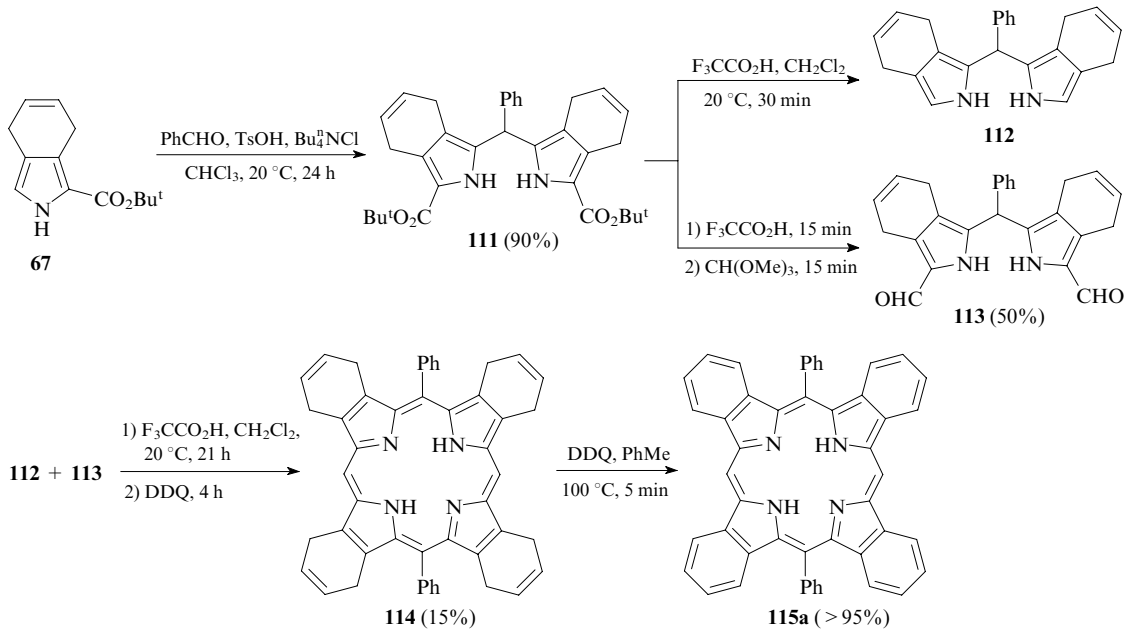
The second method for synthesis of 5,15-diaryl-substituted tetrabenzoporphyrins was realized[83] using *meso*-unsubstituted dipyrrolylmethane **116** (see Scheme 27). Compound **116** can be prepared starting from ethyl 4,7-dihydro-2*H*-isoindole-1-carboxylate (**117**) synthesized similarly to compound **67**. The condensation of pyrrole **117** with dimethoxymethane in the presence of an acidic catalyst leads to di(ethoxycarbonyl)-substituted dipyrrolylmethane **118**, which is subjected subsequently to the alkaline hydrolysis of ester groups followed by the decarboxylation.

Scheme 25

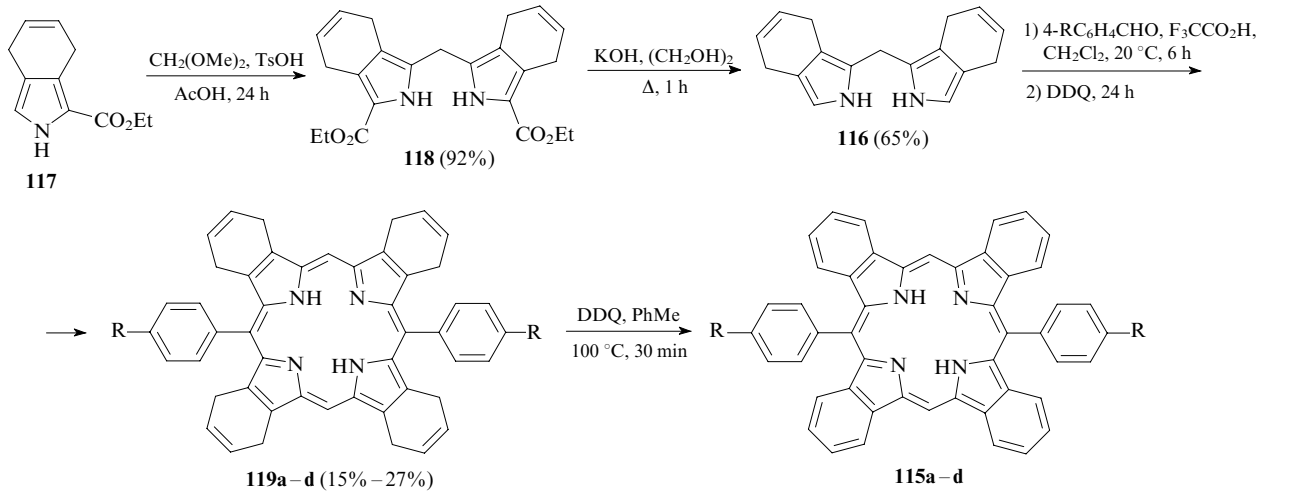


R = H (**a**, 27%), CO_2Me (**b**, 45%), Br (**c**, 48%), OMe (**d**, 23%)

Scheme 26



Scheme 27



The condensation of dipyrrolylmethane **116** with substituted benzaldehydes affords porphyrins **119a–d**. Their oxidative aromatization proceeds in quantitative yields and leads to the corresponding 5,15-diaryl-substituted tetrabenzoporphyrins **115a–d** having functional groups in the *meso*-substituents.

