Chemistry of Heterocyclic Compounds, Vol. 45, No. 3, 2009

BROMINATION OF PORPHYRINS (REVIEW)

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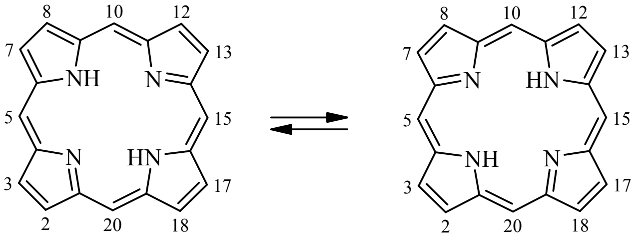
Methods for the bromination of porphyrins and their derivatives at the meso and β-positions are examined. The dependence of the course of the reactions on the conditions and on the structure of the initial compounds is discussed.

Keywords: benzoporphyrins, bromoporphyrins, porphyrins, chlorins, bromination, electrophilic substitution.

Interest in the halogenation of porphyrins has continued for many decades, beginning with the investigations of Hans Fischer in the twenties of the last century.

The simplest porphyrin **1** (porphin), which is an aromatic molecule, is the parent of many natural and synthetic porphyrins.



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The porphyrin molecule is characterized by a large number of electrons in two degenerate aromatic systems with the electron density extended over a large area. As a result of this porphyrins enter into electrophilic substitution reactions, which can take place at two types of carbon atoms differing both in position and in reactivity. These are the *meso* carbon atoms (positions 5, 10, 15, and 20 in compound **1**) and the β-carbon atoms positions (2, 3, 7, 8, 12, 13, 17, and 18 in compound **1**).

Initially, the interest in the halogenation of porphyrins was purely academic. In the nineties of the last century, however, it was found that some of the bromine-substituted porphyrins can be used as intermediates in the production of new materials having nonlinear optical and other interesting characteristics.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 323-353, March, 2009. Original article submitted September 1, 2008.

Brominated porphyrins were widely used in cross-coupling reactions (see the reviews [1-5]): Heck [6], Sonogashira [7-15], Stille [6, 16-21], Suzuki [7, 14, 15, 21-34], Takahashi [35], Negishi [16, 17, 36]. By these methods it is possible to form not only a C–C bond but also a C–heteroatom bond (O, N, S, P, B) [25, 37, 38]. In addition, porphyrins with carbon–metal bonds were obtained [37, 39].

By nucleophilic substitution it is possible to replace the bromine in porphyrins by a cyano group [40] (the Rosenmund–Braun reaction) and a hydroxyl group [41] and to form a C–S bond [42]. Specific reactions characteristic only of porphyrins are also of interest [43].

Brominated porphyrins themselves have also often been subjects of investigation during the study of their acid–base equilibria and complex formation [44-47], the effect of substituents on the stereochemical structure of the porphyrin ring [48-51], and their catalytic [52-57], electrochemical and optical [44, 50, 58-67], and antitumor [68] characteristics.

Among the halogenation reactions of aromatic compounds, on the one hand, chlorination and bromination take place quite easily. On the other hand, aromatic bromine and iodine substrates enter most readily into coupling reactions catalyzed by compounds of palladium and other transition metals. The production of iodinated porphyrins is represented by an extremely limited range of methods [18, 68-71], including the substitution of bromine by iodine [72]. These circumstances gave rise to the increased interest in the bromination of porphyrins from the standpoint of subsequent modification of the obtained compounds.

This review covers the bromination of porphyrins at the *meso* and β-positions.

BROMINATION AT THE *meso* POSITION

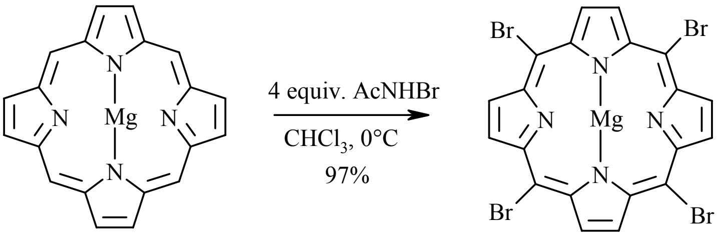
Porphin

Of the two positions capable of substitution of the proton by bromine in the porphin molecule the *meso* positions have higher reactivity.

Although it was reported in [71] that β-monobrominated porphin is formed during the bromination of porphin with bromine in $CHCl_3$ or with N-bromosuccinimide (NBS) in carbon tetrachloride and boiling subsequent attempts to reproduce the obtained results were unsuccessful [62].

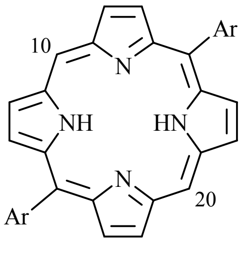
A more detailed investigation of the bromination of nonmetallated porphin demonstrated that the yields and degree of substitution depend on the conditions of the process. The use of Br_2 or the perbromide of pyridinium bromide leads to mixtures containing ~50% of 5-bromoporphin and 15% of 5,15-dibromoporphin. The content of 5-bromoporphin can be increased to 71% if these reagents are replaced by N-bromosuccinimide [62]. 5,10,15-Tribromoporphin can be obtained by the reaction of porphin with bromine in 90% acetic acid. By the methods described in this paper it was later also possible to obtain 5,15-dibromo-10,20-diphenylporphyrin [10, 17, 73] with yields approaching 88% [17].

Magnesium porphyrinate can be brominated by the use of N-bromoacetamide. Here it was noted that the presence of magnesium in the coordination cavity of porphyrin is critical for successful realization of this reaction [30].



meso-Substituted Porphyrins

One of the substrates widely used for *meso* bromination is the 5,15-diarylporphyrin **2**.



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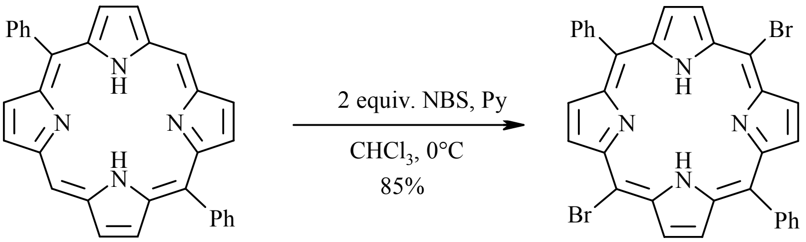
This is due to the fact, first, that such an arrangement of the substituents leaves the opposite *meso* atoms C(10) and C(20) free, and this has often been used in the production of linear high-molecular compounds based on porphyrin. Second, the presence of the aryl substituents leads to an increase of the electron density in the porphyrin π-electron system, affecting its electronic and optical characteristics. Third, as will be demonstrated below aryl substituents, unlike most other substituents, significantly facilitate the bromination of porphyrins at the *meso* position.

The selective production of 5,15-dibromo-10,20-diphenylporphyrin (**3)** from 10,20-diphenylporphyrin (with the complete absence of β-brominated porphyrins in the reaction products) was first realized with two equivalents of N-bromosuccinimide in chloroform at 0°C [16]. This method has often been used [8, 11, 73].



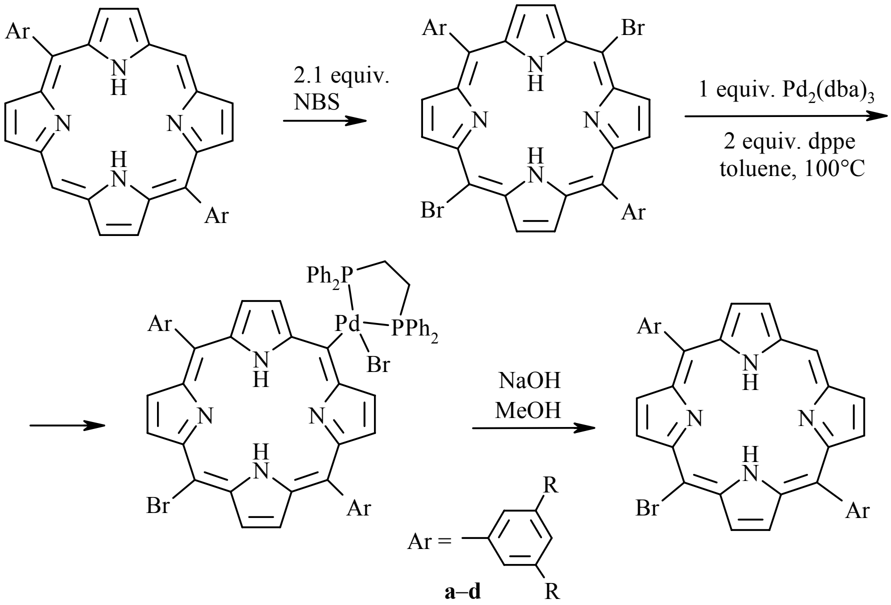
3

In [6] it was reported that high yields were obtained during the bromination of 5,10,15-triphenylporphyrin (98%) and 5,15-diphenylporphyrin (95%) at the free *meso* positions. It was also noted this method cannot be used for the production of *meso*-monobrominated 5,15-diphenylporphyrin on account of the difficulty of separating the reaction mixture. However, when this method was used in conjunction with chromatographic separation of the reaction products it was possible to obtain 5-bromo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin with a yield of 52% [74]. 5-Bromo-10,20-diphenylporphyrin was obtained with the even higher yield of 66% [19]. It is worth noting that the obtained monobromoporphyrin was then iodinated at the remaining free *meso* position, while the reverse order of introduction of the halogen atoms (iodination followed by bromination) led to a mixture of halogenation products [37, 39, 75].

Small modifications to the procedure for the production and isolation of monobrominated diarylporphyrin were made in [28]. The bromination of the triarylporphyrin in cold chloroform in the presence of pyridine takes place with a yield of 96%, while the same reaction with 1 equiv. of N-bromosuccinimide was used for the production of the monobrominated diarylporphyrin [25].

Reversed-phase chromatography can be used for the isolation of *meso*-monobrominated porphyrins containing charged groups [76].

