

Novel Aspects of Corrole Chemistry

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Abstract: Corrole is one of the first examples of porphyrin analogs reported in the literature. This class of compounds has received a great attention, because of their promising exploitation in different fields, ranging from medicine to material chemistry. Among them, corrole can be considered the prototypical example of contracted porphyrins, with one of the meso carbon bridges missing. Although this macrocycle was first reported more than thirty years ago, only recently more attention has been devoted to the chemistry of corrole. The recent availability of efficient and facile syntheses of *meso*-substituted corroles has probably been the shuttle for the impressive flourishing of corrole-related papers appearing in literature in the last few years. The aim of this review is to highlight the latest reports in the synthetic chemistry of corrole, with special attention to the synthetic strategies and peripheral functionalizations of this macrocycle.

INTRODUCTION

Porphyrins play essential functions for life and for this reasons these macrocycles have been studied for centuries. Furthermore porphyrins have been a useful arena for researchers belonging to different disciplines, because of the richness of their properties. More recently an increasing attention has been devoted to porphyrin analogs, macrocycles bearing some skeletal variation to respect the porphyrin molecular framework. The close structure-properties relationship can indeed allow the modulation of the macrocycle behavior for a particular application. This is what happens in Nature, where a wide range of modified tetrapyrroles is operating other than porphyrins. A peculiar attention has been devoted to contracted porphyrins, macrocycles having a missing carbon atom to respect the parent macrocycle, which have been of peculiar interest because they are related to the chemistry of the corrin nucleus of Vitamin B₁₂.

Corrole is the prototypical example of a contracted porphyrin, with one of the *meso*-carbon atoms substituted by a direct pyrrole-pyrrole link, (Fig. 1).

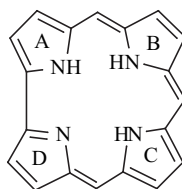


Fig. (1).

The genesis of this macrocycle is related to the Johnson's approach to the synthesis of Vitamin B₁₂, because the corrole ring was proposed as precursor of the corrin nucleus of the biological compound [1]. Unfortunately this route was not successful, because all the attempts to reduce corrole to corrin failed; the catalytic hydrogenation of corrole, in fact, occurred at the meso positions to give a "corrologen"

species, which was readily re-oxidized to corrole in presence of oxygen, (Fig. 2) [1]. This failure reduced the attention on corrole chemistry, that, for some time, has not been intensively pursued, although this macrocycle features some peculiar and interesting properties [2].

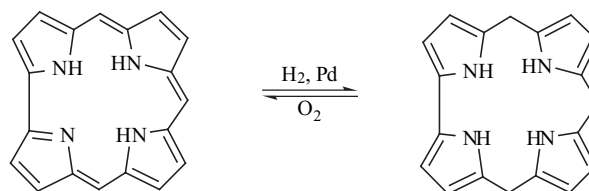


Fig. (2).

Like porphyrins, corrole presents in solution acid-base equilibria, with the formation of the cationic or the anionic species by reaction with acid or base, (Fig. 3).

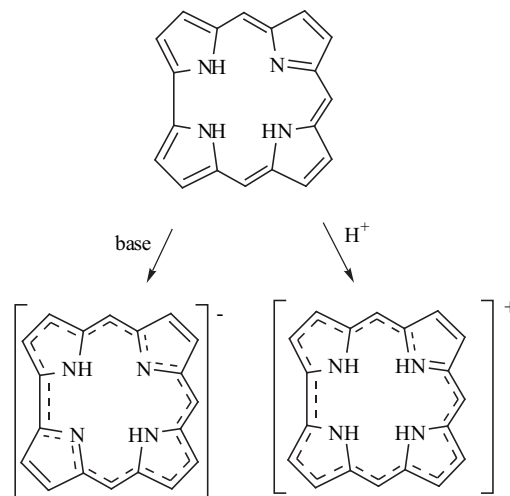
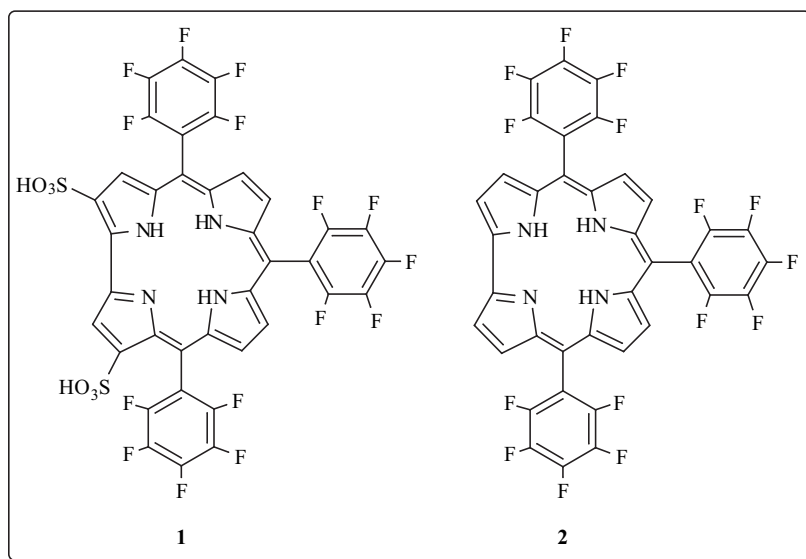


Fig. (3).

However corrole is a trianionic ligand, having three amino and one imino nitrogen atoms in the macrocyclic inner core, and this feature results in a peculiar behavior to the macrocycle. Corrole is in fact more acidic than porphyrin and the anionic species is easily formed in organic solvents by addition of bases. The higher acidity of corrole has been

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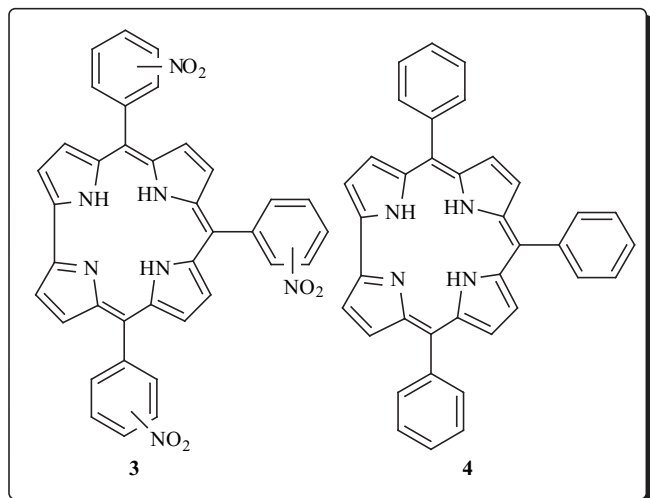


attributed to the steric relief produced by the loss of one inner core hydrogen atom.

The protonation/deprotonation equilibria for the water soluble corrole derivative (**1**) have been recently measured by spectroscopic techniques, following the changes in the absorption and luminescence spectra at different pH values [3]. It has been observed that the neutral form has a very narrow pH range of existence. This has been interpreted on the basis of steric hindrance between the inner NH groups. Both protonation and deprotonation induce a steric relief in the structure and reduce, as a consequence, the stability of the neutral form.

Variation in the neutral or charged form has also a significant influence on the photophysical properties of the macrocycle. A large increase in the fluorescence emission has been observed on going from the cationic to the anionic species and a similar behavior has been reported for the 5,10,15-tris(pentafluorophenyl)corrole (**2**) [4].

A variation of the luminescence spectra has also been observed for nitrophenyl derivatives (**3**). Interestingly, the emission almost disappeared on increasing of the dielectric constant of the solvent [5].



Another peculiar feature of corrole is its molecular structure, which is, again, strictly related to the presence of three NH groups in the macrocycle inner core. Although only few examples of X-ray molecular structures of corrole free base have been reported in the literature [5-9], recently we have been able to obtain the crystal structure of the 5,10,15-triphenylcorrole (**4**) [5], where it is confirmed the deviation from the planarity observed for this macrocycle, with the pyrrole ring A tilted out from the macrocyclic plane, caused by the steric repulsion between the inner core proton atoms, (Fig. 4). One of the most compelling features of corrole rings, arising from both the trianionic character and the reduced dimensions of the inner cavity with respect to that of porphyrin, is their ability to stabilize higher formal oxidation states of coordinated metals [10]. Furthermore the non-innocent character of corrole as ligands, makes particularly interesting its coordination chemistry [11,12].

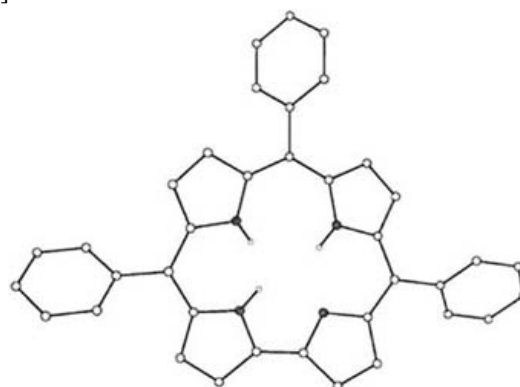


Fig. (4).

Although some of these characteristics of corroles were already known in the past, the chemistry of this macrocycle remained for long time overshadowed among porphyrin analogs. One of the reasons of this lack of interest was probably due to the multi-steps, lengthy and laborious preparation of the macrocycle, which precluded the study of corrole to researchers not familiar with pyrrole chemistry. This scenario changed in 1999, when Gross [13] and our group [14] reported almost contemporaneously the

preparation of 5,10,15-triarylcorroles from the reaction of pyrrole and benzaldehydes.

These two seminal reports constituted the starting point for a tumultuous and impressive growth of corrole-devoted papers and the chemistry of this macrocycle has then undergone an unprecedented development. The synthetic approaches to corrole have been further refined and the synthetic chemistry of corrole, yet not developed like that of porphyrins, is nowadays quite versatile.

The aim of this review is to cover these latest results in the synthetic chemistry of corrole, along with some example of peripheral elaboration of this macrocycle.

SYNTHESES OF CORROLES

Synthesis from Monopyrrolic Precursors

We reported the first example of the preparation of corrole from single pyrrole precursors in 1994, by reaction of 2-hydroxybenzylpyrrole in the presence of Co(II) ions to give corrole (**5**), (Fig. 5) [15].

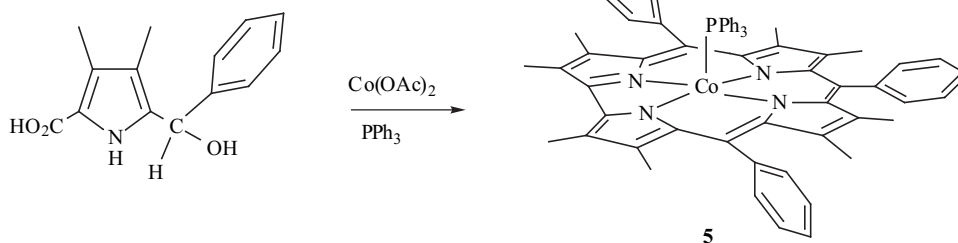
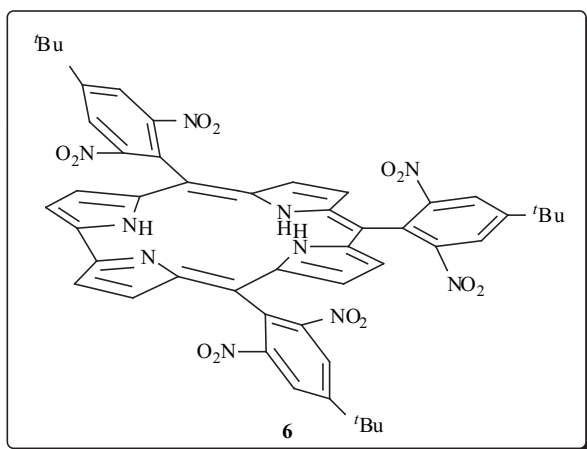


Fig. (5).