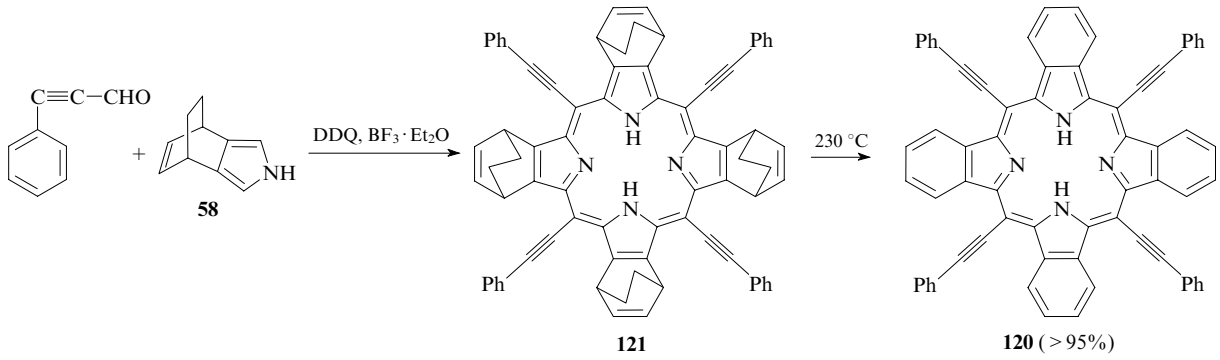
4. Synthesis of *meso*-substituted tetrabenzoporphyrins based on 4,7-ethano-4,7-dihydro-2*H*-isoindoles

Like hydrogenated isoindoles **56**, **57**, tricyclic pyrrole **58** is condensed with aldehydes. The synthesis of 5,10,15,20-tetrakis(phenylethynyl)tetrabenzoporphyrin (**120**) by the reaction of compound **58** with phenylpropynal in the presence of a catalyst and an oxidant was described.[84] The heating of initially formed 5,10,15,20-tetrakis(phenylethynyl)-substituted porphyrin **121** to 230 °C under vacuum for 30 min (retro-Diels–Alder reaction) leads to target product **120** in a quantitative yield (Scheme 28).

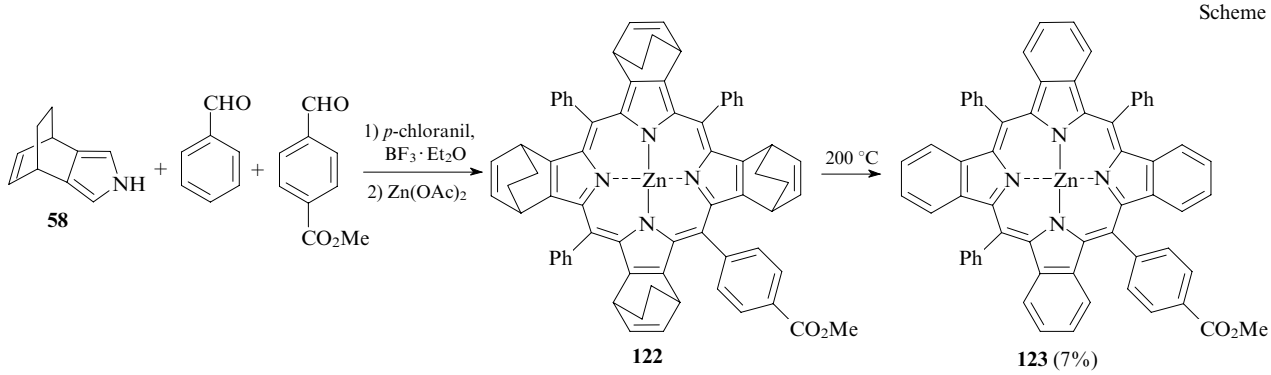
Pyrrole **58** was employed also in the synthesis of low-symmetry tetrabenzoporphyrins.[85] Its interaction with a mixture of benzaldehyde and 4-methoxycarbonylbenzaldehyde in the presence of $BF_3 \cdot Et_2O$ and zinc acetate gives the corresponding zinc porphyrin **122** as a component of a mixture of porphyrins with different combinations of *meso*-aryl substituents. After heating to 200 °C for 10 min, tetrabenzoporphyrin **123** was isolated by column chromatography in 7% yield in relation to the starting pyrrole **58** (Scheme 29).

5-Aryl-substituted tetrabenzoporphyrin **124** was synthesized[85] by the MacDonald's [2 + 2] method (Scheme 30). The co-condensation of dipyrrolylmethanes **125** and **126** under conditions of acid catalysis in the presence of zinc acetate and air oxygen leads to complex **127**, which is transformed into tetrabenzoporphyrin **124** without isolation (yield after purification 15%).