The authors of [77] proposed their own version of the solution to the production of monobrominated porphyrins. While observing the complexity and difficulty of the chromatographic separation of mono- and dibrominated porphyrins they proposed to obtain dibromodiarylporphyrins by known methods [16] and then to substitute one of the bromine atoms by the complex of palladium with 1,2-bis(diphenylphosphine)ethane and hydrodepalladize the obtained compound with a solution of alkali in methanol. The total yield of monobrominated porphyrins obtained in this way exceeded 60%.



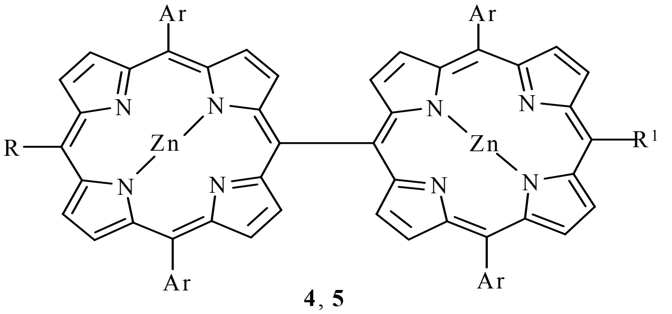
a–**d**

a R = H, **b** R = Me, **c** R = *t*-Bu, **d** R = $-O(CH_2)_2CHMe_2$

dppe = 1,2-bis(diphenylphosphine)ethane

The method presented in [16] was also used in the first attempts at the *meso* bromination of the metallated diarylporphyrin, zinc 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrinate [35].

The method has subsequently been widely used for the production of *meso*-brominated porphyrins with different aryl substituents at neighboring or opposite *meso* positions. The bromination of 5,15-diphenyl-substituted porphyrins with various functional groups (*tert*-butyldiphenylsiloxyl, and nitro [29], octyloxy, and pinacolatoboronate [7]) in the aryl substituents was realized by this method. The method was also used for the production of monobrominated diporphyrins **4**, which were isolated from mixtures with the *meso*, *meso'*-dibromodiporphyrins **5** [7].

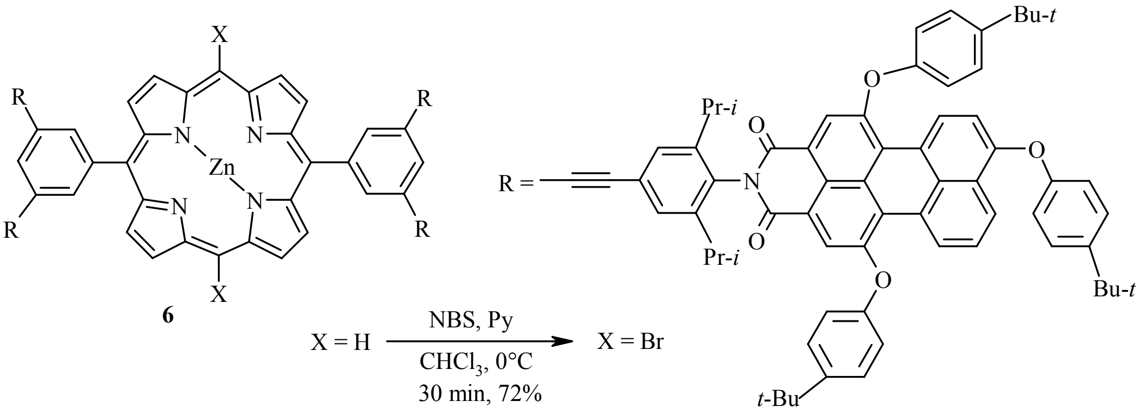


4, **5**

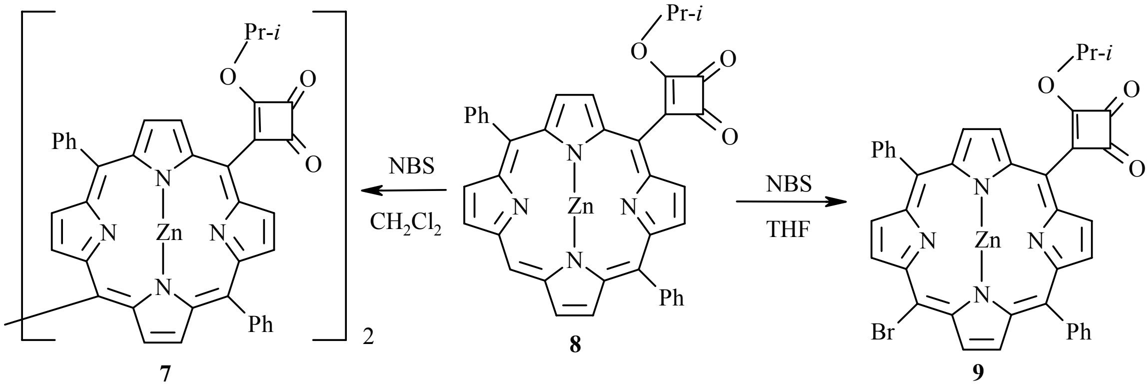
4 R = Br, R^1 = H; **5** R = R^1 = Br

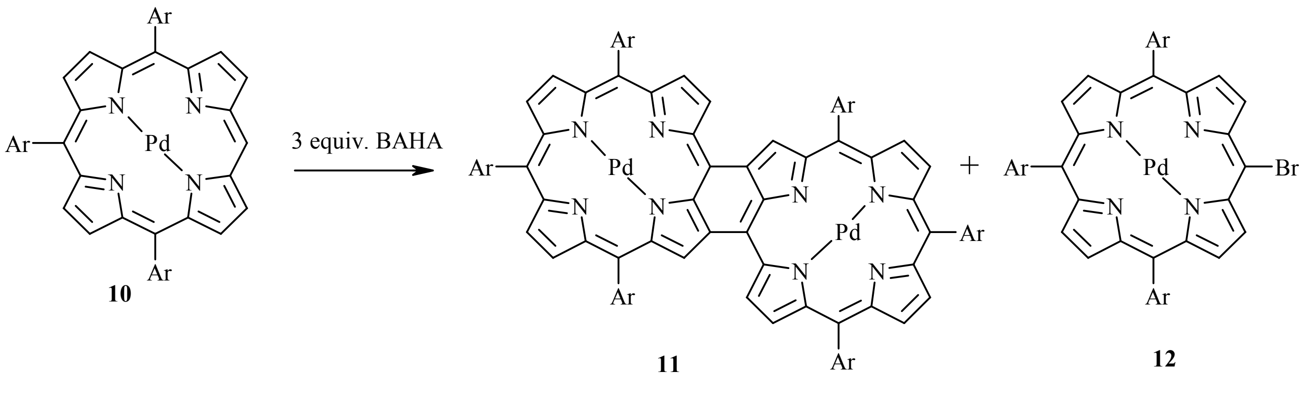
Longer *meso*,*meso'*-dibromo(polydiarylporphyrin) oligomers were also obtained [7, 22]. A lower temperature (−20°C) is required for the bromination of nickel 5,10-bis(3,5-di-*tert*-butylphenyl)porphyrinate [13].

The high regioselectivity of bromination according to the previously proposed procedure [16] made it possible to substitute hydrogen by bromine in the molecule of compound **6** exclusively at the free *meso* positions of porphyrin and to leave the large perylene aromatic system unaffected [27].



Dimerization is observed as a side reaction during bromination of the porphyrin **8** with N-bromosuccinimide. If CH_2Cl_2 is used as solvent the dimer **7** is formed with a yield of 15%. With THF it is possible to avoid the side process and to obtain a high yield of the bromide **9**.

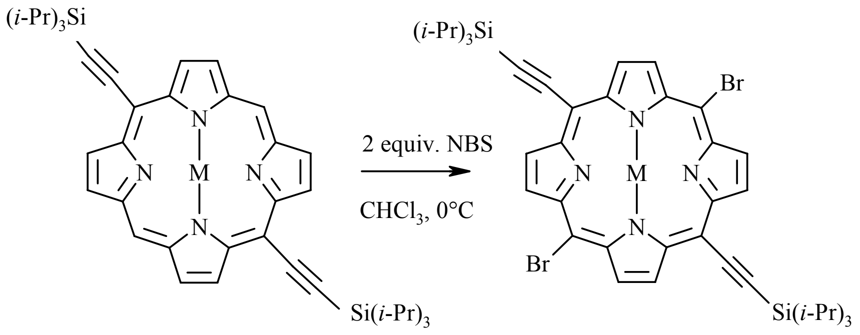




BAHA = tris(4-bromophenyl)aminium hexachloroantimonate

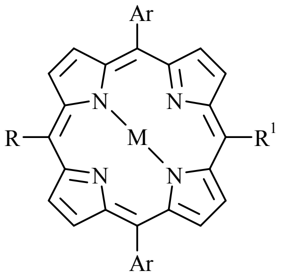
Brominated porphyrins can be formed as side products, for example, in the oxidative coupling of porphyrins. Thus, treatment of 5,10,15-triaryl-substituted palladium porphyrinate **10** with 3 equiv. of tris(4-bromophenyl)aminium hexachloroantimonate leads to the formation of the biporphyrin **11** and also to the porphyrin **12** brominated at the *meso* position [78].

The ease of the *meso*-bromination of porphyrins is characteristic of molecules in which the *meso* positions are occupied by aryl or alkyl [36, 79] substituents. If there are acetyl substituents in the porphyrin molecule the selectivity of the reaction is significantly reduced. The electron-withdrawing nature of these functional groups leads to deactivation of the porphyrins in the substitution reaction. During the bromination of 5,15-bis[(triisopropylsilyl)ethynyl]porphyrin [12, 80] with M = 2H and M = Zn a significant amount of β-bromination products is formed. Such a situation is explained by the fact that the electron-deficient acetylene substituents deactivate the porphyrin in *meso* substitution.