The presence of cobalt ions was necessary to obtain the corrole ring, because other metal ions, such as copper, nickel or rhodium, afforded the expected octamethyltetraphenylporphyrin. A plausible mechanism proposed for the formation of (**5**) involves the Co(II) catalyzed self condensation of two units of dipyrromethene, generated by the coupling of the 2-hydroxybenzylpyrrole in the acidic media [15]. The formation of corrole from the direct reaction of pyrrole and an aromatic aldehyde was reported in 1996, with the formation of corrole (**6**) as by-product of the synthesis of 5,10,15,20-tetrakis-(2,6-dinitrophenyl)porphyrin [16].



The generality of this approach was however demonstrated in 1999, by Gross group and us and after these papers other examples have been reported in the literature and it is now possible to choose, among different methods, the best ones for the particular corrole desired.

Reaction of Pyrrole and Aldehyde in the Absence of Solvent

The Gross approach consists in the reaction of pyrrole and the aldehyde in the absence of solvent, catalyzed by basic alumina. The yields of the reaction were satisfactory in the presence of pentafluorobenzaldehyde, while in the presence of less reactive aldehydes a significant reduction of yields or the complete failure of the reaction was observed [13]. The analysis of the different reaction products showed the presence of linear pyrrolic species [7]. Although with these limitations in the scope, this facile preparation of the corrole ring allowed a detailed study of the coordination chemistry of this macrocycle [17], and (**2**) became the first example of commercially available corrole. Following this route the same group was able to prepare the first meso-alkyl

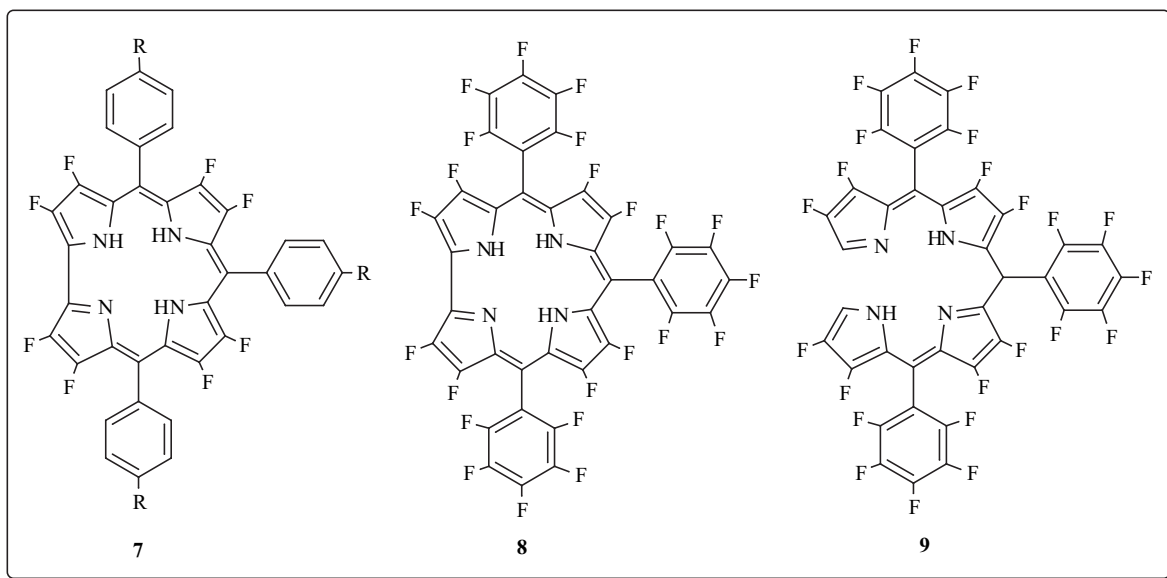
substituted corrole [6]. It is worth mentioning that the reaction is carried out to open air, which simplify the experimental protocol and it is necessary for the success of the reaction, because under inert atmosphere no macrocycles are formed [13].

Ghosh and coworkers later demonstrated that this approach is more general than previously reported and a wide range of different corroles could be prepared with small modifications of the reaction procedure [18]. This reaction is in indeed sensitive to experimental conditions and a critical point is the effective stirring of the heterogeneous mixture, due to the absence of solvent. Following this route it has also been possible to prepare β -octafluorocorrole derivatives (**7**), reacting 3,4-difluoropyrrole with benzaldehydes [19].

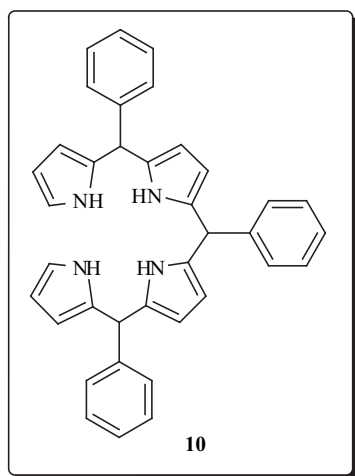
In the same way Chang and co-workers have been able to prepare the perfluorocorrole (**8**), by reaction 3,4-difluoropyrrole with pentafluorobenzaldehydes [20]. In this case it was necessary to prolong the heating of the reaction to obtain the desired product, because in the usual condition the linear tetrapyrrolic precursor (**9**) was in fact isolate, giving a further evidence that the ring closure is the final step of the reaction pathway.

Collman and co-workers recently reported a further increase in the reaction yields, by using a microwave instead of the conventional heating of the reaction mixture [21].

These results show that the reaction of pyrrole and aromatic aldehydes, which has been considered for long time



the classic preparation of porphyrins, can afford corrole, as well as isomeric and expanded porphyrins, by simple modifications of the reaction conditions. In the case of corrole the precursor is the linear bilane (**10**); Lee and co-workers, as later reported, demonstrated that the reaction of pyrrole and benzaldehyde catalyzed by trifluoroacetic acid (TFA), following the conditions usually adopted for the formation of meso-aryl dipyrromethane [22], can afford (**10**), other than higher linear polypyrroles, by variation of the reagent molar ratio [23]. Subsequent oxidative ring closure, generally carried out with DDQ or chloranil in open air, gives the corrole ring. Following this pathway, Gryko *et al.* proposed a further modification of the reaction protocol between pyrrole and benzaldehydes, carrying out the reaction in two steps: in the first the neat reaction of pyrrole and aldehydes was carried out with the addition of TFA as catalyst and then the reaction was diluted with CH_2Cl_2 and the mixture oxidized with DDQ [24].



Gryko and Koszarna optimized the conditions for the formation of corrole from the TFA reaction of pyrrole and benzaldehydes, and they refined three different experimental protocols, depending on the reactivity of the aromatic aldehyde [24]. Highly reactive aldehydes, like pentafluorobenzaldehyde, gave higher yields of corrole in the

presence of low amount of the acid catalyst, while less reactive aldehydes needed higher amounts of TFA and an excess of pyrrole. In this way it has been possible to prepare a quite large variety of substituted corroles in the range of 10-20% yields.

Modified Rothmund Method

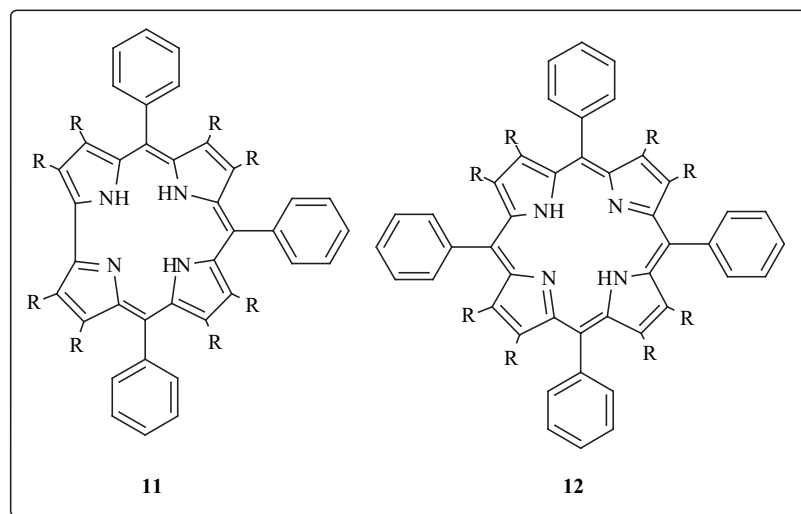
A different approach for the preparation of meso-arylc corrole has been developed by a simple modification of the experimental conditions of the conventional Rothmund method for the preparation of tetraarylporphyrins [25], which performs the reaction between pyrrole and aromatic aldehyde in refluxing acetic or propionic acid. To obtain corrole the reaction was carried out in the presence of a 3:1 molar excess of pyrrole [14,26]. In this way a mixture of corrole and porphyrin is generally obtained, although in some particular cases, such as the reaction with 4-nitrobenzaldehyde, the corrole is the exclusive macrocyclic product of the reaction, in a surprisingly high 22% yield. The scope of the reaction is quite general with mono-substituted benzaldehydes and a wide range of corroles has been prepared following this approach.

In the case of sterically hindered benzaldehydes, such as 2,6-disubstituted derivatives, this approach is not successful and corrole has not been obtained or has been observed in discouraging low yields (0.3 % [22]).

One of the major drawbacks of this approach is however the concomitant formation of the corresponding tetraarylporphyrin, which makes difficult the chromatographic separation of corrole from the corresponding porphyrin, with the consequent reduction of the total yield of the reaction.

Modified Lindsey Method

As a third example of preparation of meso-substituted corroles we studied the reaction of pyrrole and benzaldehydes in acidic CH_2Cl_2 , a route that can be considered a modification of the Lindsey procedure for the preparation of tetraarylporphyrins [25]. This route involves a two-step



reaction, where pyrrole and benzaldehyde are first reacted in acidic dichloromethane to give the porphyrinogen, which is then oxidized by DDQ to the final porphyrin. Also in this case the aim was to slightly modify the experimental conditions to define a protocol that drove the reaction to the preparation of corrole, through the formation of (10), avoiding in the same time the competitive formation of porphyrin. Our group carried out the reaction of benzaldehyde and pyrrole, in 1:10 molar excess, in CH_2Cl_2 with TFA as catalyst [5]. Subsequent oxidation with p-chloranil afforded corrole in satisfactory yields, while the corresponding porphyrin was not present or was observed only in traces among reaction products. This approach was also working in the case of 2,6-disubstituted aldehydes, where the modified Rothmund approach failed. Furthermore following this approach it was possible to prepare fully substituted β -octaalkyl, *meso*-triphenylcorroles (11) [5].

In this case the reaction afforded higher yields if the first step was carried out without solvent and acid catalyst, heating 3,4-dialkylpyrrole and benzaldehyde. The formation of the corresponding dodecasubstituted porphyrin (12) was in this case always observed and the undecasubstituted corrole was obtained in lower yields than the corresponding 5,10,15-triphenylcorrole.