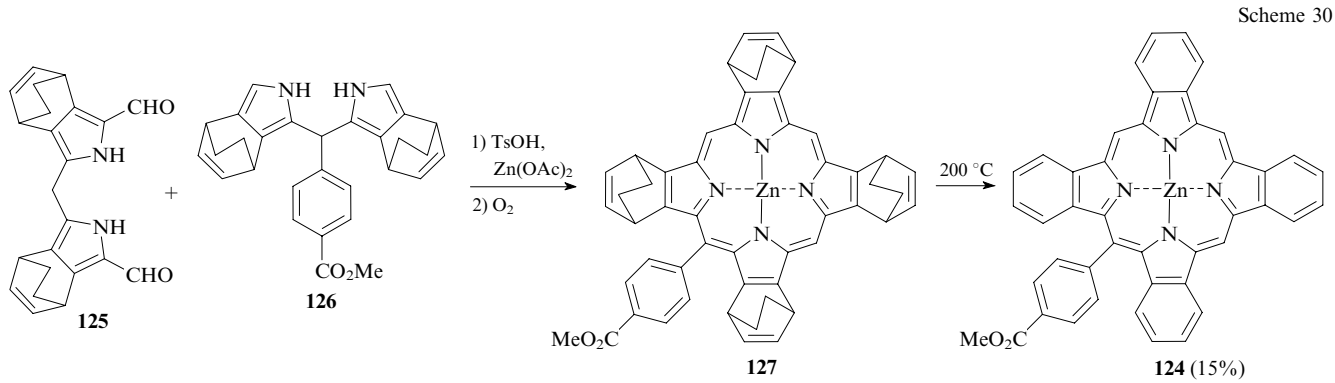
Scheme 28



Scheme 29



Scheme 30

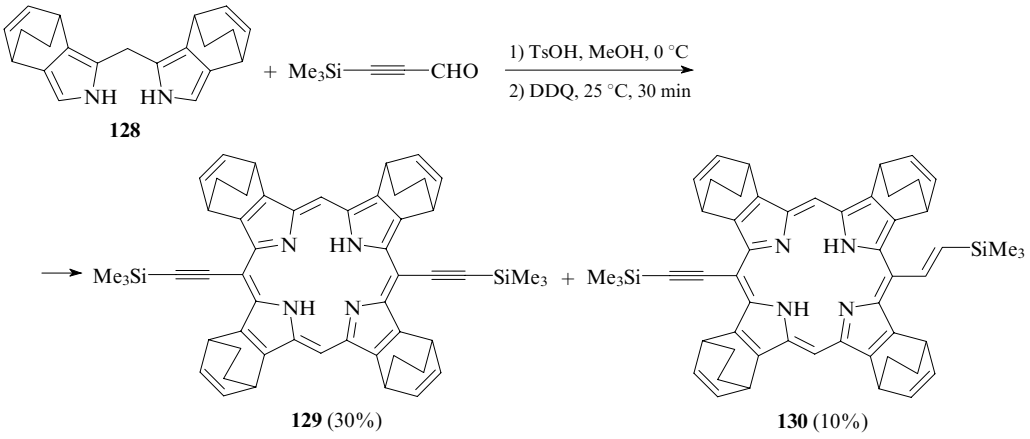


An interesting result was obtained [86] upon condensation of dipyrrolylmethane **128** with trimethylsilylpropynal in methanol (Scheme 31). It was found that, besides expected 5,15-dialkynyl-substituted porphyrin **129**, the reaction results in 5-alkynyl-15-alkenyl-substituted porphyrin **130**. Subsequently, it was established [87] that the ratio of porphyrins **129** and **130** depends on the reaction conditions. The reaction in chloroform in the presence of $BF_3 \cdot Et_2O$ gave product **129** in only 3% yield, while the yield of product **130** increased to 42%.

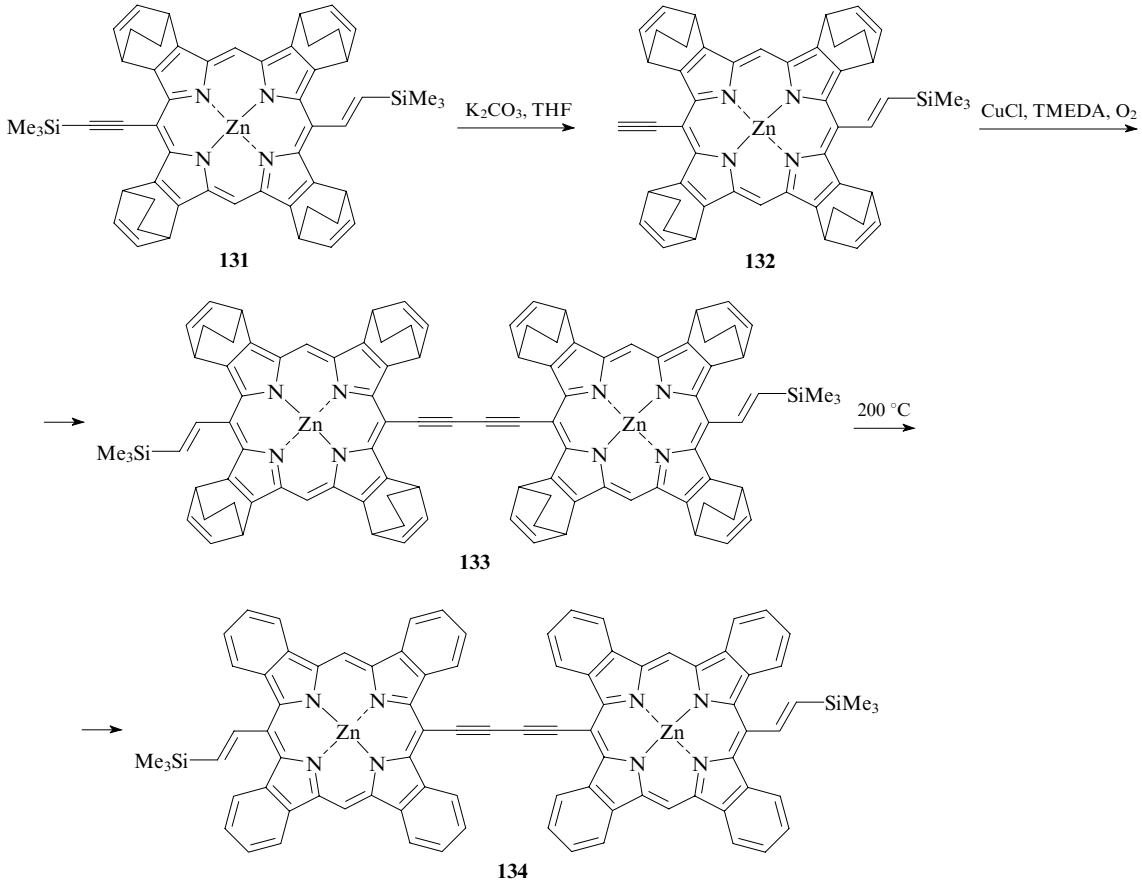
The unsymmetrical substitution in benzoporphyrin **130** appeared to be advantageous for its further functionalization.[86] For example, on treatment with potassium carbonate in tetrahydrofuran, zinc complex **131** was converted to alkyne **132**, which was subjected to the oxidative dimerization under the action of oxygen in the presence of CuCl and tetramethylenediamine (TMEDA). The subsequent aromatization of dimer **133** led to dimeric tetrabenzoporphyrin **134** in which two macrocycles are linked *via* the butadiene group (Scheme 32).

The low-temperature methods for synthesis of *meso*-substituted tetrabenzoporphyrins considered in this Section are much more flexible compared to the template method. They provide tetrabenzoporphyrins of most diverse structures in relatively high yields. Since the process is performed under mild conditions, there are no by-products of the thermal decomposition of the reactants or target compounds in the reaction mixtures, which substantially facilitates the purification by column chromatography. The high degree of purity of tetrabenzoporphyrins synthesized by these methods enables their application in the design of film electronic devices such as organic field effect transistors (OFET) [88–92] and photovoltaic cells (OPV).[93,94] The disadvantages of low-temperature methods consist in the multistep processes and high cost of some initial compounds. However, the advantages of this approach significantly reweighs its drawbacks; therefore, nowadays the low-

Scheme 31



Scheme 32



temperature condensation of saturated isoindole analogues with aldehydes is the main method for synthsis of *meso*-substituted tetrabenzoporphyrins.