This difficulty can be overcome by the insertion of a more electropositive metal into the porphyrin cavity. In fact, in the case of M = Mg the results are significantly improved, and bromination takes place selectively at the *meso* position [12, 80].

A formyl group at the *meso* position has a similar effect of deactivation of *meso* substitution and directs the reaction to the β-position. During the bromination of copper 5,15-dimesityl-10-formylporphinate **13** it was necessary to introduce additional stages involving demetallation and protection of the formyl group with neopentyl glycol in order to prevent β-bromination side processes [23].



13, 14a–d

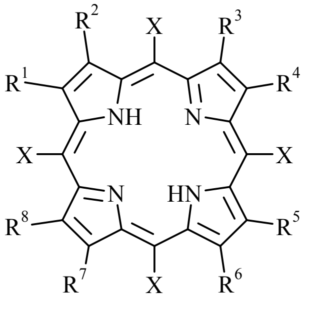
13 M = Cu, Ar = $Me_3C_6H_2$, R = H, R^1 = CHO;
14 a–d M = Ni, Ar = Ph, **a** R = H, R^1 = CHO,
b R = Br, R^1 = CHO, **c** R = H, R^1 = –CH=C(CN)$_2$,
d R = H, R^1 = –CH=CHCHO

The reaction is more selective if there is a nickel cation in the coordination cavity of the porphyrin. Thus, nickel 5-bromo-15-formyl-10,20-diphenylporphyrinate **14b** was obtained from the porphyrinate **14a** with a yield of 76% [81]. Here partial β-bromination occurred.

According to [81], if the formyl group is replaced by a dicyanoethenyl group (**14c)** bromination gives an even higher yield (90%). At the same time the formylethenyl group in the porphyrin **14d** itself undergoes bromination.

β-Polyalkylporphyrins

β-Polyalkylporphyrins are among the first porphyrin derivatives that became known to investigators. The first papers on study of the reactions of β-polyalkylporphyrins and bromination in particular were produced in the first quarter of the twentieth century by Hans Fischer [82, 83]. The possibility of bromination of etioporphyrin **15**, β-octaethylporphyrin **16**, and other β-polyalkylporphyrins and also of chlorin **22** and its derivatives with a solution of bromine in acetic acid was demonstrated.



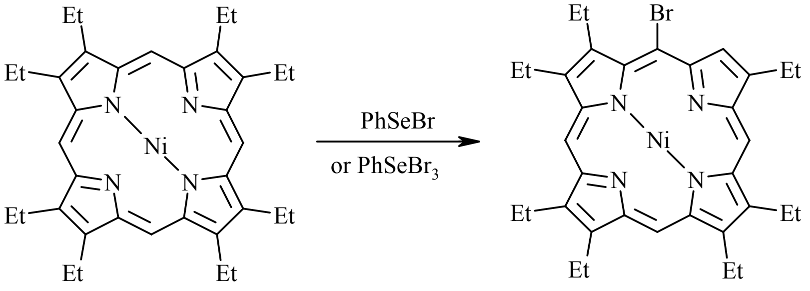
15–17

15 $R^1 = R^3 = R^5 = R^7 = H$, $R^2 = R^4 = R^6 = R^8 = Et$, X = H;
16 R^1–R^8 = Et, X = H; **17** R^1–R^8 = Et, X = Br

Since then certain conclusions concerning the composition and structure of the newly obtained compounds were defined more precisely and re-examined [84, 85]. The use of a mixture of HBr with H_2O_2 for the bromination of octaethylporphyrin and octaethylchlorin **22a** (ethyl substituents at positions 2, 3, 7, 8, 12, 13, 17, and 18) only leads to positive results in the case of octaethylchlorin [85]. γ-Bromooctaethylchlorin was obtained with a yield of 40%, and its subsequent dehydrogenation made it possible to obtain *meso*-monobromooctaethylporphyrin.

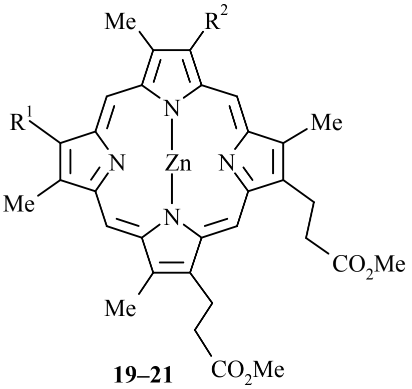
The bromination of β-octaethylporphyrin **16** with bromine leading to the formation of the *meso*-tetrabrominated compound **17** takes place in hot acetic acid and does not take place in boiling chloroform [71].

With phenylselenyl bromide or phenylselenyl tribromide as brominating agents it is possible to obtain *meso*-monobrominated nickel heptaethylporphyrinate **18** since the ethyl group closest to the bromine atom is lost during the reaction process [86]. The same dealkylation is observed when N-bromosuccinimide is used.



18

During the bromination of bismercurated zinc deuteroporphyrinate-IX **19** with 2.2 equiv. of Br_2 substitution takes place first at the mercurated β-positions, and *meso*-bromination then takes place if the concentration of bromine is increased. Coupling of the zinc deuteroporphyrinate-IX with 1,2-dibromopropene leads to a mixture containing 8% each of the monobrominated deuteroporphyrins **20** and 20% of the dibrominated deuteroporphyrinate **21** [18].

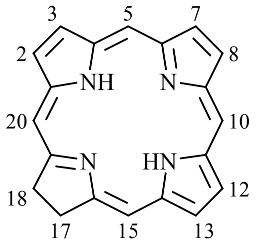


19 $R^1 = R^2 =$ HgCl;
20 $R^1 =$ Br, $R^2 =$ H and $R^1 =$ H, $R^2 =$ Br;
21 $R^1 = R^2 =$ Br

19–21

Chlorin Derivatives

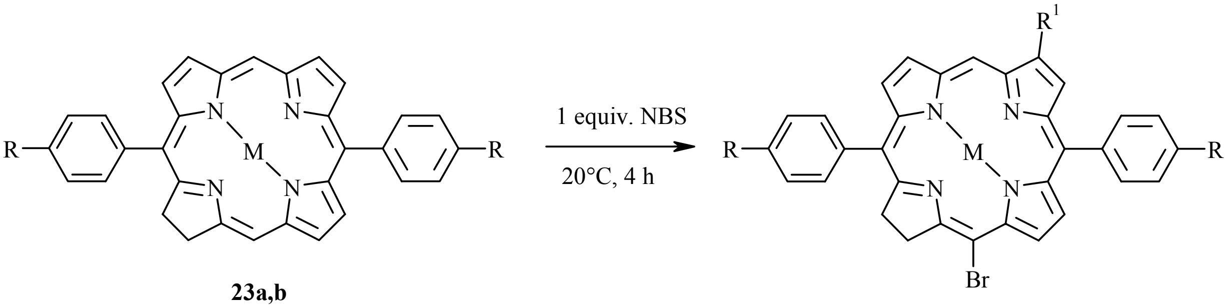
Until recently the possibilities for the production of substituted derivatives of chlorin **22** were limited. As a rule the substituents were inserted into the precursors before the final assembly of the chlorin ring. Here the possibilities for selective insertion of substituents at positions 7, 8, 15, and 20 were substantially restricted.



22

These difficulties were overcome by means of bromination.

10,20-Diphenyl-substituted chlorin **23a** is brominated by N-bromosuccinimide in the CH_2Cl_2–0.5% pyridine system at positions 7 and 15, giving a mixture of the monosubstituted **24a** (26%) and disubstituted **24b** (20%) derivatives. By the bromination of the chlorin **23b** in THF it is possible to obtain a mixture with a significantly larger content of the monobrominated compound: 44% of **24c** and 12% of **24d** [34].



23a,b

24a–d

23 a R = H, **b** R = OPr–*i*; **24 a** R = R^1 = H, **b** R = H, R^1 = Br, **c** R = OPr–*i*, R^1 = H,
d R = OPr–*i*, R^1 = Br

The chlorin **25a** (R^1, R^2 = H) and also its *meso*-aryl-substituted analogs **25b** (R^1 and/or R^2 = Ar) are easily brominated at position 15 [14, 21, 33].

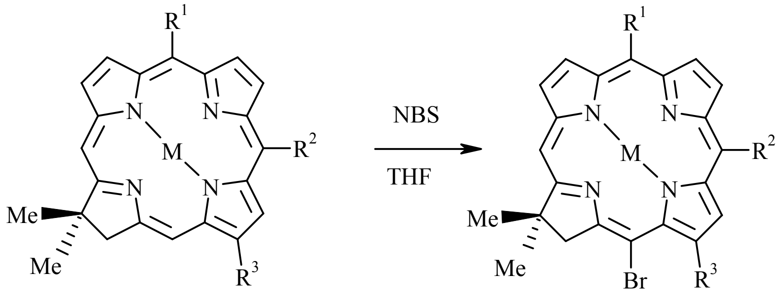


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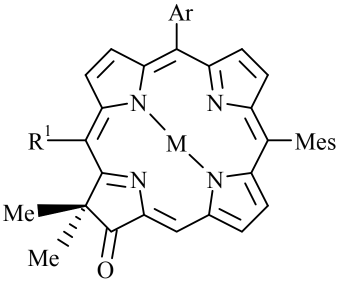
TABLE 1. Dependence of the Yield of the Bromination of Chlorin **25** on the Substituents Present in the Molecule

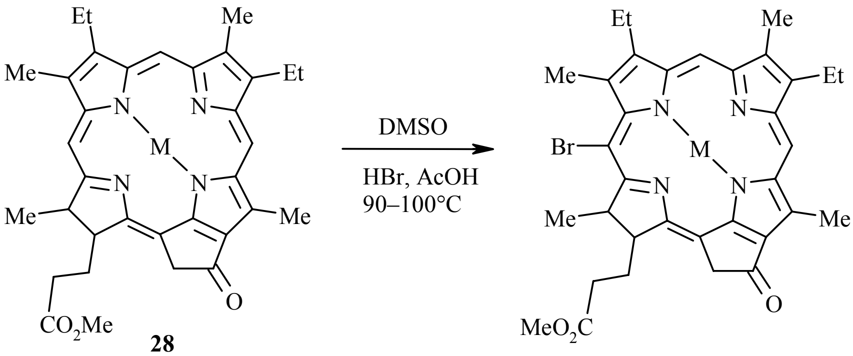
M	R^1	R^2	R^3	Yield, %
2H	H	H	H	51
Zn	H	H	H	78
2H	H	Mesityl	H	55
Zn	H	Phenyl	H	51
2H	H	*n*-Pentyl	H	54
2H	*p*-Tolyl	Mesityl	H	70
Zn	*p*-Tolyl	Mesityl	H	81
2H	*p*-Tolyl	Mesityl	Acyl	70 [20]

Under the same conditions the unmetallated oxochlorin **26** gives a complex mixture of products, whereas the introduction of zinc into its coordination cavity makes it possible to realize selective bromination at position 20 with the formation of the oxochlorin **27**.