Synthesis from Dipyrrromethanes

A wide range of *meso*-substituted corroles has been obtained using dipyrrromethane as starting material. Two different approaches can be followed, as reported in (Fig. 6).

In the first pathway two *meso*-substituted dipyrrromethanes are reacted with an aromatic aldehyde, while the other approach is reminiscent of the McDonalds synthesis of β -alkylporphyrins, with the [2+2] acid catalyzed

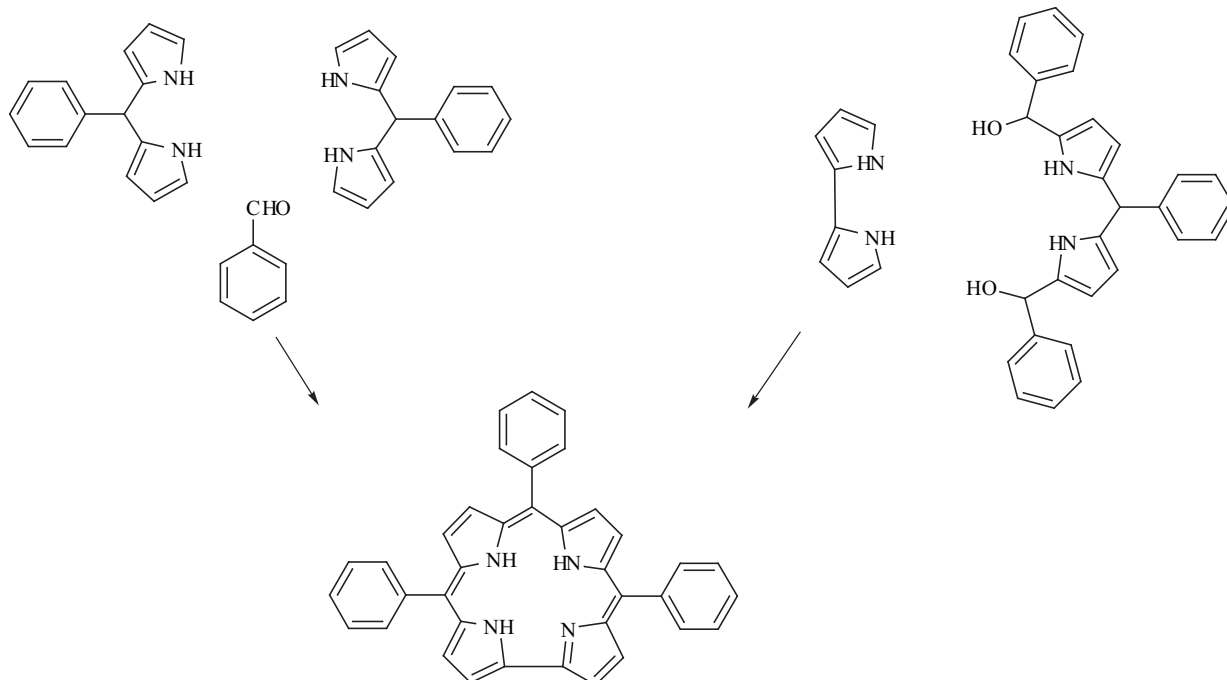


Fig. (6).

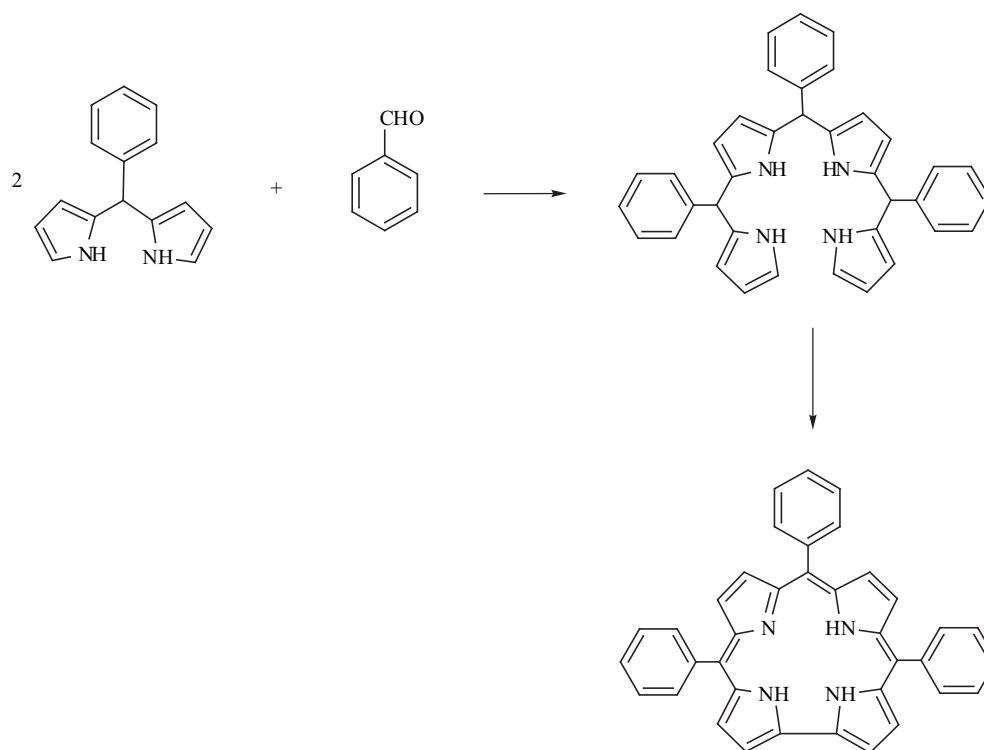


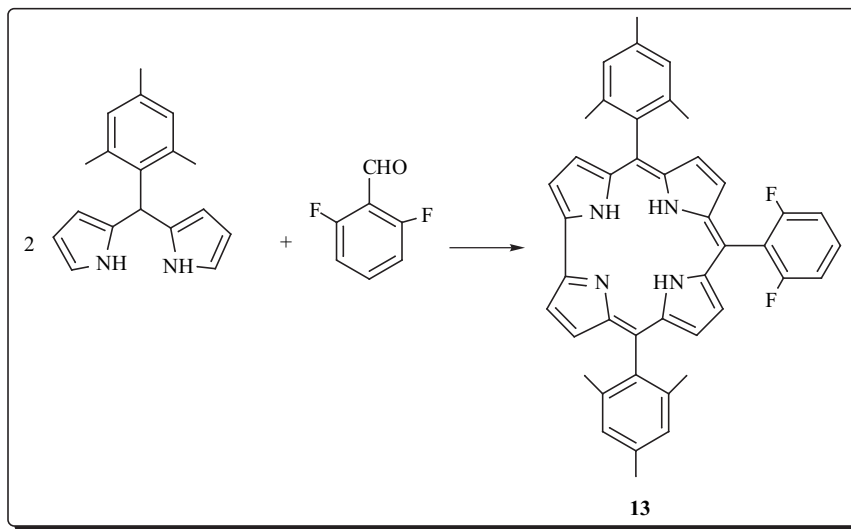
Fig. (7).

condensation of dipyrromethane and bipyrrin to give the corresponding macrocycle.

The more general pathway, however, is represented by the acid catalyzed reaction of two units of dipyrromethane with a benzaldehyde. Although no evidences have been reported in the literature, it is reasonable that the formation of corrole goes through an intermediate bilane, (Fig. 7), which is then oxidatively cyclized to give the final corrole ring.

Following this approach, it is also possible to prepare A_2B -substituted corrole, if the final aldehyde is different from that present in the starting dipyrromethane. The first example of this approach was reported in 2001 by Gryko [27]. The reaction of mesityl dipyrromethane with fluoro

substituted benzaldehydes afforded the corresponding A_2B corroles (**13**) in satisfactory yields. In the preliminary communication the reaction has been reported to be successful only with activated liquid aldehydes and was carried out without the addition of acid as a catalyst. However a detailed study from the same author rationalized this unexpected results [28], showing that the acid catalysis is necessary for the success of the reaction, and in the first reactions the catalysis was performed by the presence of small amounts of benzoic acids present as contaminants in the liquid aldehydes. Gryko and co-workers pointed out the optimal reaction conditions to increase the corrole yields and to avoid scrambling in the formation of A_2B corroles, using the reaction of mesityldipyrromethane and 2,6-difluorobenzaldehyde as reference reagents [28]. Differently



from the protocol used in the porphyrin synthesis, low concentration of acid and high concentrations of substrates favored the formation of corrole ring. TFA and dichloromethane were found to be the best choices for the reaction, while no increase of reaction yields were observed using propionitrile as solvent. The scope of the reaction is quite general and a wide range of different substituted A_2B corroles, including macrocycles bearing pyridine or other nitrogen aromatic bases in the meso positions [29].

A two-steps one-pot approach was proposed by Brückner and Briñas [30]; in this case the dipyrromethane formed *in situ* by the acid catalyzed reaction of pyrrole and benzaldehyde was then further reacted in 6:1 molar excess with a second aldehyde unit. Subsequent oxidative ring closure by DDQ gave the corrole. This route allows also the formation of A_2B corroles if the aldehyde used in the second step is different from that exploited for the dipyrromethane formation. This approach has however the disadvantage to use an excess of dipyrromethane and furthermore the presence of porphyrin as by-product in these conditions has been later observed by other researchers [28].

Dehaen and coworkers reported a similar two-steps synthesis of corrole by reaction of sterically hindered dipyrromethane and 2,6-disubstituted electron-poor benzaldehydes; in the other case, in fact, the reaction product is always the corresponding porphyrin [31].

The first example of a superstructured chiral corrole has been reported by Andrioletti and Rose following the above reported synthetic pathway, (Fig. 8) [32]. In this case 2,6-dinitro-4-tertbutylphenyl dipyrromethane was reacted with pentafluorobenzaldehyde to give the corresponding corrole (14) in a 24% yield, with no formation of the corresponding porphyrin. Reduction of the nitro groups to the corresponding amino derivatives and subsequent reaction with a bis-naphthyl acyl chloride afforded the corresponding chiral strapped corrole (15) in a 25% yield.