IV. Introduction of substituents at the *meso*-positions of the preformed macrocycle

Two above groups of methods for the synthesis of *meso*-substituted tetrabenzoporphyrins are based on the condensation of isoindole derivatives with nucleophilic or electrophilic reagents, the *meso*-substituents being parts of these reagents. The third group includes the methods based on the introduction of substituents at the *meso*-positions of the macrocycle *via* electrophilic or nucleophilic substitution of the hydrogen atoms.

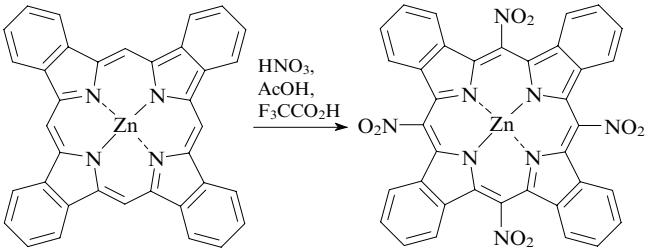
1. Synthesis of *meso*-substituted tetrabenzoporphyrins *via* electrophilic substitution

One of the ways to modify tetrabenzoporphyrin is the introduction of functional groups into the macrocycle molecule using the reactions of electrophilic substitution. Up to the mid-1980s, halogenation,[95] sulfonation,[96–98] chloromethylation,[99] and nitration[100] of tetrabenzoporphyrins and their metal complexes were studied. However the compounds obtained were often poorly soluble in organic solvents, which complicated their purification and exact elucidation of the structure. For example, the nitra-

tion of cadmium tetrabenzoporphyrin with a nitrating mixture (20.4% HNO_3, 77% H_2SO_4, and 2.6% H_2O) at 0 °C afforded mononitro derivative of tetrabenzoporphyrin in 23% yield; however, the position of the nitro group was not confirmed unambigously, it was only assumed that the nitro group is situated in one of the isoindole moieties.[100]

Later, the nitration was studied in detail by the example of zinc tetrabenzoporphyrin (**135**).[101] It was established that its nitration with 1% aq. HNO_3 in trifluoroacetic/acetic acid mixture at 25 °C for 1 h gives a mixture of tetrabenzoporphyrins having different numbers of the nitro groups at the *meso*-positions of the macrocycle. Preparative thin layer chromatography wa used to isolate zinc 5,10,15,20-tetranitrobenzoporphyrin (**136**) in 17% yield (Scheme 33).

Scheme 33



135 **136** (17%)

The nitration of zinc tetrakis(4-*tert*-butylbenzo)porphyrin (**137**) with 1% aq. HNO_3 in acetic acid (25 °C, 1 h) affords a mixture of zinc 5,10,15,20-tetranitrotetrakis(4-*tert*-butylbenzo)porphyrin (**138**) and zinc 5,10,15-trinitrotetrakis (4-*tert*-butylbenzo)porphyrin (**139**) in 60% and 6% yields, respectively (Scheme 34).[101] It was found that complex **138** cannot be reduced to *meso*-amino-substituted tetrabenzoporphyrin **140** on treatment with $SnCl_2$ in acetic acid, sodium borohydride and sodium hydrogen sulfite in aqueous alkaline medium or upon hydrogenation on palladium catalyst in ethanol. It was reduced only with metallic tin in boiling acetic acid. Porphyrin **140** appeared to be unstable and was characterized as *N*-acyl derivative **141**.[101]

Nowadays, the nitration is the only one method of introduction of the substituents at the *meso*-positions of tetrabenzoporphyrin using the reactions of electrophilic substitution.

2. Synthesis of *meso*-substituted tetrabenzoporphyrins by nucleophilic substitution

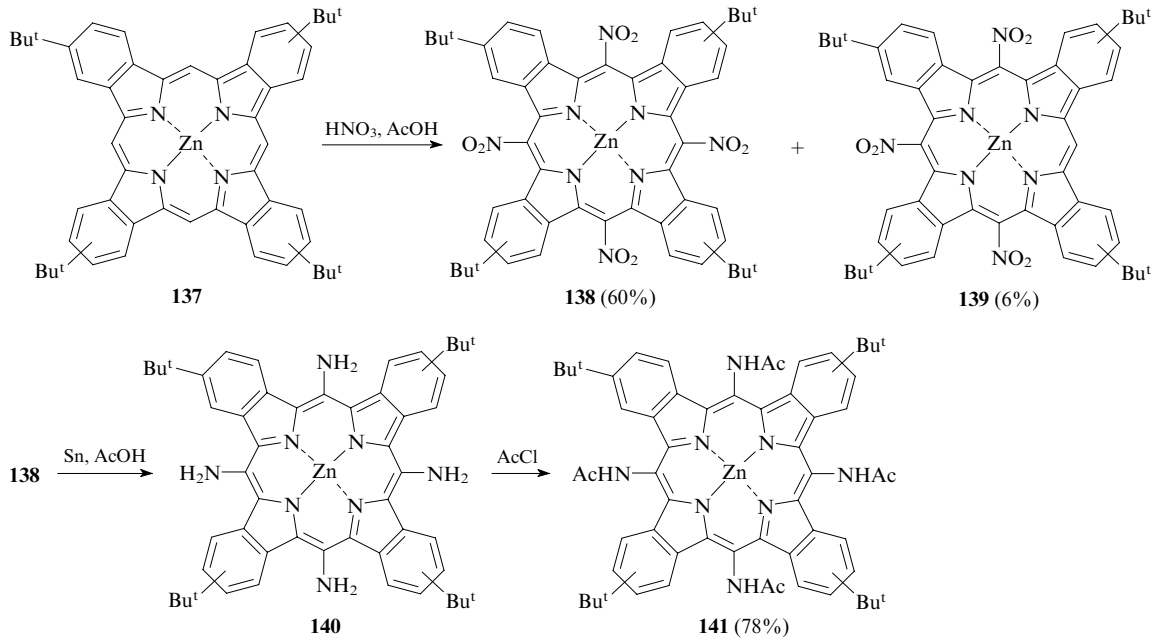
As the first example of the application of nucleophilic substitution in the modification of tetrabenzoporphyrin macrocycle, one should consider the interaction of complex **135** with n-hexyllithium (5 equiv.) in THF at −30 °C followed by treatment with water and DDQ, which gave rise to three free bases, namely, tetrabenzoporphyrin (**142**), 5-hexyltetrabenzoporphyrin (**143**) and 5,10-dihexyltetrabenzoporphyrin (**144**) in 32%, 38%, and 9% yields, respectively (Scheme 35).