26, 27

26 M = 2H, R^1 = H; **27** M = Zn, R^1 = Br



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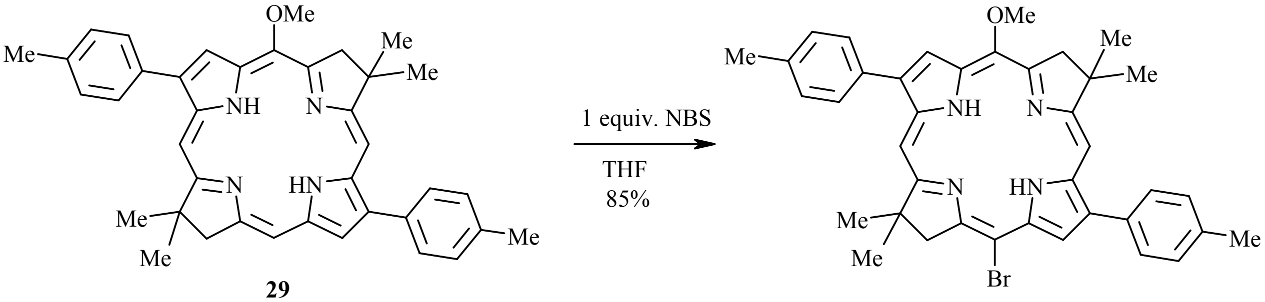
With the use of hydrobromic acid it is possible to achieve selective bromination of methyl *meso*-pyropheophorbide **28** at the δ-position. By heating a solution of the porphyrin in DMSO with a 48% solution of HBr in acetic acid for 5 min it is possible to obtain the monobrominated porphyrin with a yield of 54%.

By bromination with pyridinium bromide perbromide it is possible to increase the yield of this reaction to 62% [87].

Bacteriochlorin **29** is brominated selectively by N-bromosuccinimide at the *meso* position opposite to the methoxy group [15].



Bromination of the analogous bacteriochlorin without the methoxy group under such conditions led to a mixture of substitution products. Attempts to increase the regioselectivity of the reaction by changing the conditions and the bromination reagents were unsuccessful.

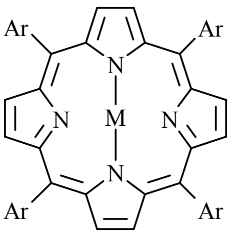
BROMINATION AT THE β-POSITION

Substituents at the β-position have greater steric and electronic effects on the porphyrin ring than substituents at the *meso* position [3]. In addition they are often the reason for the change of porphyrins to the nonplanar conformation, which has a substantial effect on the characteristics of these molecules. The direct halogenation of porphyrins at the β-position has a number of advantages over the synthesis of bromine-substituted porphyrins from 3-bromo- or 3,4-dibromo-substituted pyrroles since the latter case requires more stages and laborious separation of the mixture of reaction products.

meso-Tetraarylporphyrins

As in the case of *meso* bromination, papers relating to bromination at the β-position can also be classified according to the type of substituents already present in the porphyrin ring. First of all we will consider the bromination of *meso*-tetrasubstituted porphyrins not having β-substituents since the latter have a significant effect on the course of the reaction and require special attention.

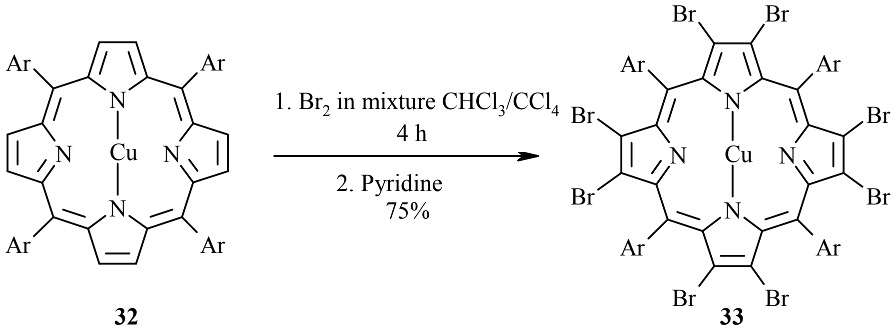
We will begin with methods for the bromination of 5,10,15,20-tetraaryl-substituted porphyrins **30** and their metallated derivatives **31**, where Ar is any aromatic substituent (usually phenyl, tolyl, mesityl, more rarely naphthyl):



30, 31

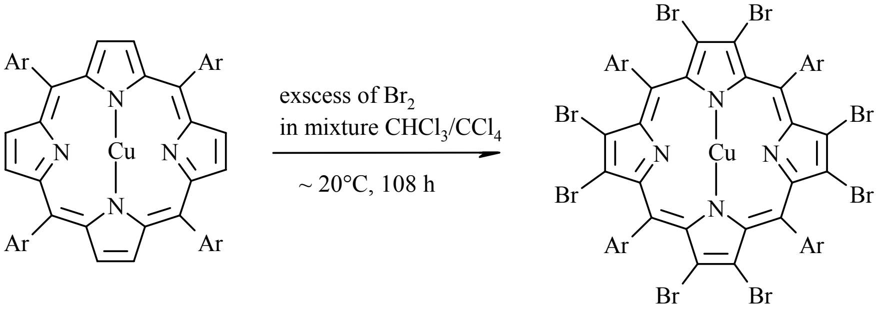
30 M = 2H; **31** M = Zn, Mg, Ni(II), Cu, Mn

Fundamental in this respect is the paper [58], in which a method is proposed for the production of copper octabromotetraphenylporphyrinate **33** (Ar = Ph) by the bromination of copper tetraphenylporphyrinate **32** (Ar = Ph) with a solution of bromine at room temperature.



32 **33**

This method was subsequently used in a large number of works often with one or the other modification. Thus, a series of tetraaryloctabromoporphyrins were obtained: 5,10,15,20-tetra(*o*-, *m*-, and *p*-tolyl)octabromoporphyrins **34** and 5,10,15,20-tetra(α- and β-naphthyl)octabromoporphyrins **35** with yields of 70 and 80% respectively [60]. The modifications in this case were an increase in the time for which the reagents were present and agitation of the reaction mixture. The authors indicate that the porphyrins undergo partial demetallation during bromination.

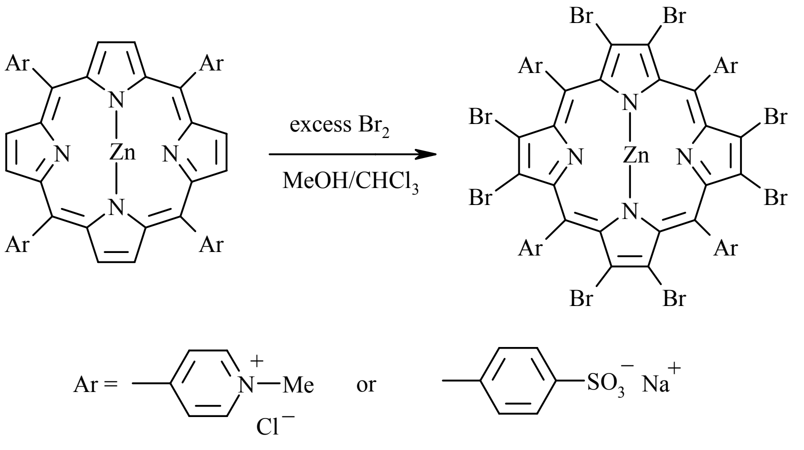


34, **35**

34 Ar = tolyl, **35** Ar = naphthyl

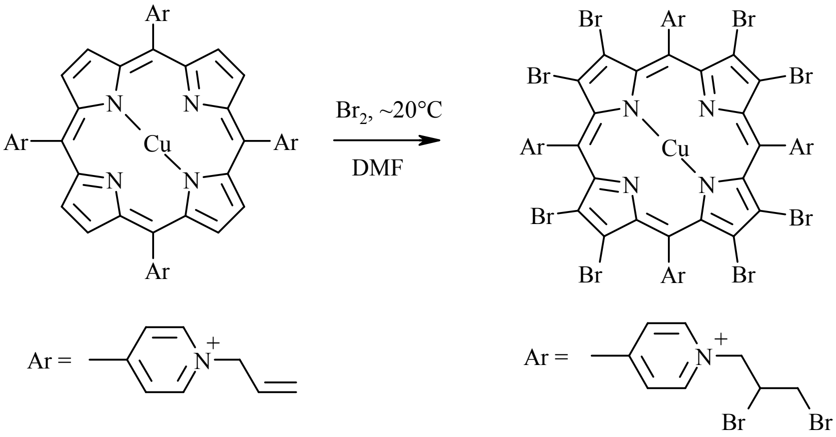
The bromination of manganese *meso*-tetra(*p*-carboxymethylphenyl)porphyrinate by this method also requires an increase in the reaction time [61].

The reaction can be used for the bromination of tetraarylporphyrinates in which the aryl groups carry a positive or negative charge [45, 46].



In [46] DMF was used as solvent, and it was noted that its replacement by methanol or DMSO and also the addition of pyridine to the reaction mixture led to incomplete bromination.