Recently Collman and co-workers have proposed a synthetic route to corroles reminiscent of the McDonald approach to porphyrin, involving the condensation of a dipyrromethane dicarbinol with a bipyrrrole unit, (Fig. 9) [33]. It is interesting to note that a similar reaction in the β -

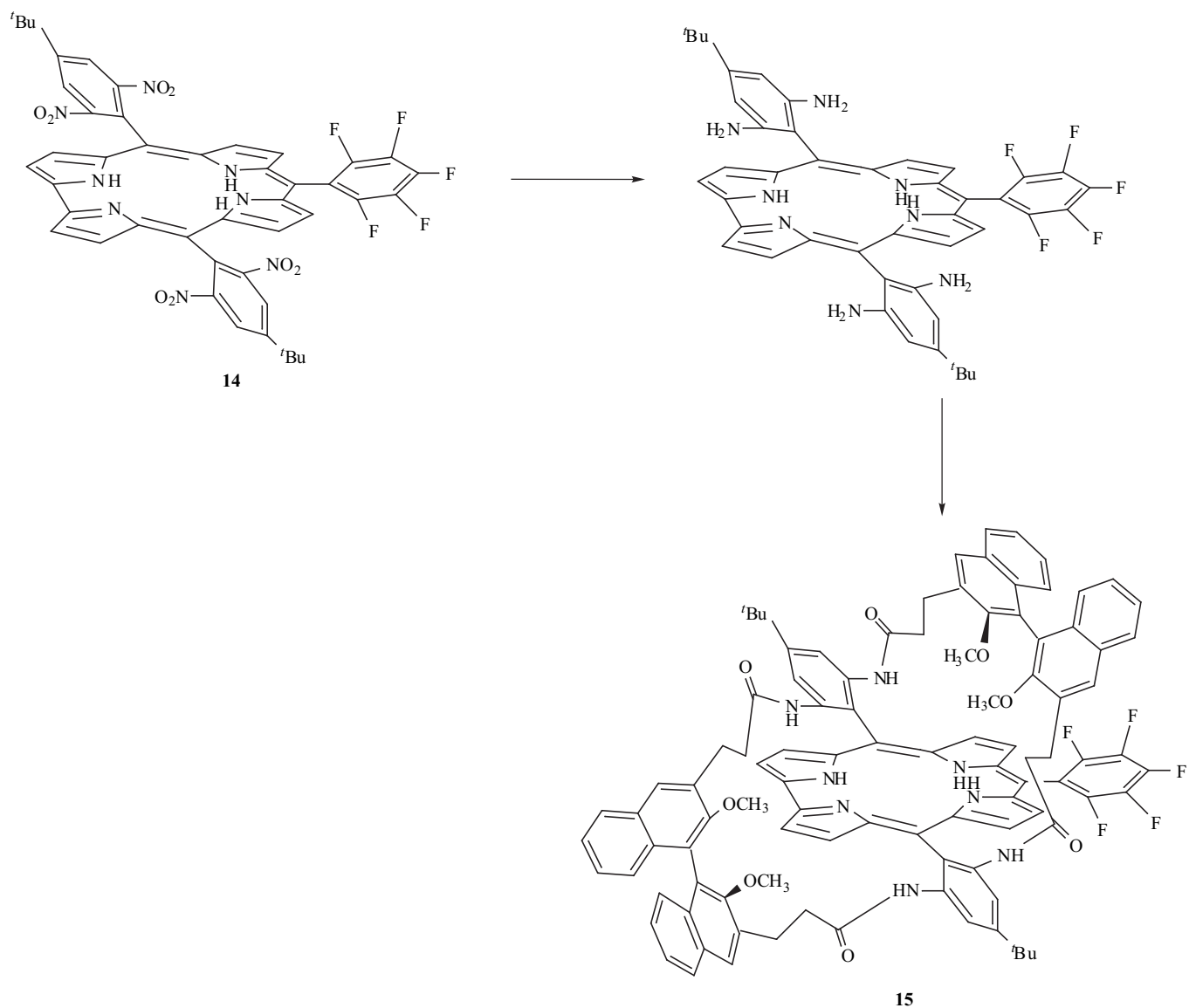


Fig. (8).

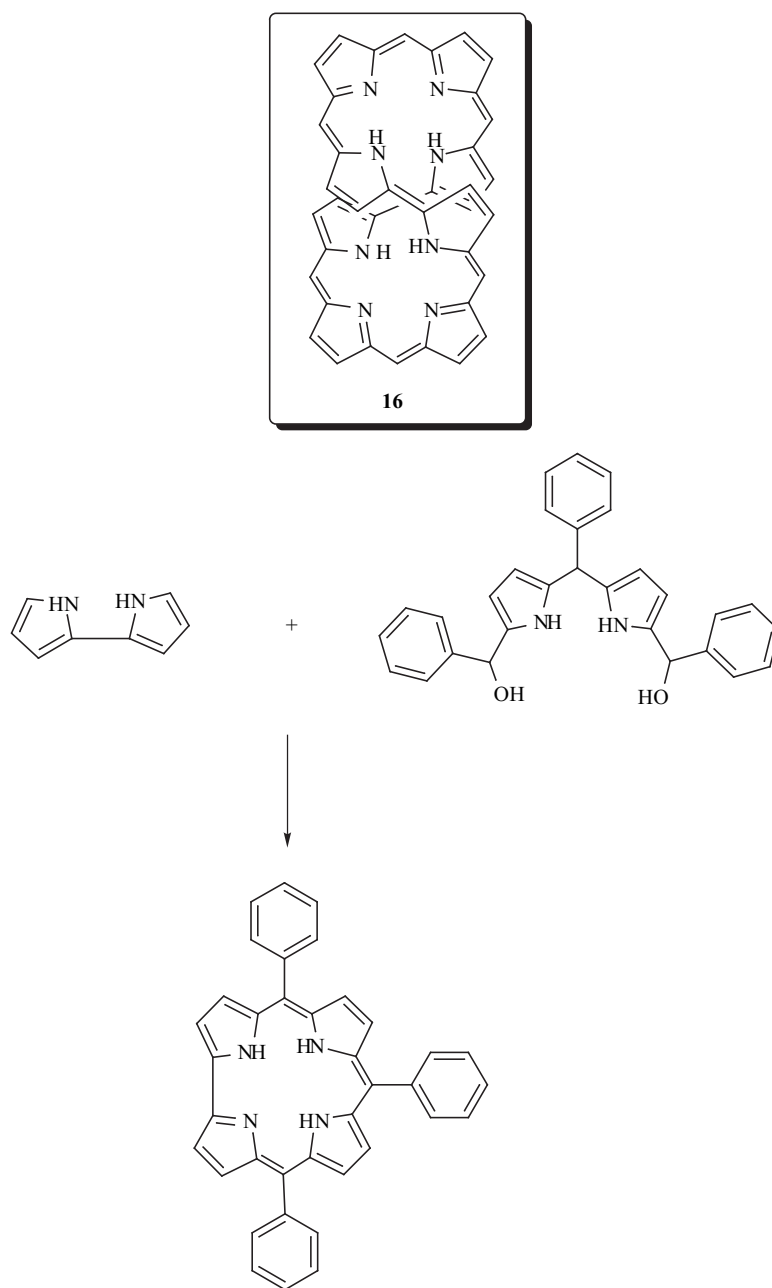


Fig. (9).

octaalkylcorrole series was attempted by Vogel, but in this case the product was not the corrole, but a figure eight macrocycle (**16**) [34].

The reaction was tested for mesityl- and phenyl derivatives and the influence of both reaction time and acid catalyst was investigated. Best yields were obtained using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and prolonging the reaction time to 24 hours.

This approach can be also adopted for the preparation of A_2B or ABC -substituted corroles, by the opportune modifications of the pyrrolic precursors.

Synthesis [3+1]

A [3+1] approach for the preparation of diphenyl substituted corrole has been recently proposed [35].

Although this route works better in the case of oxacorrole derivative (as later reported in this article), it was also tested for the preparation of corroles. Reaction of diaryltirpyrrane (**17**) with 2-pyrrole carbaldehyde in $\text{TFA}/\text{CH}_2\text{Cl}_2$ afforded the corresponding corrole (**18**) in low yields, being the tetraarylporphyrin (**19**) the main reaction product, (Fig. 10). The porphyrin originated from the acidolysis of the starting tripyrrane species.

Synthesis from Tetrapyrrolic Precursors

The cyclization of a linear tetrapyrrole has been for long time the unique general route for the preparation of corroles. The oxidative cyclization of the *a,c*-biladiene (**20**), (Fig. 11), has been also the first successful approach for the preparation of this macrocycle [1].

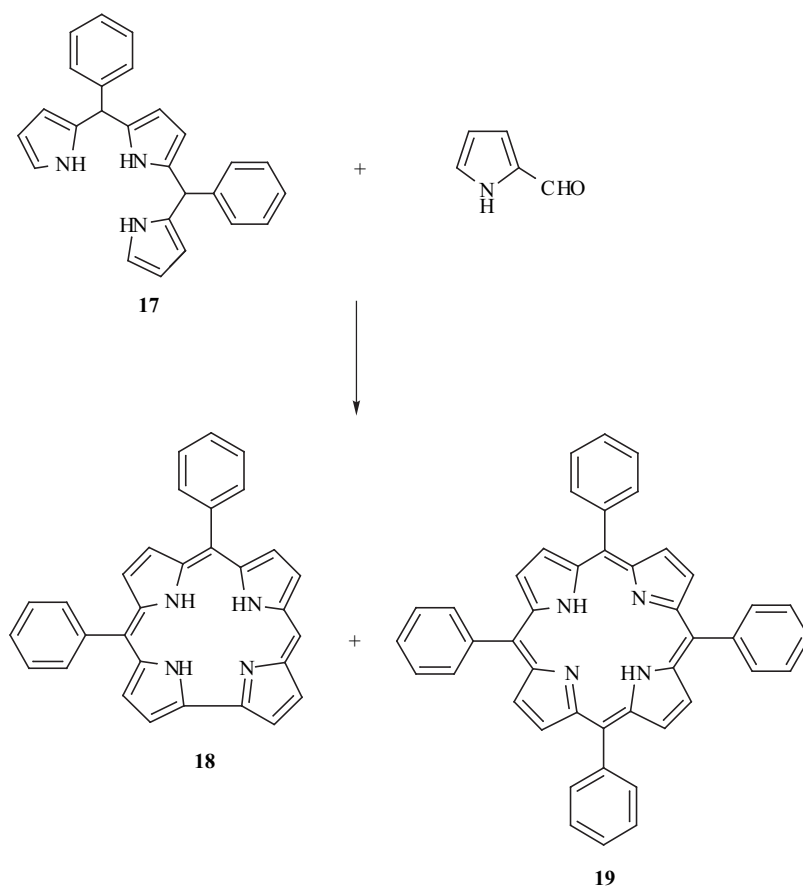


Fig. (10).

This linear tetrapyrrolic precursor is generally prepared by the acidic condensation of a dipyrromethane with two equivalents of a 2-formylpyrrole and the obtained a,c-biladiene is separated as dihydrobromide salt. For long time

basic conditions have been considered as an essential requisite for the formation of corroles [36], necessary to induce the formation of the dihydrobilatriene, the linear precursor that undergoes the final cyclization step to give

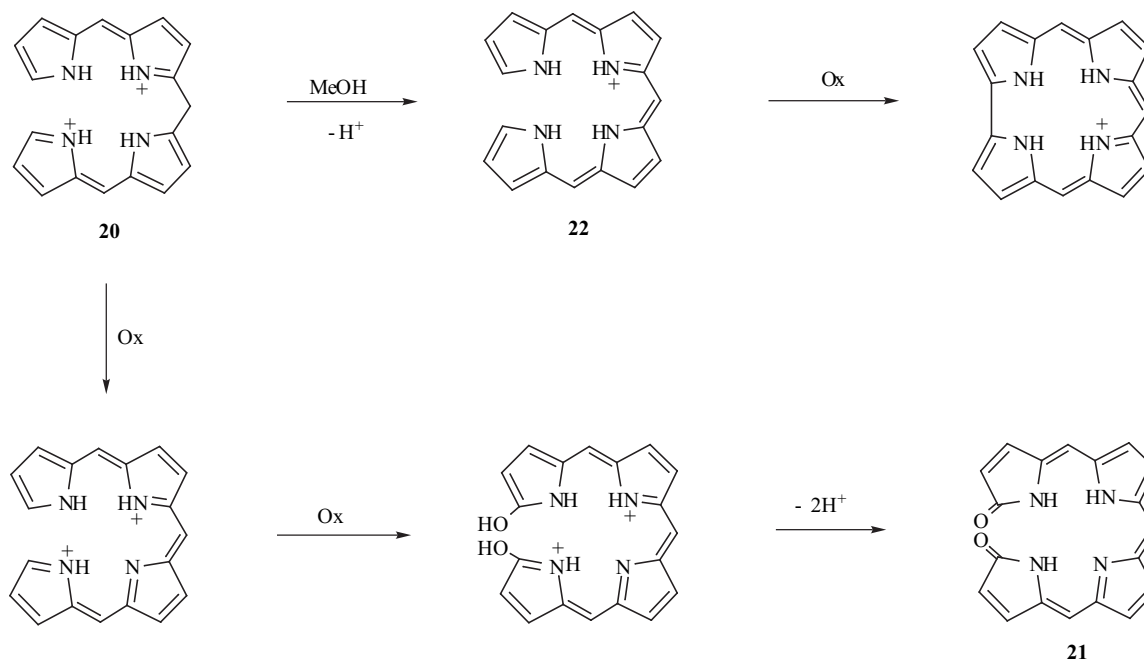


Fig. (11).