The increase in the amount of n-hexyllithium to 8 equiv. leads to the increase in the yields of alkyl-substituted tetrabenzoporphyrins **143** and **144** to 46% and 14%, respectively, whereas the yield of porphyrin **142** reduces to 6%. The application of n-butyllithium (9 equiv.) in the reaction with zinc complex **135** resulted in the isolation of 5-n-butyltetrabenzoporphyrin (42%), 5,10-di-n-butyltetrabenzoporphyrin (42%) and unsubstituted benzoporphyrin (**142**) (10%).[102]

The authors explain the formation of porphyrins in the form of free bases by transmetallation of zinc complexes to dilithium derivatives, which are demetallated upon quenching with water.[102] A similar result was obtained previously[103] upon the interaction of zinc octaethylporphyrin with organolithium reagents.

The attempts to synthesize *meso*-aryl-substituted tetrabenzoporphyrins **145**, **146** *via* the reaction of complex **135** with phenyllithium appeared to be unsuccessful.[102] These products were derived by the treatment of porphyrin **147** with phenyllithium; porphyrin **147** was obtained by the condensation of ester **70** in the presence of lithium alumi-

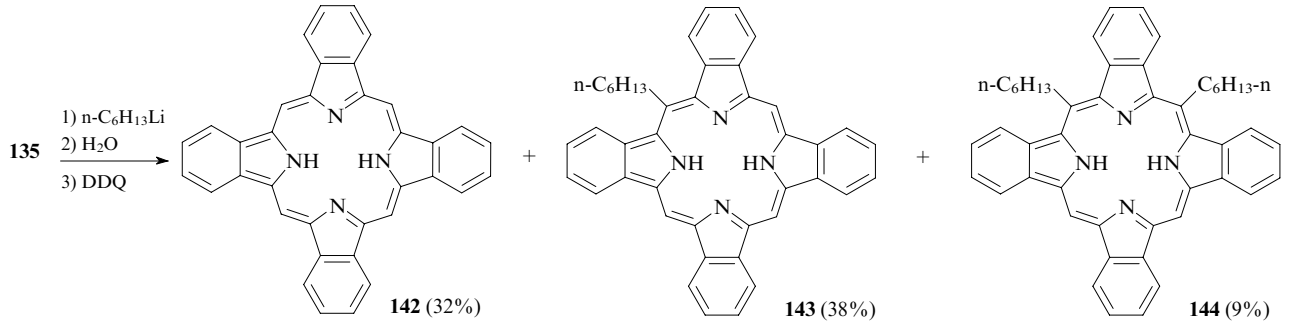
Scheme 34



137 **138** (60%) **139** (6%)

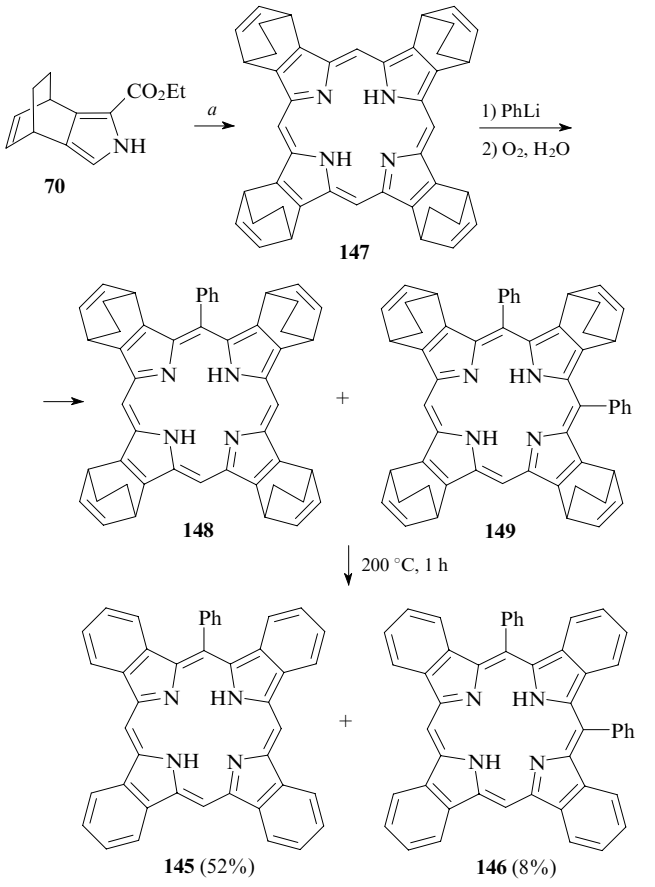
140 **141** (78%)

Scheme 35



nium hydride, serving as an acidic catalyst and oxidant, according to the published procedure.[79] The following transformation of phenyl-substituted porphyrins **148**, **149** into tetrabenzoporphyrins **145**, **146** was accomplished by the retro-Diels–Alder reaction (Scheme 36).[102]

Scheme 36



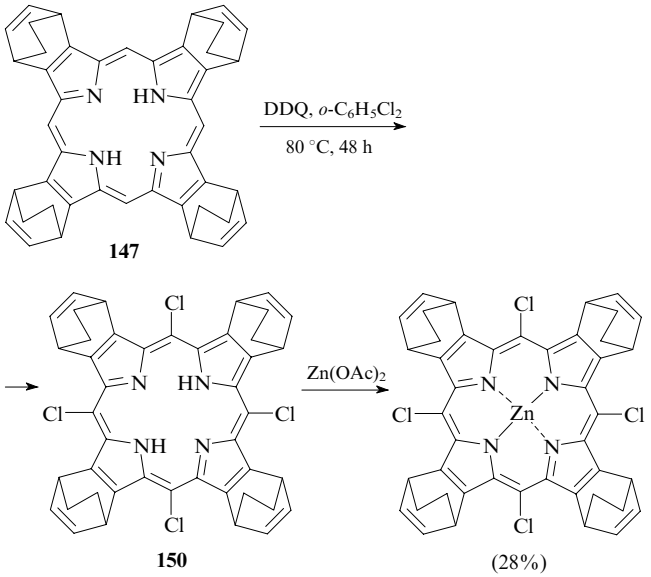
(*a*) 1) $LiAlH_4$, THF, 0 °C, 3 h; 2) TsOH, $CHCl_3$, 20 °C, 24 h; 3) *p*-chloranil, $CHCl_3$, 20 °C, 48 h

Of note is the high selectivity of the nucleophilic substitution. The reaction of porphyrins **135** and **147** with organolithium reagents affords only two *meso*-substituted tetrabenzoporphyrins; in the case of disubstituted compounds **144** and **146**, the *meso*-substitutents are situated at the *cis*-positions of the macrocycle. Hence, nowadays this method is the only one giving 5,10-disubstituted tetrabenzoporphyrins in satisfactory yields.