Dimethyl formamide was also used for the bromination of methylated and allylated copper tetrapyridylporphyrinates. In the latter case both the β-positions of the porphyrin ring and the allyl groups were brominated [88].



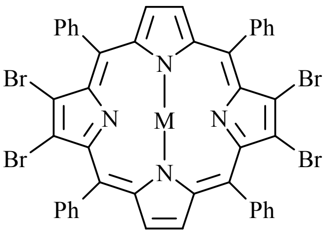
This procedure was also used for the production of octabromotetraphenylporphyrin from tetraphenylporphyrin (yield 76%) [26].

Treatment of copper tetraphenylporphyrinate partially fluorinated at the-β position with bromine leads to substitution of all the remaining β-hydrogen atoms by bromine [89].

It can be concluded from analysis of the published data that the use of molecular bromine has a substantial limitation: The reaction affects all the free β-positions present in the molecule being brominated. The method for the bromination of *meso*-tetraarylporphyrins with N-bromosuccinimide, which as will be shown below makes it possible to vary the number of bromine atoms inserted into the porphyrin molecule, has therefore become more widely used.

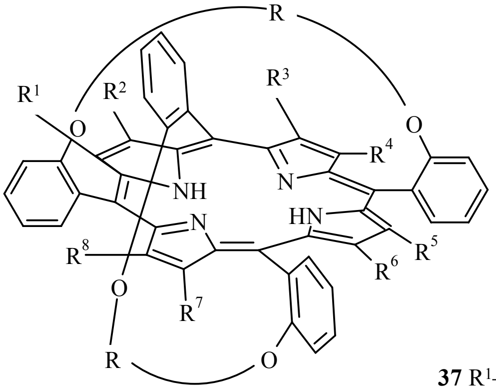
N-Bromosuccinimide can be used for the production of octabromotetraarylporphyrinates [55, 90]. Special attention must be paid to the possible bromination of unmetallated porphyrin [47]. Only metallated porphyrins have been used in reaction with a solution of molecular bromine since an excess of bromine in the reaction mixture is capable of breaking down the molecule of unmetallated porphyrin [61]. This property made it necessary to carry out additional metallation/demetallation stages in the porphyrins.

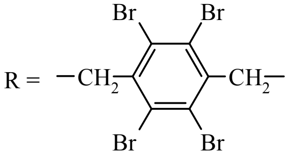
The paper [91] is one of the fundamental papers concerning the bromination of porphyrins at the *meso* position. However, having obtained a series of substituted porphyrins with N-bromosuccinimide, the authors sometimes deduced their structures incorrectly. Thus, the previously proposed structure of tetra-β-brominated porphyrin containing one bromine atom in each pyrrole fragment was disproved, and the structure containing two bromine atoms in each of two opposite pyrrole fragments **36** was proved [24, 40, 41].



36

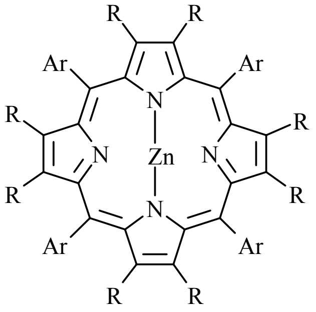
Nevertheless, it was reported that the tetrabrominated porphyrin **38**, in which one hydrogen atom in each pyrrole fragment is substituted, is formed during the bromination of the porphyrin **37** with 4.4 equiv. of N-bromosuccinimide in boiling chloroform [67].



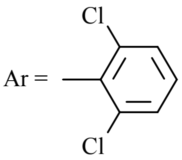


37 R^1–R^8 = H; **38** $R^1 = R^3 = R^5 = R^7$ = Br

The authors of [49, 52, 53, 57, 92] also reached their own conclusion in favour of N-bromosuccinimide during the production of octabromotetraarylporphyrinates [93]. Here such parameters as the solvent, rate of addition of the reagents, and reaction time were varied. Comparative analysis and modification of the various bromination procedures were used during the production of octabrominated zinc *meso*-tetrakis(2,6-dichlorophenyl)porphyrinate **39** from the β-unsubstituted porphyrin **40** [94] (Table 2).



39, **40**



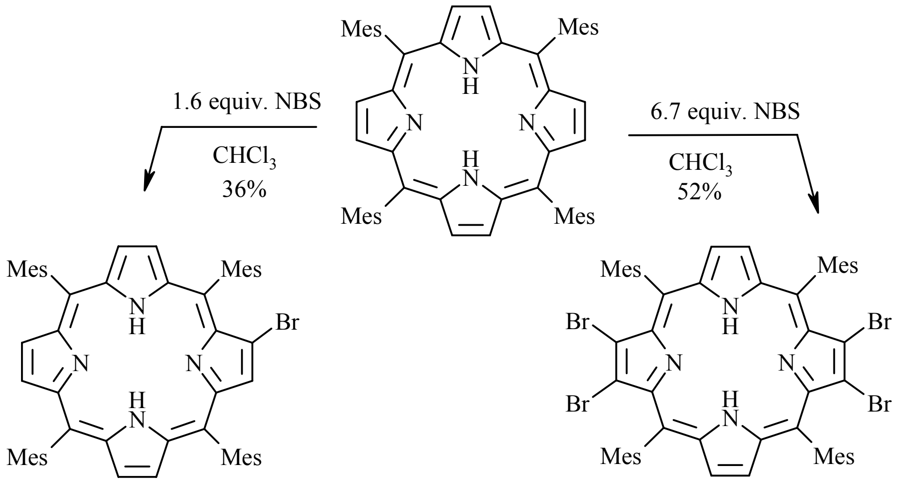
39 R = Br; **40** R = H

TABLE 2. Dependence of the Bromination of Zinc *meso*-Tetrakis(2,6-dichlorophenyl)porphyrinate **40** on the Reaction Conditions

Brominating agent	Solvent	Conditions	Yield
NBS	CCl_4	Boiling	Partial bromination
NBS	MeOH	Boiling	63%
Br_2	CCl_4	~ 20°C	Partial bromination
Br_2	CCl_4	Boiling/longer reaction time	Destruction of porphyrin system
Br_2	MeOH	~ 20°C	79%
N-Bromoacetamide	MeOH	Boiling	75%

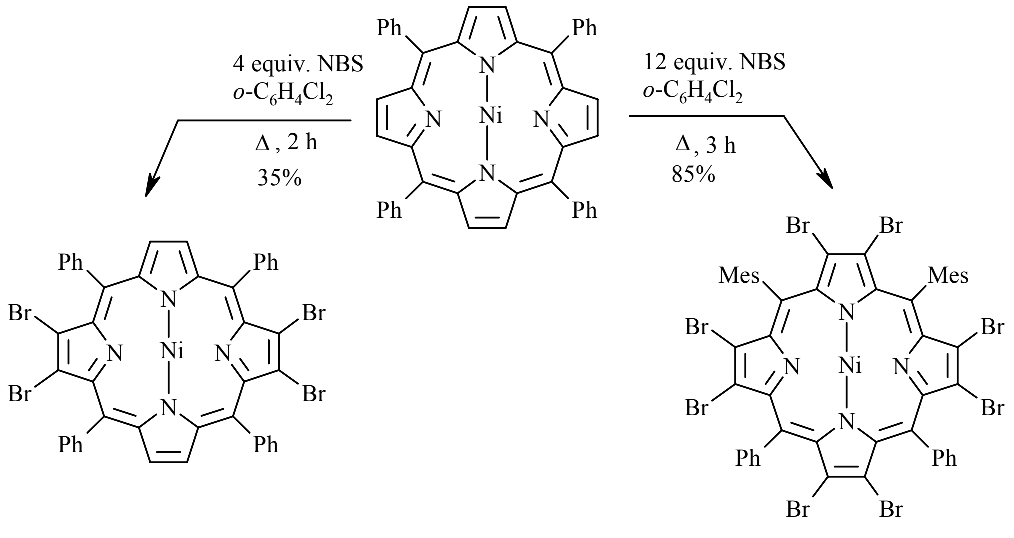
Taking account of the different direction of the reaction during bromination with molecular bromine in CCl_4 and methanol, the authors assumed that the active particle for the reaction in methanol was not bromine but the product of its reaction with the alcohol – MeOBr.

Greatly significant is the possibility of varying the number of bromine atoms in the porphyrin molecule. Interesting in this respect is the paper [32], where both mono- and tetrabromo-substituted tetramesitylporphyrins were obtained.

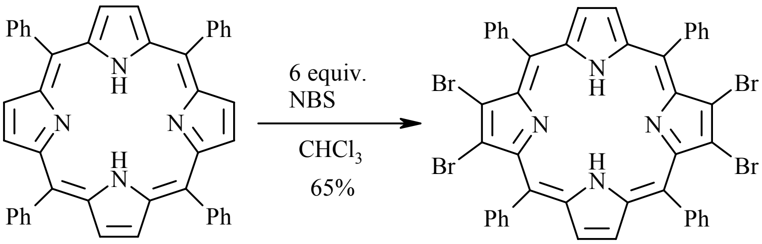


However, the authors were unable to obtain octabromo-substituted porphyrin under these conditions. For this they used the reaction with molecular bromine, having previously metallated the porphyrin.

Nevertheless, it is possible to obtain both tetra- and octabromotetraphenylporphyrinates with N-bromosuccinimide [63]. The reaction was conducted with boiling in *o*-dichlorobenzene, and nickel tetraphenylporphyrinate was used as substrate.



While stressing the lack of modern bromination procedures, the authors of [48] published a detailed method for the production of β-tetrabromotetraphenylporphyrin with a high yield. They showed that compounds with a smaller or larger number of bromine atoms in the molecule were not formed under the given conditions. Increase in the amount of N-bromosuccinimide to 12 equiv. did not lead to an increase in the degree of bromination, but the yields were reduced. These data confirm the result obtained in [32].