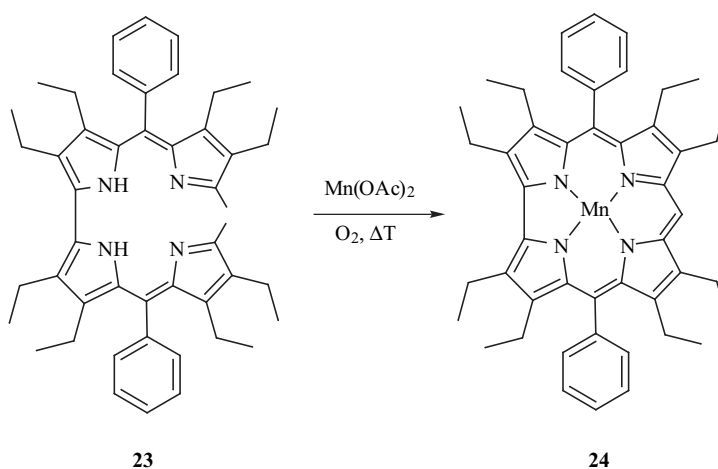


Fig. (12).

corroles. However we recently noted that corroles can also be obtained from a,c-biladienes directly in acetic acid or acidic ethanol, demonstrating that the addition of bases is not necessary [37]. More recently we have studied the reaction of a,c-biladienes with chloranil in different solvents. Good yields of corrole can be obtained in methanol and the addition of base is not necessary for the cyclization. In CHCl_3 the reaction has a completely different pathway, with the formation of the corresponding biliverdin (**21**) [38]. Addition of small amounts of methanol to the CHCl_3 solution, however, induces again the formation of corrole in yields similar to that observed in pure methanol. These results indicated that it is necessary the formation of a fully conjugated species, the dihydrobilatriene cation (**22**), to allow the subsequent formation of corrole, (Fig. 11). Methanol or other protic species, induce the formation of this precursor after tautomeric shift of a hydrogen atom, and then the corrole formation. When the formation of this species is prevented, such as in CHCl_3 , the direct oxidation of the biladiene leads to the biliverdin. When both deprotonation and oxidation are not allowed, as in the case of 10-alkyl substituted a,c-biladienes, no reaction is observed and the tetrapyrrole slowly decomposes in solution. The possibility to carry out the reaction with *p*-chloranil also in acidic conditions, offers the possibility to point out a two-steps, one-pot synthesis of corroles starting from dipyrromethane and 2-formylpyrroles, avoiding the isolation of the linear precursor [38].

While in the usual preparation of corrole the last synthetic step is the formation of the direct pyrrole-pyrrole link, a different route has been proposed by Bröring and

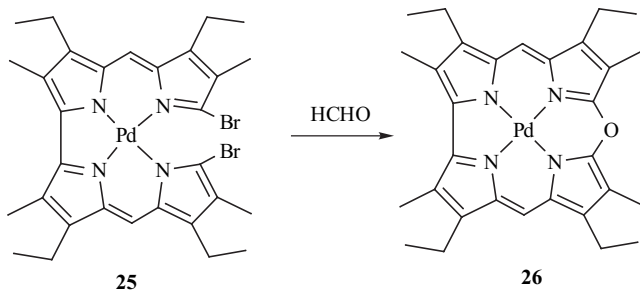
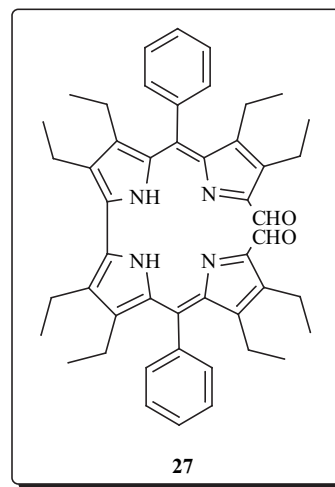


Fig. (13).

Hell, which used as linear precursor a 2,2'-bisdipyrrin (**23**), where the pyrrole-pyrrole bond is already present [39]. The cyclization of this precursor was catalyzed by Mn(OAc)_2 and the final product is the corresponding Mn(III)Corrole complex (**24**), (Fig. 12). It is to note that the 2,2'-bisdipyrrin route was also one of the first Johnson's attempts for the preparation of corrole [40]. Johnson used the Pd(II) complex of 2,2'-bisdipyrrin (**25**), but after reaction with formaldehyde the product was 10-oxacorrole (**26**), (Fig. 13), instead of the expected corrole ring [40]. The free base corrole can be obtained in good yields following this route by removal of the Mn(III) ion in HAc/HBr solution. This is also the first example of demetallation of a corrole ring reported in the literature. By using substituted bis-dipyrrins, Bröring and Hell were able to prepare 5,15-diarylcorroles, which could not be prepared by the usual a,c-biladiene route [39].

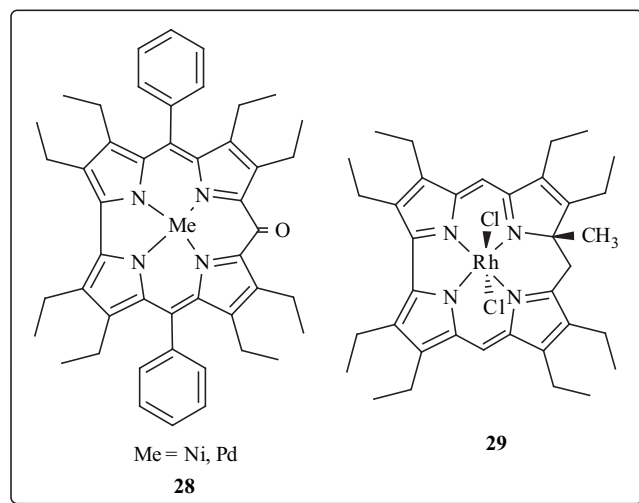
Both Mn(II) ion and oxygen are necessary for the success of this reaction, as more recently reported by the same authors [41]. When Mn(II) ion was reduced to catalytic amount (5 mol%), no ring closure of the linear precursor was observed, and the reaction product was the dialdehyde (**27**), obtained by oxidation of the terminal methyl groups. This interesting result arouses the question of the effective oxidant in the reaction, which can be either a Mn(III) or a partially reduced dioxygen species. However the reaction



with Mn(III) acetate led to the decomposition of the bisdipyrrin, ruling out the role of this ion as oxidant. When the reaction was carried out using KO_2 as oxidant, a quantitative formation of (27) was observed [41].

The next step of this study was to investigate the reaction of Ni(II), Pd(II) and Cu(II) complexes of 2,2'-bisdipyrrin with K_2O , to study the influence of the template ion on the cyclization step. The reaction of the Ni(II) and Pd(II) complexes was fast, but the product obtained in both cases was the corresponding 10-oxocorrole (28). On the other hand the Cu(II) derivative reacted very slowly and afforded the corresponding Cu(III)corrole in low yields. In the case of Ni and Pd derivatives the formation of the metallocorrolate is followed by a further oxidation to give the final 10-oxocorrole complex and this result is in good agreement to the different oxidative behaviour of these metallocorrolates. While the formation of (27) as an intermediate in the cyclization to corrole of the 2,2'-bisdipyrrin was excluded by Bröring and co-workers, because (27) is able to afford the corresponding 10-oxocorrole complexes with different transition metal ions [41], the preparation of the intriguing Rh(III) complex (29) by Bröring and co-workers [42] seems to indicate a reaction pathway similar to that elucidated for the cyclization of a,c-biladienes to porphyrins [43].

In the case of 5,10,15-triarylcorroles, the linear precursor is the bilane (10), formed from the acid catalyzed, neat condensation of pyrrole and benzaldehyde [44]. Highest yields of (10) were obtained by reduction of the pyrrole:benzaldehyde molar excess to 3:1. The bilane can be purified by chromatography from the other oligo-pyrrolic species formed in this reaction, and subsequently reacted with DDQ, to give the corresponding corroles in good yields. To optimize the experimental protocol the reaction was carried out in different solvents and the influence of the



addition of some inorganic salts was also studied. Best results (65 % yield) were obtained by using propionitrile as solvent, where inorganic salts showed no influence. On the other hands, a significant increase of reaction yields by addition of these inorganic salts were observed in acetonitrile or CH_2Cl_2 ; DDQ was also found to be a better oxidant for the ring closure than p-chloranil.

More recently Guilard and co-workers have reported a different route to the formation of the bilane, by the reaction of a dipyrromethane dicarbinol (30) with pyrrole, which is reminiscent of the a,c-biladiene pathway, (Fig. 14) [45].