In a more recent work [104] dealing with thermal transformations of porphyrin **147** in *o*-dichlorobenzene at 120 °C in the presence of an excess of DDQ, it was found unexpectedly that the proceeding reactions result in a mixture of porphyrins consisting of *meso*-chloro-substituted tetrabenzoporphyrins with different numbers of the chlorine atoms. The interaction of macrocycle **147** with DDQ (15 equiv) at 80 °C for 48 h leads to 5,10,15,20-tetrachloro-substituted porphyrin **150**, which was isolated after metallation with zinc acetate by column chromatography in the form of the corresponding zinc complex (Scheme 37).

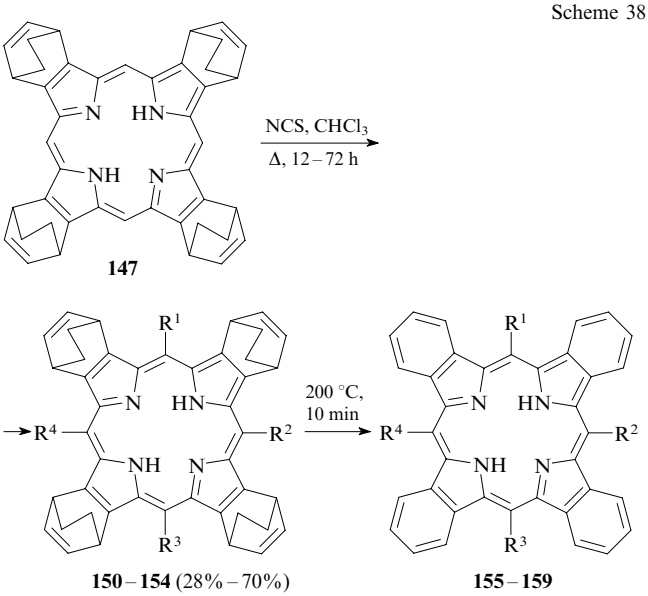
Further invetsigations showed [104] that it is more reasonable to use *N*-chlorosuccinimide (NCS) as the chlorinating agent. The reaction of NCS (1.1–4.4 equiv.) with porphyrin **147** in boiling chloroform for 12–72 h gives rise to chlorinated porphyrins **150**–**154**; the yeild of each product depends on the porphyrin : NCS ratio (the maximal yields of compounds **150**, **151**, **152**, **153**, and **154** are 70%, 28%, 32%, 33%, and 43%, respectively).

Scheme 37



On heating to 200 °C under vaccum, porphyrins **150**–**154** transform into the corresponding *meso*-chlorotetrabenzoporphyrins **155**–**159** in quantitative yields (Scheme 38).

Scheme 38



147

150–154 (28%–70%) **155–159**

$R^1 = R^2 = R^3 = Cl$: $R^4 = Cl$ (**150**, **155**), H (**151**, **156**); $R^1 = R^2 = Cl$, $R^3 = R^4 = H$ (**152**, **155**); $R^1 = R^3 = Cl$, $R^2 = R^4 = H$ (**153**, **158**); $R^1 = R^2 = R^3 = H$, $R^4 = Cl$ (**154**, **159**)

* * *

Hence, nowadays three main methods for synthesis of *meso*-substituted tetrabenzoporphyrins are used, which comprise the template synthesis, condensation of saturated isoindole analogues with aldehydes, and introduction of substituents at the *meso*-positions of the porphyrin macrocycle *via* the reactions of electrophilic or nucleophilic substitution. Each of these approaches possesses its own advantages and drawbacks, the choice of the particular method and reaction depends on the structure of the target macrocycle, and their combination provides the relative availability of *meso*-substituted tetrabenzoporphyrins for their investigation and application in different fields of science and engineering.