With N-bromosuccinimide it is possible to obtain a full range of substituted porphyrins containing various numbers of bromine atoms – from one to eight [59, 64, 71, 91]. Hexabrominated porphyrin was isolated as a side product during the production of the octabrominated porphyrin [56]. Later on hexa- and hepta-β-substituted polybromotetraphenylporphyrins were obtained specifically with a total yield of 40% [59]. We note that the reaction of copper tetraphenylporphyrinate with molecular bromine was used for the production of the octabromide in this work.

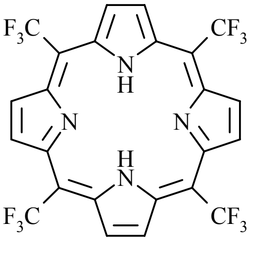
Previously proposed procedures were used for the production of brominated tetraphenylporphyrins with one, two, three, four, six, seven, and eight bromine atoms [64]. For the production of tetraphenylporphyrin containing five bromine atoms (yield 20%) a solution of zinc porphyrinate was boiled for 4 h with 7 equiv. of N-bromosuccinimide in anhydrous CCl_4. Porphyrinates containing between one and eight substituents were obtained with the use of various methods described above [65, 66].

Searches for optimum conditions for the production of monobrominated tetraphenyltetrabenzoporphyrin made it possible to increase the yield to 78% [38].

Phenylselenyl bromide can also be used for the production of β-monobromo-substituted nickel tetraphenylporphyrinate. The use of phenylselenyl tribromide leads to a mixture of bromination products [86].

meso-Tetraalkylporphyrins

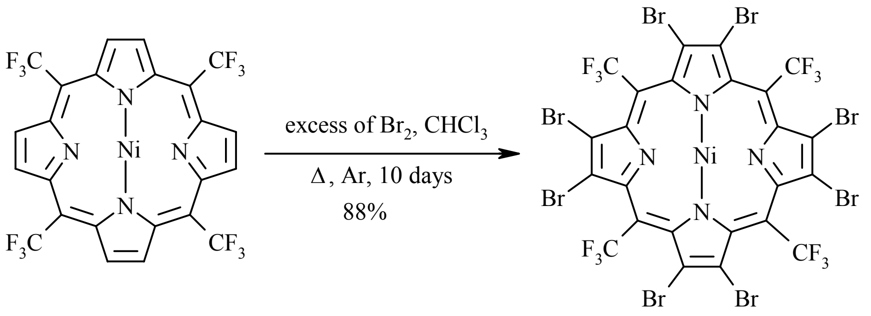
Among *meso*-tetraalkylporphyrins greatest attention has been paid to *meso*-tetra(trifluoromethyl)-porphyrin **41**.



41

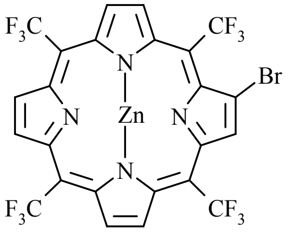
This is due to the fact that the electron-withdrawing trifluoromethyl group strengthens the lipophilicity and also the catalytic activity of metalloporphyrins in some organic oxidation reactions (e.g., epoxidation) [50, 95].

Nickel octabromotetra(trifluoromethyl)porphyrinate was first obtained with an excess of bromine in chloroform as brominating agent [59].



The development of the method is reflected in [31], where the effect of the concentration of the brominating agent on the degree of bromination was demonstrated. As in the case of the bromination of *meso*-tetraarylporphyrins, this requires bromination with N-bromosuccinimide, and the unmetallated porphyrin does not undergo bromination. By using different numbers of equivalents of N-bromosuccinimide it was possible to obtain mono-, di-, and tetrabromoporphyrinates **42**, **43**, and **44** with yields of 47, 70, and 23% respectively.

The procedure was subsequently used by other authors [9]. This paper reports on an unsuccessful attempt to realize a reaction similar to that described earlier [50] (the production of the octabromo derivative) with copper *meso*-tetra(trifluoromethyl)porphyrinate.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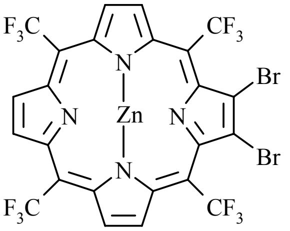
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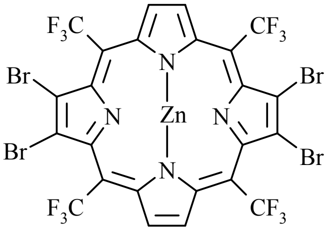
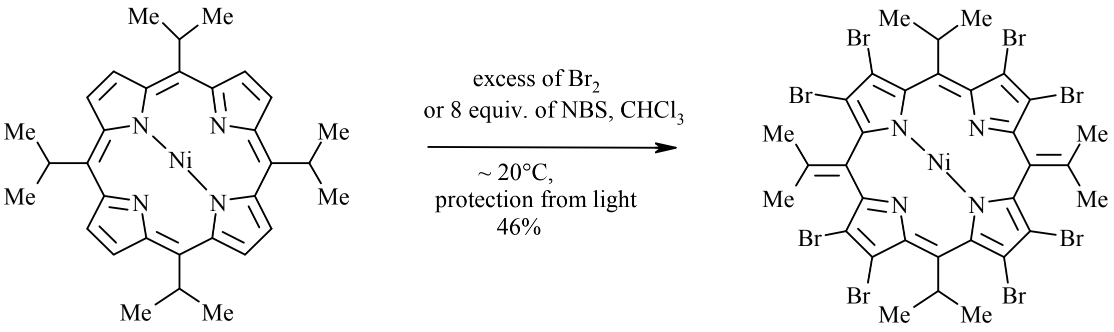
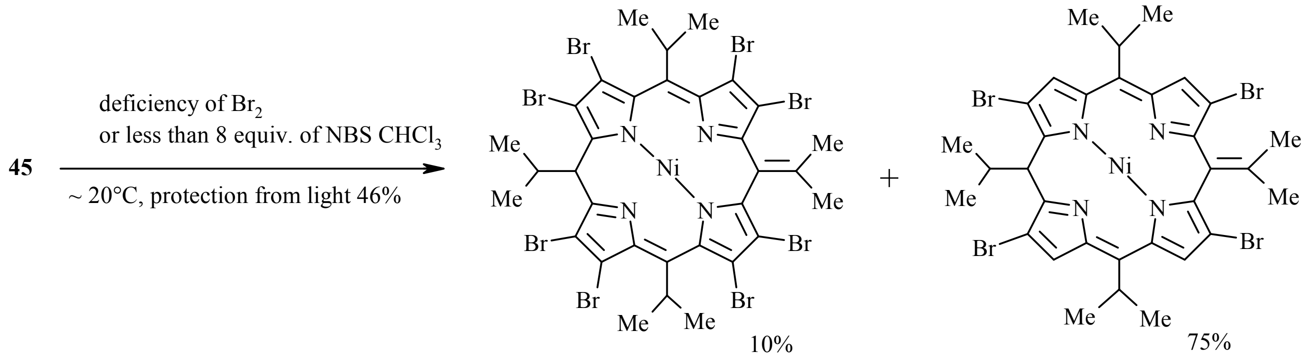

44

Unexpected results from the bromination of *meso*-tetraalkylporphyrins with longer alkyl substituents **45** were presented in [95]. In the authors' opinion apart from the bromination reaction, leading to octabromo-substituted porphyrin, addition of Br_2 or HBr to the opposite *meso*-carbon atoms also occurs, and they are subsequently detached leading to destruction of the porphyrin π-system and the formation of a porpho-dimethine-like structure.



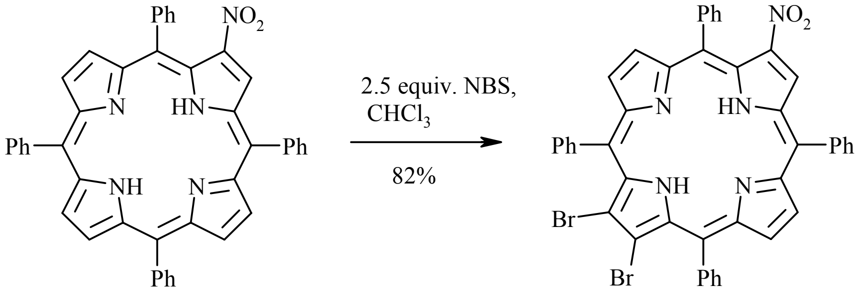
45

A similar situation is observed if a deficiency of the brominating agent is used.



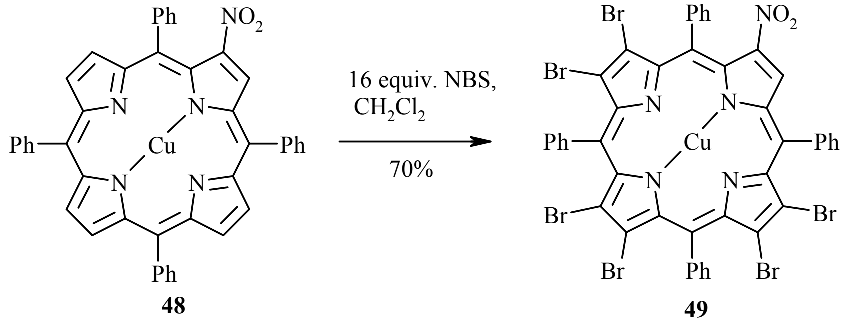
meso-Tetraarylporphyrins with Substituents at the β-Position

As already mentioned above, the bromination of *meso*-tetrasubstituted porphyrins in which there are already substituents at the β-position must be considered specially in view of the effect that they have on the course of the reaction. Thus, it is clear that the effect of the nitro group in 2-nitrotetraphenylporphyrin **46** leads to the regioselective entry of two bromine atoms into the pyrrole fragment opposite to the one that carries the nitro group [96].