In this case a diacyl dipyrromethane (31) is reduced by NaBH_4 and then condensed in acidic conditions with pyrrole to give the linear species, which is then cyclized with DDQ under the usual conditions to give the corresponding corrole. The bilane can be purified by chromatography and then

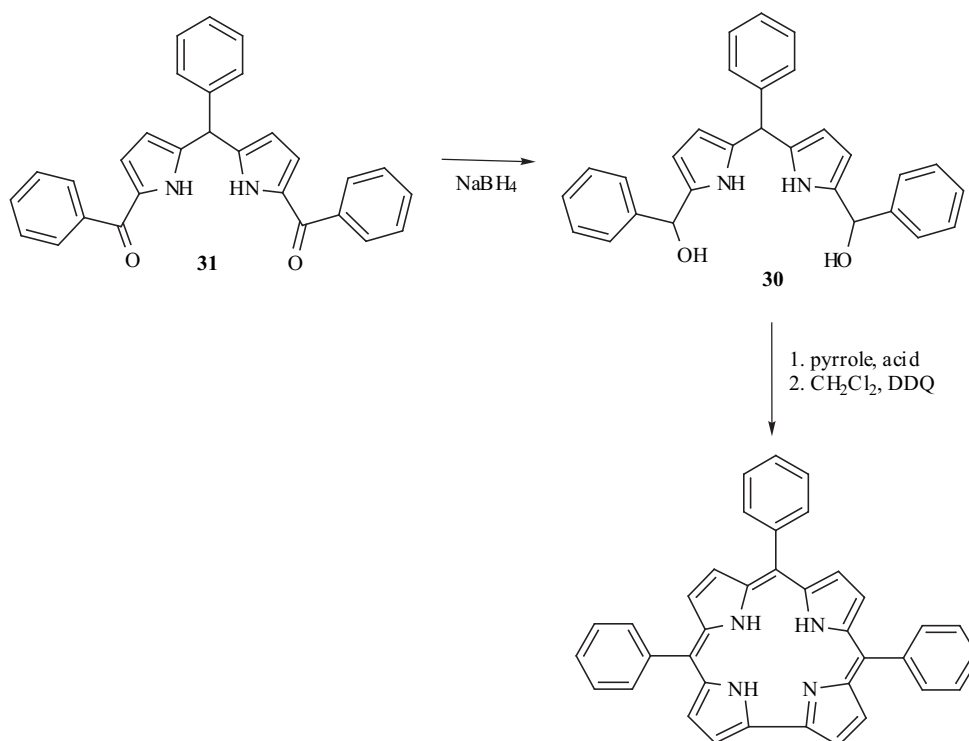
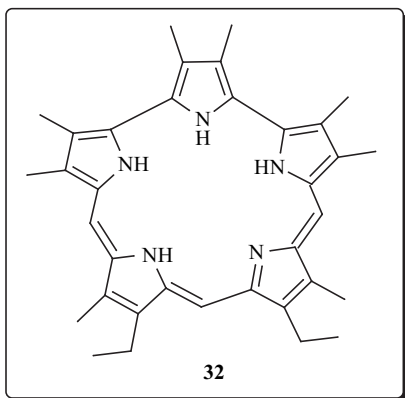


Fig. (14).

reacted to give corrole, or the reaction can be carried out one-pot, without the isolation of the linear intermediate. In both cases no porphyrin was observed among reaction products.

Unsymmetrical ABC-corroles can be prepared following this route, starting from unsymmetrical diacyl dipyrromethanes, prepared following the procedure reported by Lindsey and co-workers [46].

More recently Gryko and co-workers have reported an improved preparation of diacyldipyrromethane, the key intermediates in this route, by definition of a modified Vilsmeier approach [47]. This method afforded many advantages to respect the usual Grignard route, such as the higher yields, the absence of monoacyl species and the preparation of dipyrromethanes bearing functional groups not compatible with the Grignard approach, such as CN or NO₂ groups. The improvement in the preparation of diacyl dipyrromethane can facilitate the exploitation of this approach to the preparation of both symmetrical and unsymmetrical substituted 5,10,15-triarylcorroles. During this study Gryko and co-workers reported also the formation of the pentaphyrin (**32**), probably originated from the reaction of the intermediate bilane with excess of pyrrole. This result can explicate the unexpected low yields obtained during the preparation of some corrole following this method [47].



FUNCTIONALIZATION OF CORROLES

The modification of the substitution pattern on the corrole ring by the introduction of different groups was a quite unexplored field until the preparation of 5,10,15-triarylcorroles. Indeed these macrocycles constitute a convenient starting platform for the achievement of more elaborated molecular architectures, by analogy with the corresponding 5,10,15,20-tetraphenylporphyrins. Following this idea, interesting examples of β -functionalization of *meso*-triphenylcorroles have been reported in the literature, although this field is still in its infancy when compared with that achieved in porphyrin synthetic chemistry [48]. Furthermore, β -functionalization of corroles presents higher potential complexity compared with porphyrins, because of the lower symmetry of the corrole system, which can lead to a larger number of possible isomers.

The functionalizations performed on the corrole ring can be divided in two main groups, namely the addition to the inner core nitrogen atoms or substitutions on the peripheral positions.

N-Alkylcorroles

The introduction of alkyl groups at the inner core nitrogen atoms is the first functionalization attempted of corrole ring and Johnson and Kay in fact reported the reaction of corrole with alkyl iodides together the first preparation of this macrocycle [1]. The facile formation of corrole anion in dilute alkaline solutions is probably the reason of the early attempt of this reaction. The presence of three NH groups in the corrole inner core, however, leads to the formation of two regioisomers, the N-21 or the N-22 alkyl substituted derivatives. Although these N-alkylated corroles were known from several years, only recently their chiral character has been elucidated by Gross [49]. Due to the lower symmetry of corrole ring, in fact, these N-alkyl substituted derivatives, lacking any symmetry elements, are chiral compounds. Gross and co-workers prepared N-alkyl derivatives of (**2**) by reaction of benzyl bromide or 2-chloromethyl pyrimidine in toluene/K₂CO₃ mixture. Gross and Galili demonstrated the chiral character of these compounds by different spectroscopic techniques and they have also been able to separate the enantiomers of these N-alkyl derivatives by HPLC on a chiral column.

SUBSTITUTION OF THE PERIPHERAL POSITIONS

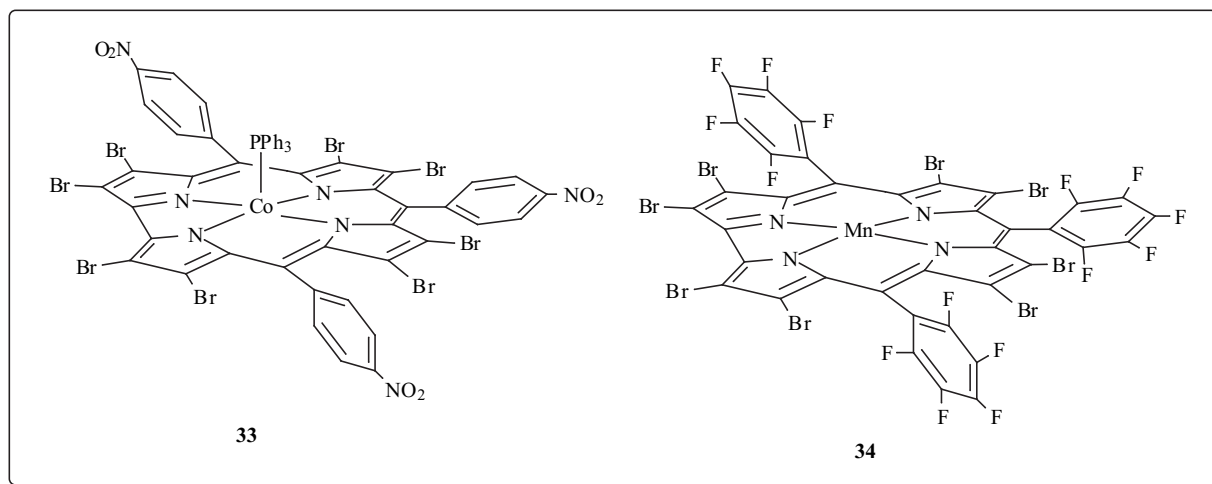
While the alkylation of the corrole inner core has been carried out on both β -alkyl and *meso*-triarylcorroles, the functionalization of the peripheral positions has been almost exclusively performed on triarylcorroles, by reaction with electrophilic reagents.

Bromination

The introduction of bromine atoms at the β -pyrrolic positions have been carried out on the free-base or on a corrole metal complex. Different from tetraaryl-porphyrins, in both cases the product of the reaction is the β -octabromo corrole derivative, where all the β -pyrrolic positions are substituted [19,26,50].

The reaction on the free base corrole (**3**) or (**4**) was performed by using N-bromosuccinimide (NBS) as brominating agent. The yields of this reaction were however quite low, probably due to the decomposition of the corrole in the reaction conditions. When the reaction was carried out using bromine in methanol, the bromination was accompanied by the ring opening of the corrole ring [26]. The β -octabromo corrole is quite unstable, probably due to the steric hindrance induced by the peripheral halogen groups, as evident from the UV-vis spectrum, which showed a red-shifted and very broad Soret-like band. Coordination of cobalt ion, using triphenylphosphine as axial ligand, afforded the corresponding penta-coordinated complex in a quantitative yield. X-ray crystallographic characterization of the cobalt complex of the corrole (**33**), showed only slight deviations from the planarity of the macroring, evidencing the steric relief due to the metal coordination [26].

When the bromination reaction of corrole was carried out on metal complexes, higher yields were obtained, probably because of the higher stability of the metal complexes of the octabromocorrole. Gross and coworkers prepared the



octabromo derivative (**34**), by reaction of the Mn(III)corrole with Br₂ in MeOH [50], while Ghosh *et al.* obtained the fully brominated product of a series of corroles after the reaction of their copper complexes with Br₂ in CHCl₃ [19].

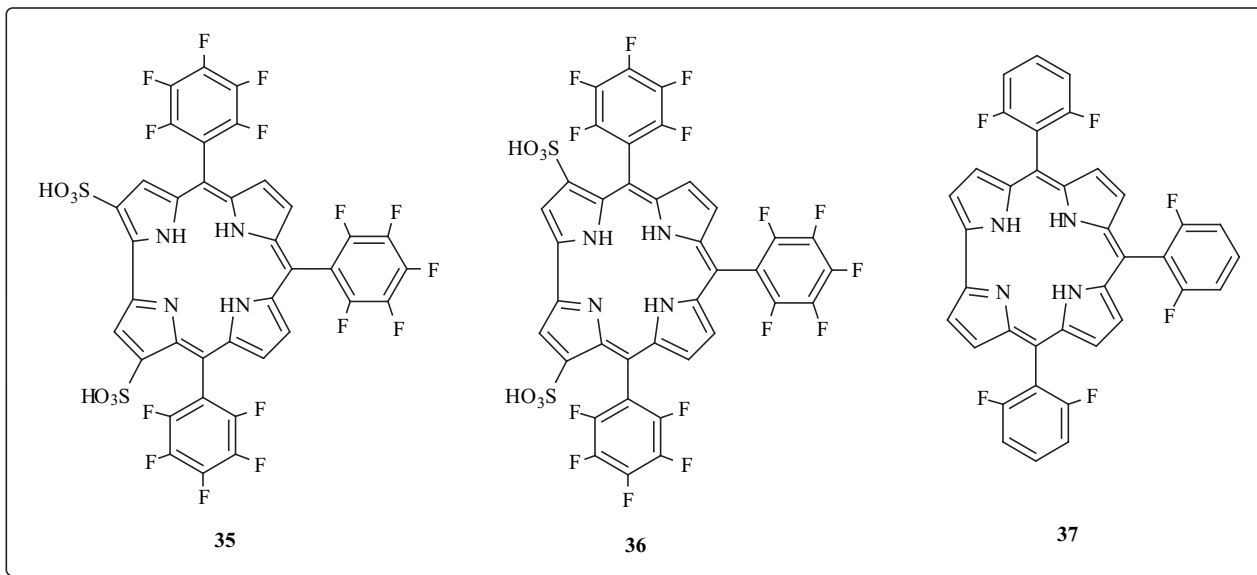
Chlorosulfonation

This reaction was carried out dissolving corrole (**2**) in chlorosulfonic acid (CSA), which served both as solvent and reagent. Following this approach, bis-substituted products were obtained and, among the different regioisomers, only two isomers were isolated, with the 2,17-

giving a mixture of different isomers, which was not separated [51].