References

1. J H Helberger, A von Rubai, D E Hever *Justus Liebigs Ann. Chem.* **533** 197 (1938)
2. P A Barret, R P Linstead, F G Rundall, G A P Tuey *J. Chem. Soc.* 1079 (1940)
3. USSR P. 889675; *Byull. Izobret.* (46) 10 (1981)
4. A A Evseev, M I Bazanov, N E Galanin, A V Petrov, G Andrijewski *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **47** (10) 24 (2004)
5. P B Shea, A R Johnson, N Ono, J Kanicki *IEEE Trans. Electron Devices* **52** 1497 (2005)
6. M Drobizhev, A Karotki, M Kruk, A Rebane *Chem. Phys. Lett.* **355** 175 (2002)
7. S A Vinogradov, L W Lo, W T Jenkins, S M Evans, C Koch, D F Wilson *Biophys. J.* **70** 1609 (1996)
8. O Ongayi, V Gottumukkala, F R Fronczek, M G H Vicente *Bioorg. Med. Chem. Lett.* **15** 1665 (2005)
9. D F Wilson, W M F Lee, S Makonnen, S Apreleva, S A Vinogradov *Adv. Exp. Med. Biol.* **614** 53 (2008)
10. USSR P. 1126581; *Byull. Izobret.* (44) 75 (1984)
11. USSR P. 765281; *Byull. Izobret.* (35) 147 (1980)
12. N Ono, S Ito, C H Wu, C H Chen, T C Wen *Chem. Phys.* **262** 467 (2000)
13. V Kral, H Furuta, K Shreder, V Lynch, J L Sessler *J. Am. Chem. Soc.* **118** 1595 (1996)
14. O Finikova, A Galkin, V Rozhkov, M Cordero, C Hägerhill, S Vinogradov *J. Am. Chem. Soc.* **125** 4882 (2003)
15. N Kobayashi *Bull. Chem. Soc. Jpn.* **75** 1 (2002)
16. N E Galanin, E V Kudrik, G P Shaposhnikov *Russ. Chem. Bull.* **57** 1595 (2008) [*Izv. Akad. Nauk, Ser. Khim.* 1565 (2008)]
17. N E Galanin, E V Kudrik, G P Shaposhnikov, in *Uspekhi Khimii Porfirinov* (Progress in Chemistry of Porphyrins) Vol. 5 (Ed. O A Golubchikov) (St Petersburg: St Petersburg State University, Scientific Research Institute of Chemistry, 2007) p. 93
18. N Ono, H Yamada, T Okujima, in *Handbook of Porphyrin Science* Vol. 2 (Eds K M Kadish, K M Smith, R Guilard) (Singapore: World Scientific, 2010) p. 1
19. A V Cheprakov, in *Handbook of Porphyrin Science* Vol. 13 (Eds K M Kadish, K M Smith, R Guilard) (Singapore: World Scientific, 2010) p. 1
20. V N Kopranenkov, S N Dashkevich, E A Luk'yanets *Zh. Obshch. Khim.* **51** 2513 (1981) [a]
21. K Ichimura, M Sakuragi, H Morii, M Yasuike, Y Toba, M Fukui, O Ohno *Inorg. Chim. Acta* **186** 95 (1991)
22. E A Luk'yanets, S N Dashkevich, N Kobayashi *Zh. Obshch. Khim.* **63** 1411 (1993) [a]
23. M Yasuike, T Yamaoka, O Ohno, M Sakuragi, K Ichimura *Inorg. Chim. Acta* **184** 191 (1991)
24. G Liu, T Shi, X Cao, X Liu *Synth. React. Inorg. Met.-Org. Chem.* **24** 1127 (1994)
25. T Shi, X Zhang, W Liu, B Jia, G Liu *Chem. J. Chin. Univ.* **19** 1026 (1998)
26. N E Galanin, N A Kolesnikov, E V Kudrik, G P Shaposhnikov *Zh. Org. Khim.* **40** 297 (2004) [b]
27. V N Kopranenkov, E A Makarova, E A Luk'yanets *Khim. Geterotsikl. Soedin.* 480 (1988) [c]
28. N E Galanin, E V Kudrik, M E Lebedev, V V Aleksandriiskii, G P Shaposhnikov *Zh. Org. Khim.* **42** 306 (2005) [b]
29. N E Galanin, E V Kudrik, G P Shaposhnikov *Zh. Org. Khim.* **39** 1254 (2003) [b]
30. N E Galanin, E V Kudrik, G P Shaposhnikov *Zh. Obshch. Khim.* **76** 151 (2006) [a]
31. V P Kulinich, G P Shaposhnikov, V E Maizlish, in *Teoreticheskie i Prakticheskie Aspekty Krasheniya Tekstil'nykh Materialov i Sinteza Krasitelei (Mezhvuz. Sb. Nauchn. Tr.)* [Theoretical and Practical Aspects of Dyeing of Textile Fabrics and Synthesis of Dyes (Intercollegiate Collection of Scientific Works)] (Ed. B N Mel'nikov) (Ivanovo: Ivanovo State University of Chemistry and Technology, 1991) p. 43
32. N E Galanin, E V Kudrik, G P Shaposhnikov *Zh. Obshch. Khim.* **67** 1393 (1997) [a]
33. N E Galanin, E V Kudrik, G P Shaposhnikov *Zh. Org. Khim.* **42** 619 (2006) [b]
34. I B Rietveld, E Kim, S A Vinogradov *Tetrahedron* **59** 3821 (2003)
35. S A Vinogradov, D F Wilson *Tetrahedron Lett.* **39** 8935 (1998)
36. N E Galanin, E V Kudrik, G P Shaposhnikov *Zh. Obshch. Khim.* **69** 1542 (1999) [a]
37. RF P. 2215003 (2003); *Byull. Izobret.* (30) 233 (2003)
38. N E Galanin, E V Kudrik, G P Shaposhnikov *Zh. Obshch. Khim.* **70** 1379 (2000) [a]
39. E V Kudrik, M K Islyaikin, S V Frantseva *Zh. Obshch. Khim.* **67** 1202 (1997) [a]
40. N E Galanin, E V Kudrik, G P Shaposhnikov *Zh. Obshch. Khim.* **72** 1198 (2002) [a]
41. N E Galanin, E V Kudrik, G P Shaposhnikov *Zh. Org. Khim.* **35** 725 (2001) [b]