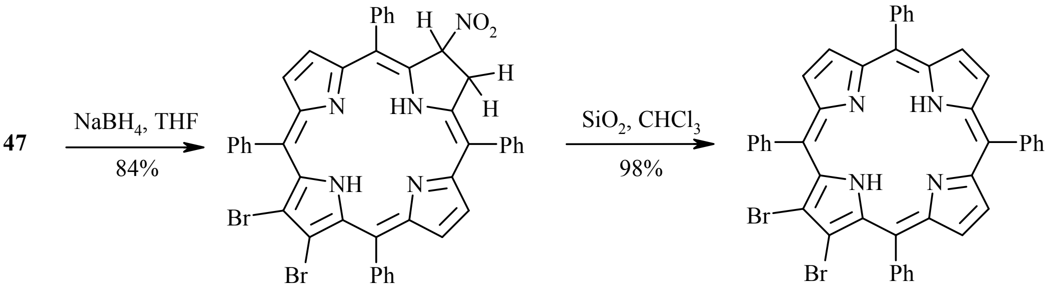
46 **47**

A difference in the reactivity of the metallated and free-base porphyrins was also demonstrated in this work. In the reaction with an excess of N-bromosuccinimide copper hexabromo-2-nitrotetraphenylporphyrinate **49** is formed from copper 2-nitrotetraphenylporphyrinate **48**, whereas the unmetallated 2-nitroporphyrin gives the dibromo derivative even in the presence of an excess of N-bromosuccinimide.



48 **49**

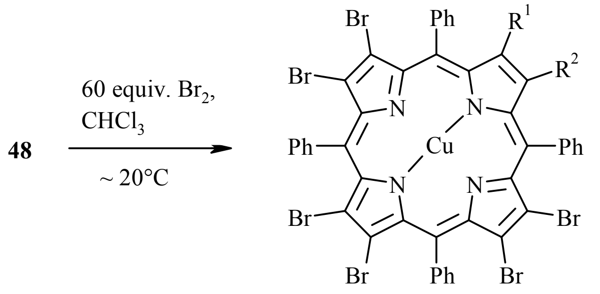
This investigation found an interesting extension in work by the same authors [97]. Thus, reduction of the double bond of the pyrrole fragment carrying the nitro group and subsequent "rearomatization" with the elimination of HNO_2 in boiling chloroform in the presence of silica gel lead to 2,3-dibromotetraphenylporphyrin **50**.



50

In the case of the hexabromo-substituted porphyrinate **49** the nitrous acid is lost spontaneously during the first reaction without additional boiling with silica gel.

It was possible to achieve full substitution of the free β-positions of 2-nitrotetraphenylporphyrin **48** by treating its copper derivative with a solution of bromine in a solvent at room temperature followed by the addition of pyridine [44]. As a result a mixture of hexa- and heptabromides **49** and **51** and octabromotetraphenylporphyrin **52** were obtained.

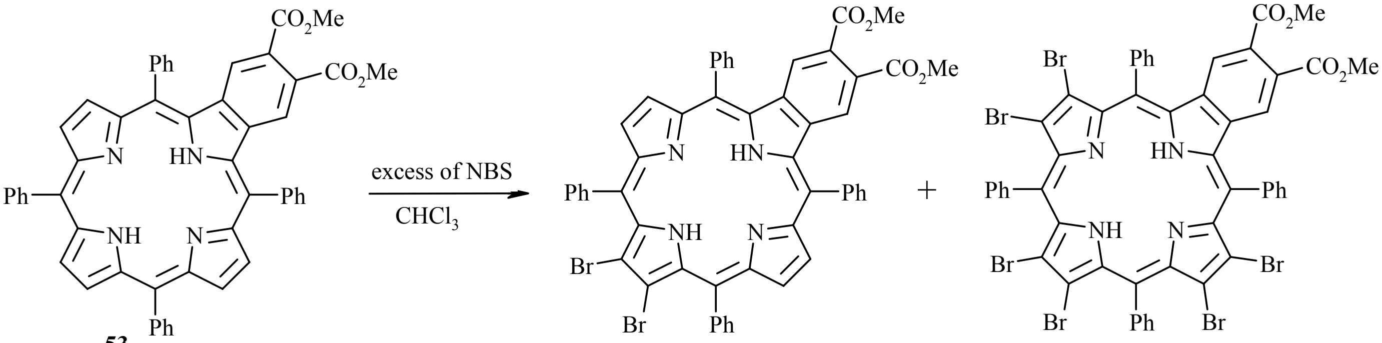


49, 51, 52

49 $R^1 = NO_2$, $R^2 = H$; **51** $R^1 = NO_2$, $R^2 = Br$; **52** $R^1 = R^2 = Br$

After the insertion of zinc in place of the copper in the coordination cavity of the porphyrin it became possible to separate these bromination products by column chromatography.

Another example of the effect of the β-substituents on the course of the reaction is the reaction of monobenzoporphyrin **53** with an excess of N-bromosuccinimide in boiling chloroform, leading predominantly to the dibromo derivative **54**, in which the hydrogen atoms of the pyrrole fragment opposite to the fragment annelated to the benzene ring are substituted [98].



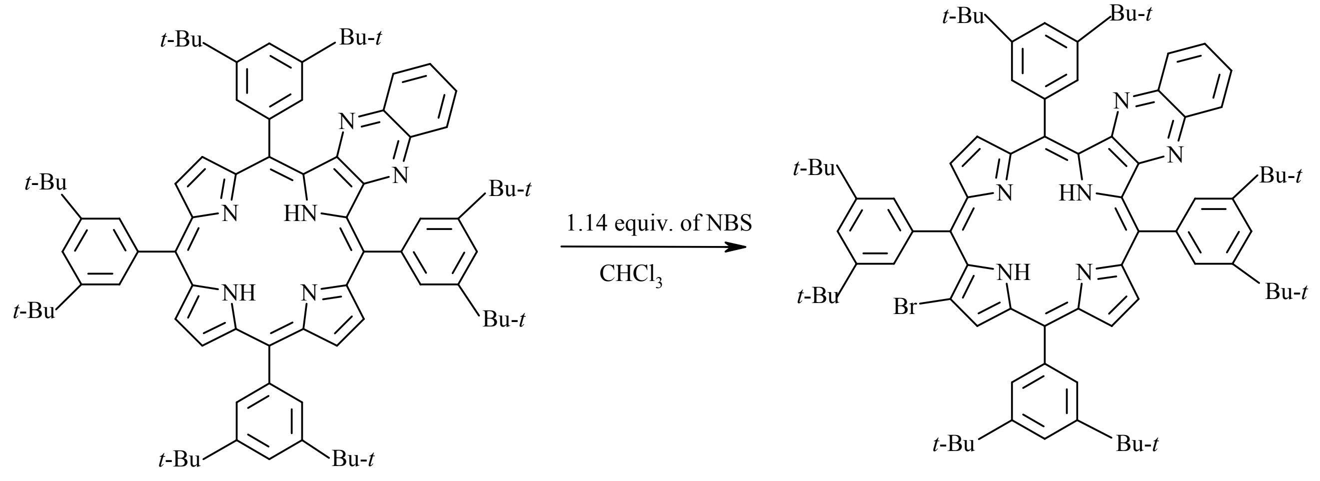
53 **54** **55**

Thus, the conjugated benzene ring, like the nitro group, can act as a fragment of a "fixing bond", leading to a preference for one of the two possible tautomers of the 18-π-electronic aromatic system of porphyrin. This in turn leads to regioselective electrophilic substitution.

The hexabromoporphyrin **55** can also be detected in the reaction mixture (up to 10% of the amount of the porphyrin **54**) by mass spectrometry. The formation of compound **55** can only arise during the initial bromination of the pyrrole ring adjacent to the annelated benzene ring, since compound **54** does not react when boiled with a large excess of N-bromosuccinimide in chloroform. Such bromination has the effect of removing the directing/blocking effect of the conjugated benzene ring. In other words the bromination of the porphyrin **53** in the pyrrole fragment adjacent to the fragment having an extended aromatic system gives rise to loss of regioselectivity and leads to the previously unobserved perbromination of the porphyrin macrocycle, and this makes its preliminary metallation essential.

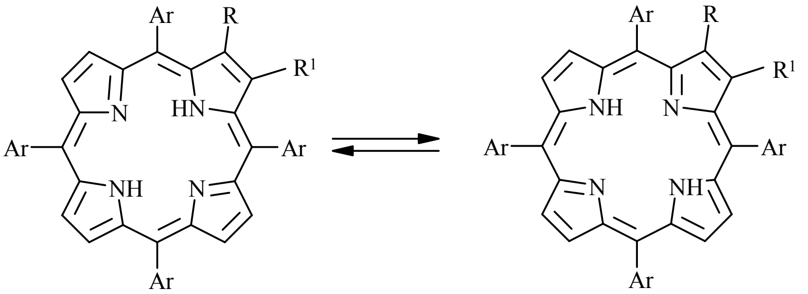
The presence of both the conjugated benzene ring and the bromine atoms of the opposite pyrrole fragment in compound **54** leads to their synergistic effect on the porphyrin π-system, thereby preventing subsequent bromination.

An identical direction of bromination, i.e., in the pyrrole fragment opposite the substituted fragment, is also observed in other cases, e.g., for porphyrinoquinoxaline **56** [41].



56

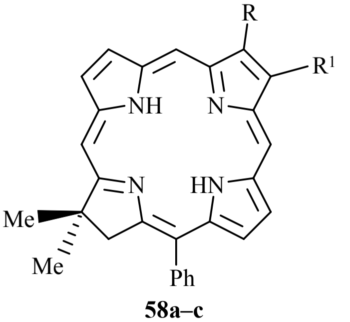
The preponderance of the tautomer **57** in the reaction mixture also follows from comparison with the reactivity of chlorins (see the next section), in which the tautomeric transition is impossible, and bromination here takes place in the pyrrole ring not entering into the aromatic system of the porphyrin.