Nitration

Nitration of Ga complex of corrole (**2**) was firstly carried out with the nitrating systems successfully used in the case of tetraarylporphyrins, but a complex mixture of polynitrated derivatives and a significant decomposition of the corrole ring was observed in these conditions, probably due to the strong oxidating character of the reagents [52]. However a successful approach was to use NaNO₂ in

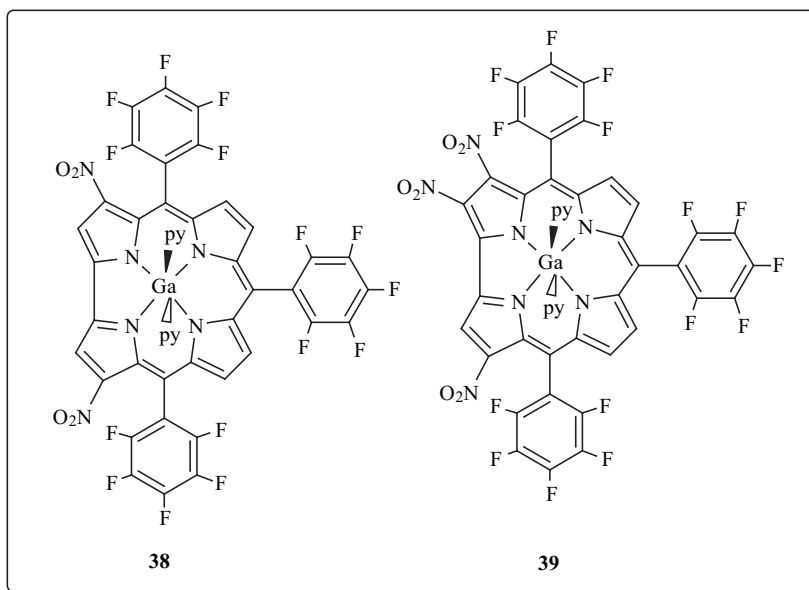


substituted derivative (**35**) as the predominant species to respect the 3,17-isomer (**36**) present in lower amount (94:6 molar ratio) [51,52].

It is worth mentioning that the reactivity of corrole with CSA is peculiar among tetrapyrrolic macrocycles, in that tetraarylporphyrins have been shown to react preferentially at the meso-aryl positions, while phthalocyanines give a complex mixtures of isomers [53].

It is also interesting to note that the Ga complex of (**2**) or corrole (**37**) showed a much lower selectivity than (**2**),

acetonitrile, with the addition of a small amount of a hexachloroantimonate salt, as one-electron oxidant [52]. In these conditions the reaction was selective and it was possible to obtain the mono-nitro, the 3,17-dinitro-**(38)** and the 2,3,17-trinitro derivative (**39**), depending on the amount of the nitrating agent used. In a first instance it can be thought, by analogy with porphyrin, that the role of the one-electron oxidant can be the formation of the π -cation radical of corrole. It must be pointed out, however, that the addition of the antimonate salt as the last reagent is essential for the



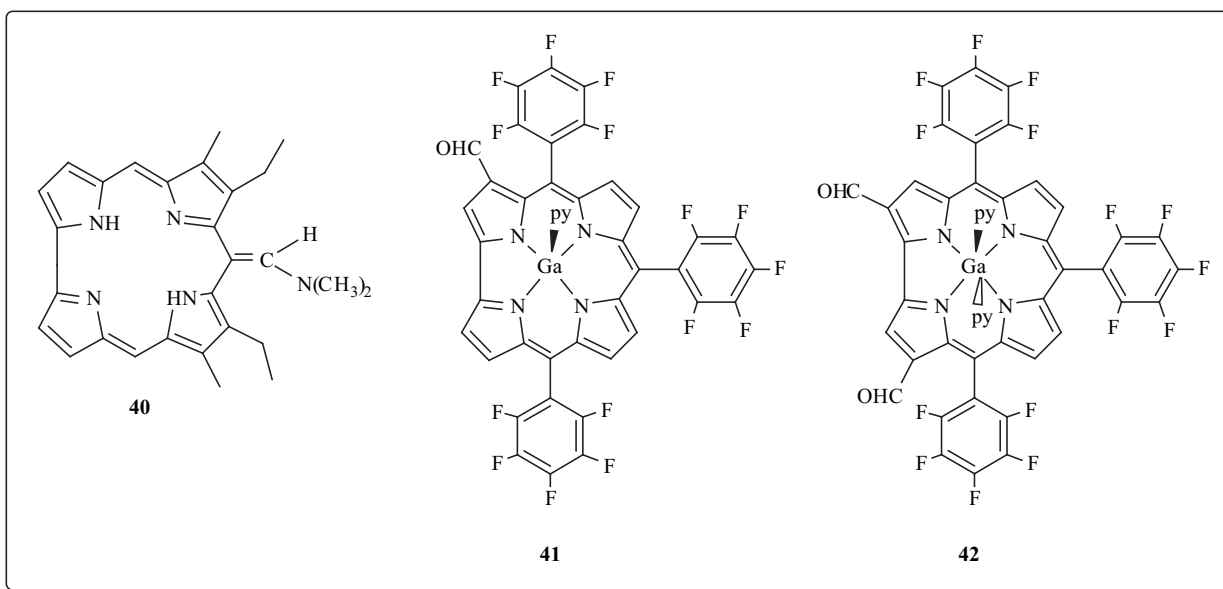
success of the reaction. This result seems to indicate a crucial role of the hexachloroantimonate in the oxidation of NO_2^- to NO_2 , which is considered the effective nitrating agent. This hypothesis can be supported by the success of the reaction also with the corresponding tin derivative, which does not form the π -cation radical and by the different regioselectivity observed in this reaction, compared to that commonly featured by other electrophilic substitutions.

Formylation

The reagent of choice for this reaction is the Vilsmeier reagent and this system has been used in the case of β -alkylcorroles, although in this case a dimethylamino derivative (**40**) is instead obtained in place of the expected product [54]. The reaction carried out on the Ga complex of corrole (**2**) afforded the 3-formyl corrole (**41**) or the 2,17-diformyl derivative (**42**) depending on the corrole:Vilsmeier

reagent molar ratio [52]. The selectivity was very high and only these regioisomers were obtained.

A peculiar behavior was observed when the reaction was carried out on the free base corrole (**4**) [55]. The expected 3-formyl derivative (**43**) was obtained along with a polar compound that became the major product in the presence of an excess of DMF. The X-ray crystallographic characterization of this product allowed us to identify this compound as an inner core ethane bridged derivative (**44**). This compound is unprecedented in the case of porphyrins and it is probably obtained from the attack of the Vilsmeier reagent to the inner core nitrogen atoms, followed by a complex series of reactions. A plausible reaction pathway is reported in (Fig. 15). Also in this case this peculiar reactivity can be probably inferred to its higher acidity with respect to that of porphyrins, biasing the formation of the corrole anion, which can drive the attack of the Vilsmeier reagent to the macrocyclic core.



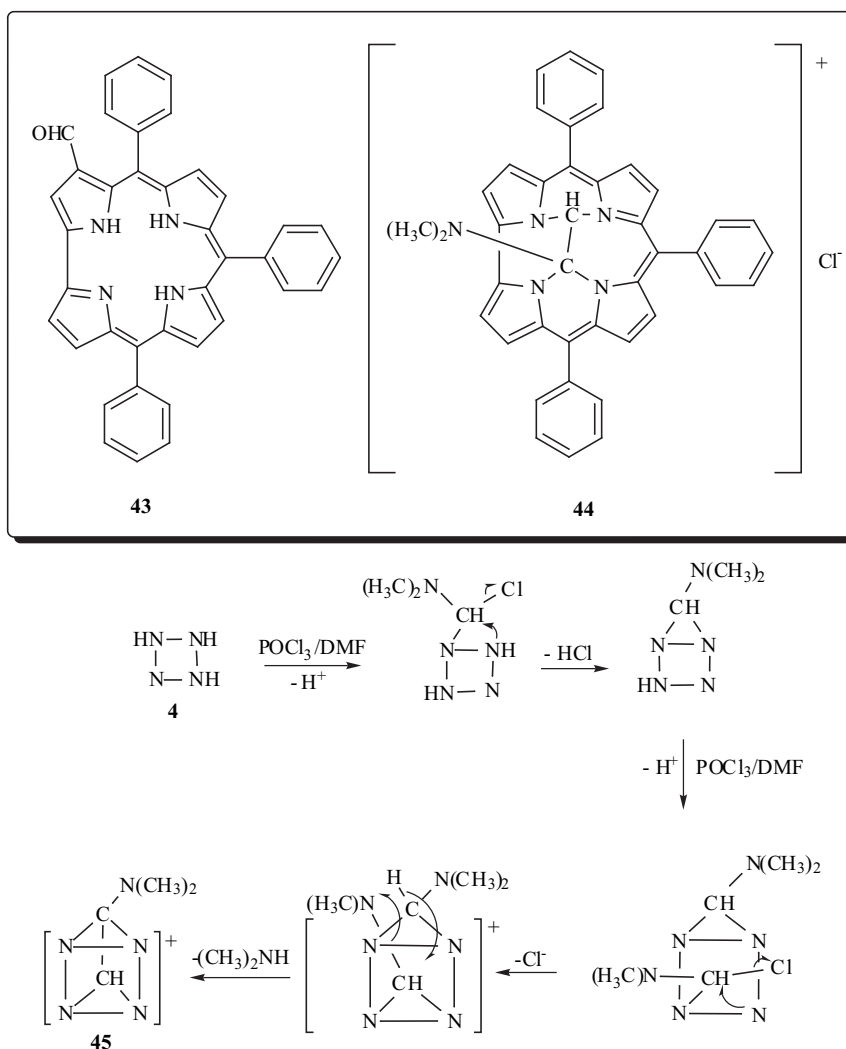
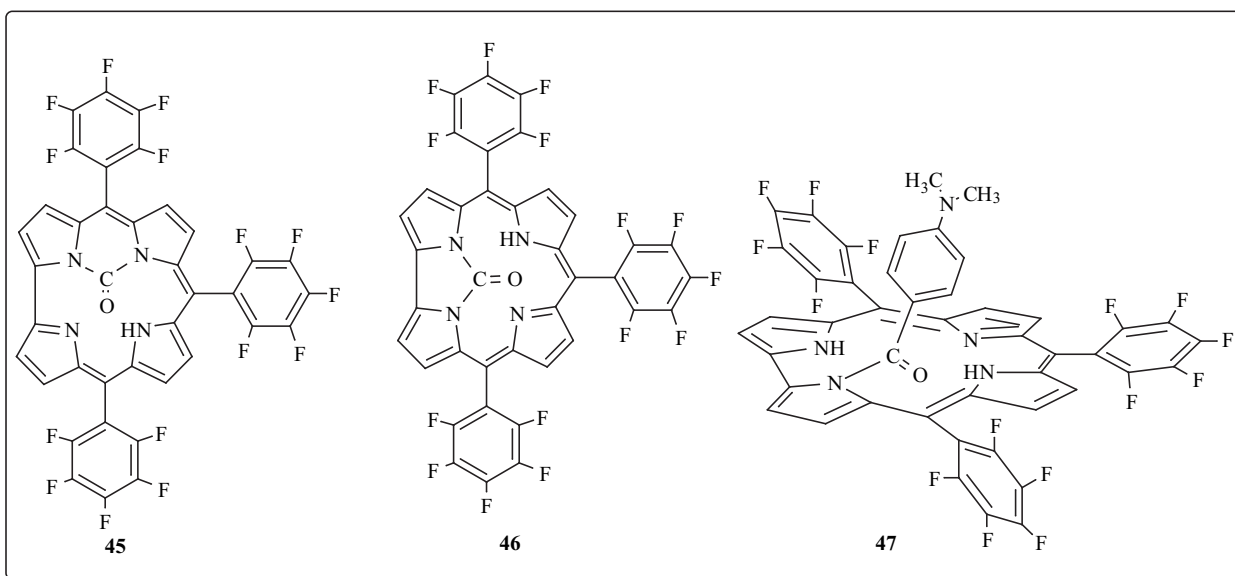


Fig. (15).