42. N E Galanin, E V Kudrik, G P Shaposhnikov *Zh. Obshch. Khim.* **68** 1740 (1998) [a]
43. N E Galanin, L A Yakubov, G P Shaposhnikov *Zh. Org. Khim.* **45** 1037 (2009) [b]
44. N E Galanin, L A Yakubov, G P Shaposhnikov *Zh. Obshch. Khim.* **78** 1572 (2008) [a]
45. A S Semeikin, N G Kuz'min, O I Koifman *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **31** (6) 39 (1988)
46. A S Semeikin, O I Koifman, B D Berezin *Khim. Geterotsikl. Soed.* 1354 (1982) [c]
47. E D Sternberg, D Dolphin, C Brückner *Tetrahedron* **54** 4151 (1998)
48. A S Semeikin, O I Koifman, B D Berezin *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **28** (11) 47 (1985)
49. S Neya, N Funasaki *J. Heterocycl. Chem.* **34** 689 (1997)
50. C Paliteiro, A Sobral *Electrochim. Acta* **50** 2445 (2005)
51. V N Kopranenkov, S N Dashkevich, V K Shevtsov, E A Luk'yanets *Khim. Geterotsikl. Soedin.* 61 (1984) [c]
52. M-H Qi, G-F Liu *J. Phys. Chem. B* **107** 7640 (2003)
53. M-H Qi, G-F Liu *J. Mater. Chem.* **13** 2479 (2003)
54. M-H Qi, G-F Liu *Solid State Sci.* **6** 287 (2004)
55. L A Yakubov, Candidate Thesis in Chemical Sciences, Ivanovo State University of Chemistry and Technology, Ivanovo, 2010
56. L A Yakubov, N E Galanin, G P Shaposhnikov, N Sh Lebedeva, E A Mal'kova *Zh. Obshch. Khim.* **78** 1028 (2008) [a]
57. N E Galanin, L A Yakubov, V E Maizlish, G P Shaposhnikov *Zh. Org. Khim.* **43** 1407 (2007) [b]
58. L A Yakubov, N E Galanin, G P Shaposhnikov *Zh. Org. Khim.* **44** 763 (2008) [b]
59. N A Tyukavkina, Yu I Baukov *Bioorganicheskaya Khimiya* (Bioorganic Chemistry) (Moscow: Meditsina, 1985)
60. L A Yakubov, N E Galanin, G P Shaposhnikov *Makrogeterotsikly* **4** 111 (2011) [d]
61. P Rothemund *J. Am. Chem. Soc.* **57** 2010 (1935)
62. P Rothemund *J. Am. Chem. Soc.* **61** 2912 (1939)
63. A D Adler, F R Longo, W Shergalis *J. Am. Chem. Soc.* **86** 3145 (1964)
64. A D Adler, L Sklar, F R Longo, J D Finarelli, M G Finarelli *J. Heterocycl. Chem.* **5** 669 (1968)
65. A D Adler, F R Longo, J D Finarelli, J Goldmacher, J Assour, L J Korsakoff *J. Org. Chem.* **32** 476 (1967)
66. J S Lindsey, H C Hsu, I C Schreiman *Tetrahedron Lett.* **27** 4969 (1986)
67. J S Lindsey, I C Schreiman, H C Hsu, P C Kearney, A M Marguerettaz *J. Org. Chem.* **52** 827 (1987)
68. D E Remy *Tetrahedron Lett.* **24** 1451 (1983)
69. G P Arsenault, E Bullock, S F MacDonald *J. Am. Chem. Soc.* **82** 4384 (1960)
70. D H R Barton, S Z Zard *J. Chem. Soc., Chem. Commun.* 1098 (1985)
71. D H R Barton, J Kervagoret, S Z Zard *Tetrahedron* **46** 7587 (1990)
72. N Ono, K Maruyama *Chem. Lett.* **17** 1511 (1988)
73. O Finikova, A Cheprakov, I Beletskaja, S Vinogradov *Chem. Commun.* 261 (2001)
74. O S Finikova, A V Cheprakov, I P Beletskaya, P J Carroll, S A Vinogradov *J. Org. Chem.* **69** 522 (2004)
75. M A Filatov, A V Cheprakov *J. Porphyrins Phthalocyanines* **10** 630 (2006)
76. M A Filatov, A V Cheprakov, I P Beletskaya *Eur. J. Org. Chem.* 3468 (2007)
77. S Ito, T Murashima, H Uno, N Ono *Chem. Commun.* 1661 (1998)
78. S Ito, N Ochi, H Uno, T Murashima, N Ono *Heterocycles* **52** 399 (2000)
79. H Uno, S Ito, M Wada, H Watanabe, M Nagai, A Hayashi, T Murashima, N Ono *J. Chem. Soc., Perkin Trans. 1* 4347 (2000)
80. S Ito, H Uno, T Murashima, N Ono *Tetrahedron Lett.* **42** 45 (2001)
81. O S Finikova, S Yu Chernov, A V Cheprakov, M A Filatov, I P Beletskaya *Dokl. Akad. Nauk* **391** 781 (2003) [e]
82. M A Filatov, S E Aleshchenkov, A V Cheprakov *Makrogeterotsikly* **2** 198 (2009) [d]
83. M A Filatov, Doctoral Thesis in Chemical Sciences, Moscow State University, Moscow, 2008
84. Z Shen, H Uno, Y Shimizu, N Ono *Org. Biomol. Chem.* **2** 3442 (2004)
85. M Giraud-Roux, G Proni, K Nakanishi, N Berova *Heterocycles* **61** 417 (2003)
86. H Yamada, K Kushibe, T Okujima, H Uno, N Ono *Chem. Commun.* 383 (2006)
87. H Yamada, K Kushibe, S Mitsuogi, T Okujima, H Uno, N Ono *Tetrahedron Lett.* **49** 4731 (2008)
88. P B Shea, J Kanicki, Y Cao, N Ono *Appl. Phys. Lett.* **87** 173506 (2005)
89. P B Shea, J Kanicki, N Ono *J. Appl. Phys.* **98** 014503 (2005)
90. P B Shea, J Kanicki, L R Pattison, P Petroff, M Kawano, H Yamada, N Ono *J. Appl. Phys.* **100** 034502 (2006)
91. P B Shea, L R Pattison, M Kawano, C Chen, J Chen, P Petroff, D C Martin, H Yamada, N Ono, J Kanicki *Synth. Met.* **157** 190 (2007)
92. P B Shea, C Chen, J Kanicki, L R Pattison, P Petroff, H Yamada, N Ono *Appl. Phys. Lett.* **90** 233107 (2007)
93. H Yamada, N Kamio, A Ohishi, M Kawano, T Okujima, N Ono *J. Porphyrins Phthalocyanines* **11** 383 (2007)
94. Y Matsuo, Y Sato, T Niinomi, I Soga, H Tanaka, E Nakamura *J. Am. Chem. Soc.* **139** 16048 (2009)
95. R P Linstead, F T Weiss *J. Chem. Soc.* 2975 (1950)
96. B D Berezin, T I Potapova, M V Platonova *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **24** 160 (1981)
97. S V Kharitonov, O P Yablonskii, V A Burmistrov, B D Berezin *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **25** 823 (1982)
98. T I Potapova, R A Petrova, B D Berezin, S V Kharitonov *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **27** 1017 (1984)
99. R A Petrova, T I Potapova, B D Berezin, S V Kharitonov, Z V Kharitonova *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **27** 1304 (1984)
100. B D Berezin, I K Barvinskaya, L I Sharova *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **23** 161 (1980)
101. V N Kopranenkov, E A Makarova, E A Luk'yanets *Khim. Geterotsikl. Soedin.* 1189 (1986) [c]
102. M O Senge, I Bischoff *Tetrahedron Lett.* **45** 1647 (2004)
103. M O Senge, W W Kalisch, I Bischoff *Chem.–Eur. J.* **6** 2721 (2000)
104. S Ito, L T Phong, T Komatsu, N Igarashi, S Otsubo, Y Sakai, A Ohno, S Aramaki, Y Tanaka, H Uno, T Oba, K Hiratani *Eur. J. Org. Chem.* 5373 (2009)

[a] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[b] — *Russ. J. Org. Chem. (Engl. Transl.)*
[c] — *Polym. Sci. (Engl. Transl.)*
[d] — *Macroheterocycles (Engl. Transl.)*
[e] — *Dokl. Chem. (Engl. Transl.)*