57

Chlorin Derivatives

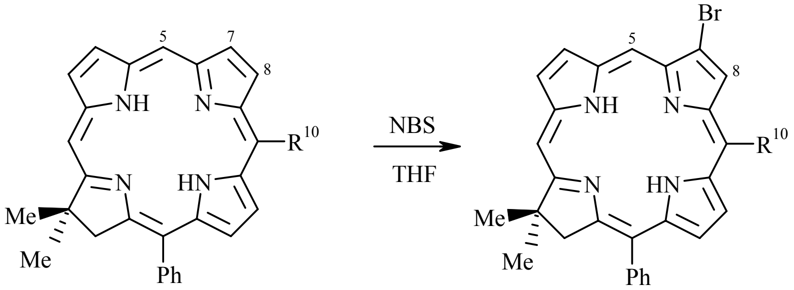
The bromination of the various *meso*-substituted chlorins takes in the pyrrole ring opposite the hydrogenated ring on the condition that the adjacent *meso* positions are hindered or substituted. Thus, bromination of the chlorin **58** leads to various reaction products, depending on the excess of N-bromosuccinimide, but only hinders positions 7 and 8.



58a–c

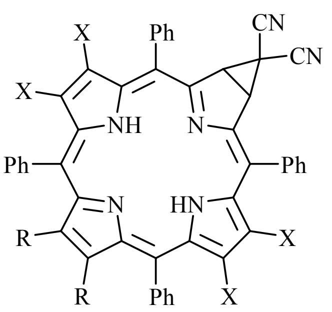
58 a R = R^1 = H, **b** R = R^1 = Br, **c** R = H, R^1 = Br и R = Br, R^1 = H

The use of 2 equiv. of N-bromosuccinimide leads to the dibromide **58b** with a yield of 31%, while the use of 1 equiv. leads to an inseparable mixture of bromides **58c**. It is possible to achieve selective bromination at position 7 by introducing a bulky group at the *meso* position 10 so that substitution at position 8 is prevented by steric hindrances.

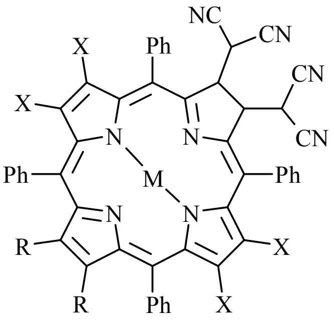


The reaction gives good yields in the case where R^{10} = *p*-tolyl or mesityl and leads to an inseparable mixture of chlorins brominated at position 7 and, presumably, at position 20 if R^{10} = C_5H_{11}.

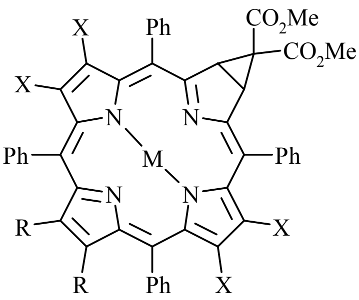
Similarly, bromination at position 8 can be directed by the presence of an aryl substituent at the *meso* position 5 [21].



59, 60



61–64



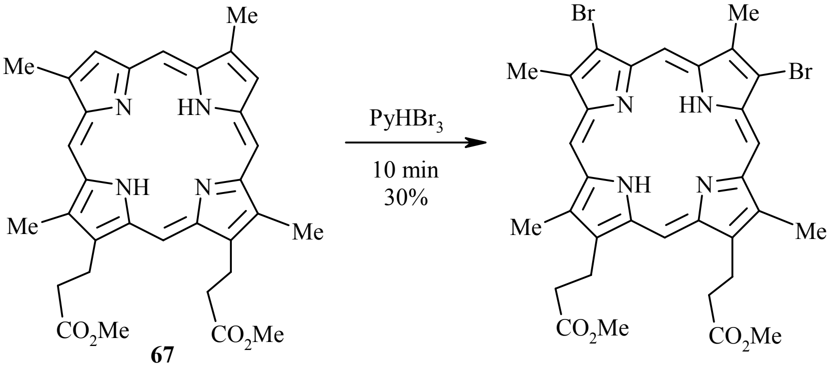
65, 66

59 X = R = H; **60** X = H, R = Br; **61**, **62** M = 2H, **61** X = R = H; **62** X = H, R = Br;
63–66 M = Ni, **63** X = R = H; **64** X = R = Br; **65** X = R = H; **66** X = R = Br

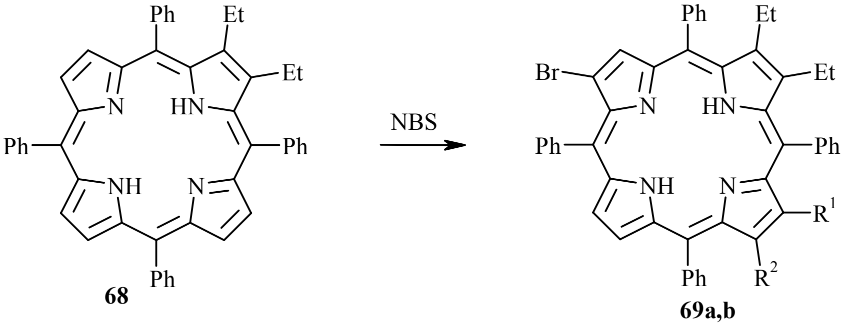
The dibrominated chlorin **60** is obtained with a 70% yield during the treatment of the chlorin **59** with 2.5 equiv. of N-bromosuccinimide in boiling chloroform. If 2.5 equiv. of bromine is used it is possible to obtain the disubstituted compound **62** from the initial compound **61**. Treatment of the metallated chlorins **63** and **65** with an excess of bromine leads to the hexabromides **64** and **66** [96, 99].

Porphyrins with Various Substituents at the β-Position

Many of the papers in this section concern polyalkyl-substituted porphyrins, among which the deuteroporphyrin **67** has been investigated most often. Thus, the bromination of deuteroporphyrin with the perbromide of pyridinium bromide [68, 100] and N-bromosuccinimide [101] leads to identical results.



An attempt at the bromination of 2,3-diethyltetraphenylporphyrin **68** with 2 equiv. of N-bromosuccinimide gave a complex mixture of reaction products, from which after repeated purification it was possible to obtain a small yield of the β-dibromo-substituted porphyrin **69a** [51].



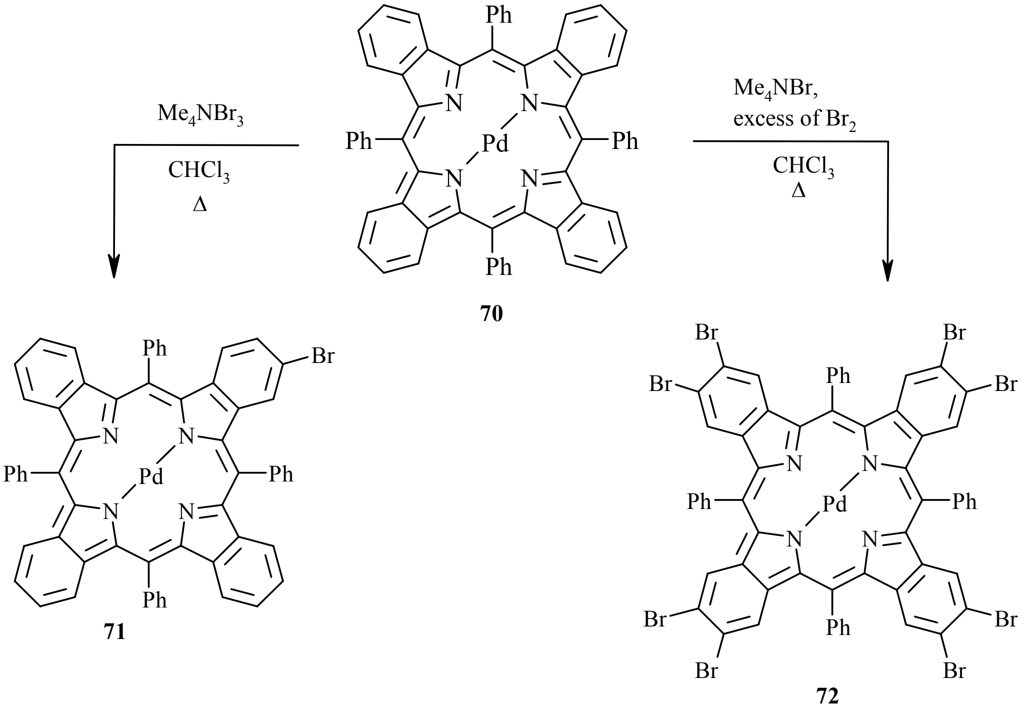
69 **a** R^1 = H, R^2 = Br; **b** R^1 = Br, R^2 = H

A similar result was obtained when 1 equiv. of N-bromosuccinimide was used – the porphyrin **69b** was obtained.

Exhaustive bromination at all the free β-positions of tetraphenylporphyrins with various number of ethyl groups [51] can be achieved by the method in [58].

Bromination of Tetrabenzoporphyrins

Palladium tetraphenyltetrabenzoporphyrinate **70** is brominated selectively in the benzene rings conjugated with the porphyrin ring if a mixture of bromine with tetramethylammonium bromide is used as brominating agent [102]. Other brominating agents not only affect the extended aromatic system of the tetrabenzoporphyrinate but also lead to substitution in the phenyl rings located at the *meso* position.



During bromination in the presence of tetramethylammonium bromide the octasubstituted tetrabenzoporphyrinate **72** is formed. With 2-4 equiv. of tetramethylammonium tribromide it is possible to obtain the monobrominated tetrabenzoporphyrin **71**, which can be separated from the dibromide impurity and unreacted porphyrin by column chromatography [103].

* * *

This review has made it possible to draw a series of conclusions concerning the reactivity of porphyrins in bromination.

First, there is a clear difference in the reactivity of the *meso* and β-positions of the porphyrin ring. Second, the presence and nature of substituents in the porphyrin substrate and also the presence and nature of the metal in the coordination cavity of the porphyrin often have a deciding effect on the possibility of reaction and its regioselectivity.

However, in spite of the numerous factors influencing the course and direction of the bromination of porphyrins, the appropriate choice of reaction conditions and brominating agents or the development of specific multistage pathways will make it possible to achieve regiospecificity during the insertion of bromine atoms into the porphyrin molecule.

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