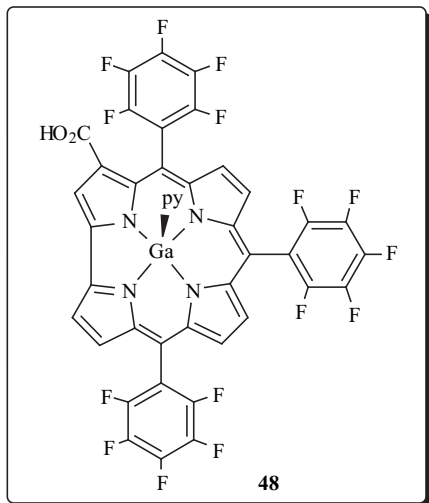
Carboxylation

This reaction is similar to the chlorosulfonation and was attempted in order to obtain corroles bearing carboxylic

groups at their peripheral positions [56]. The reagent is phosgene and the reaction was firstly attempted on the corrole free base (2). Also in this case the preferred reaction site was the corrole inner core and the product of the reaction



was the bridged carbamide (**45**). It is interesting to note that the other isomer (**46**) was not formed. In the presence of *N,N*-dimethylaniline as base, the corresponding *N*-acyl derivative (**47**) was obtained. As in the case of *N*-alkyl derivatives, also these products are chiral molecules.



When the reaction was carried out on the Ga complex, the reaction was successful and the monocarboxylated species (**48**) was obtained.

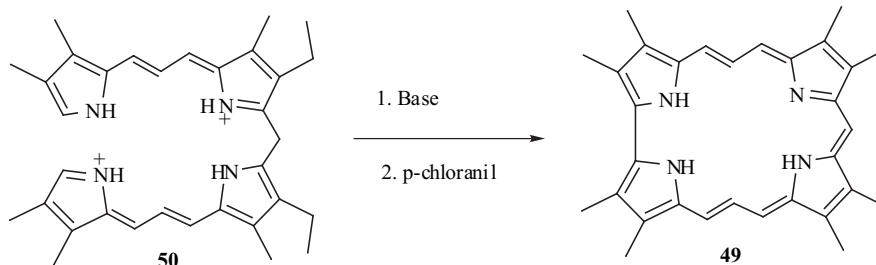


Fig. (16).

CORROLE RELATED MACROCYCLES, EXPANDED CORROLES, AND CORE-MODIFIED CORROLES

This part of the review deals with some “less familiar” aspect of the rich corrole chemistry. Within this context some general aspects of the synthesis and the properties of these modified macrocycles will be exploited.

Expanded Corroles

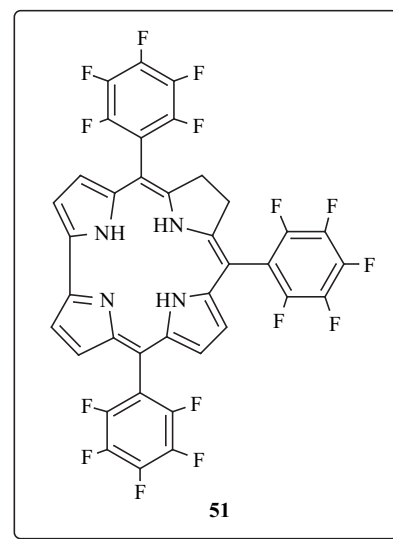
Expanded corrole such as (**49**) represent a bis-vinylous system of “progenitor” corrole. This class of macrocycles should feature interesting structural and physico-chemical properties, arising from the expanded aromatic annulenic structure.

The synthesis of (**49**) has been accomplished by base-catalyzed condensation of precursor (**50**), (Fig. 16), followed by oxidation, to give the target corrole in good yield [57]. Indeed, structural and spectroscopic studies showed the remarkable aromaticity of the π -ring system, being the “inner” protons strongly upfield shifted with respect to the “external” ones ($\Delta\delta \approx 20$ ppm). Interestingly, the electronic absorption spectra show the presence of strongly coupled

Soret bands indicating that the molecule exist as a dimeric species. The relative structure was unambiguously confirmed by X-ray analysis.

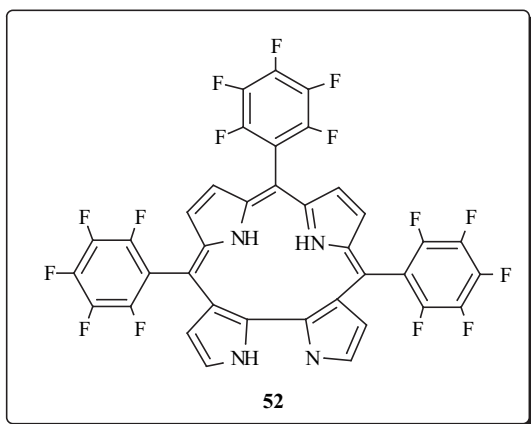
Corrolines

Corroline (**51**) can be considered as corrole-based chlorophyll analog. While the direct reduction of corrole with H_2 failed to give β -saturated derivatives [1], in this case the formally dihydrocorrole can be easily achieved by reaction of the parent macrocycle with *p*-toluenesulfonylhydrazide to give exclusively the isomer (**51**) [58]. The corresponding aluminum derivative is prepared by further reaction with $AlMe_3$. It is worth of noting that the presence of a non-transition metal (i.e. Al, Zn, or Mg) is a key factor in the photo-promoted biological function of the relative chlorophyll counterparts. The title macrocycles are strongly fluorescent, with quantum yield remarkably higher than that observed for the related porphyrin compounds. Remarkably, the insertion of either Al or Ga results in a further increase of emission intensities. This is ascribable to the increased rigidity of the carbocycle framework, with a consequent disfavoring of a non-radiative relaxation path such as the internal conversion (*IC*).



Corrorin

Corrorins (**52**) belong to the class of the “N-confused” corroles (NCC). By analogy with the N-confused porphyrins (NCP) in which one, or two, pyrrole rings point outward the macroring plane by swapping of α - or β - linkages, or both. Most of these isomers have been shown to be less stable



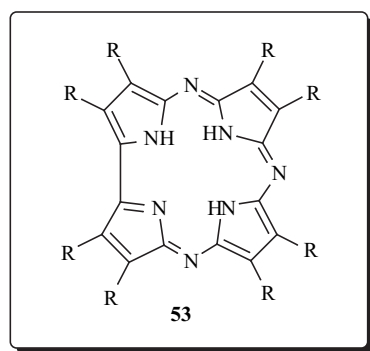
than the parent macrocycles. This lower stability, however, can be useful in the transformation of these structures into novel porphyrinoids. A noteworthy example has been provided recently by Furuta and co-workers [59]. The treatment of corrolins with SnCl_2 in refluxing benzene gave oxyindolophyrin, a new macrocycle bearing an oxo-substituted indolizine moiety and a dipyrromethene unit in the skeleton. Interestingly, this novel macrocycle features remarkable property as a fluoride receptor.

Corrolazine

Corrolazines (Cz) (**53**) are new members of corrole family. By analogy with other porphyrazines, they present a nitrogen atom replacing the *meso* carbon atom. These intriguing macrocycles have been prepared from the parent porphyrazine by an ingenious synthetic path, involving a “ring contraction” step [60]. Structural, electrochemical, and UV-visible spectroscopy studies, confirm the aromatic character of the title pyrrolic macrocycles. In particular, the red-shifted values of B and Q bands, suggests a depletion of electronic charge on the carbon skeleton. Density functional theory studies (DFT) strongly corroborate this hypothesis [61]. Indeed, the calculations indicate that Cz can be viewed as strongly electron-deficient analogs of corroles. This allows for an innocent electronic character, on stabilising high-valent P(V), Cu(III), Fe(V), or Mn(IV) metals.

Oxacorroles

Monooxacorroles (**54**) represent corrole derivatives in which a pyrrole ring is replaced by a furan moiety. This interesting class of molecules has been unprecedentedly



synthesized by α - α oxidative coupling reaction of 16-oxa tripyrrane (**55**) and dipyrromethane, upon acid-catalyzed cleavage of the dipyrromethane, (Fig. 17) [62]. $^1\text{H-NMR}$ and UV-visible spectroscopy studies attest the aromatic nature of the macrocycle. Interestingly, the B (Soret) and Q bands are hypsochromically shifted, compared to those of the parent corrole, by effect of the core oxygen atom. Surprisingly, the molecules show very strong emission efficiency, with strongly blue shifted spectral maxima. Single crystal X-ray structure indicates only small deviation of the inner-core heteroatoms from planarity. Electrochemical studies show easier oxidation and harder reduction compared to the relative porphyrin counterparts. The corresponding metalloderivatives have been easily prepared by classical reaction insertion [63]. The X-ray structures reveal that the macrocycle binds with the participation of all the heteroatoms Ni(II) Cu(II), and Co(II). Peculiarly, Rh(I) ion complexation to only one imino and one amino nitrogen of the macrocycle, retains the square planar geometry completed by two CO molecules. Cyclic voltammetry studies did not show the characteristic metal reduction, owing to the high energy of their LUMO.

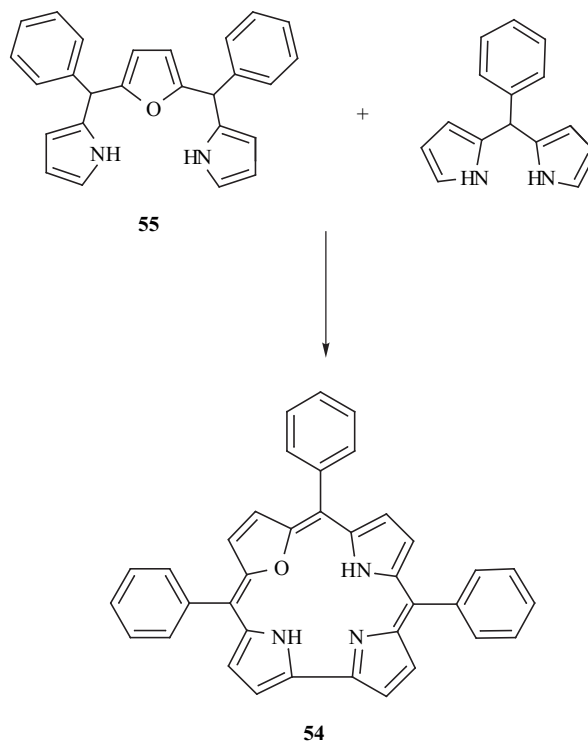


Fig. (17).

A rationalization of the synthetic strategy of monooxacorroles, has been further accomplished by some authors, as summarized in (Fig. 18). A “customized” synthesis, entailing a [2+2] condensation of dipyrromethanes, afforded different corroles bearing heteroatoms in a predesignated location [64]. A related strategy has been pursued for the preparation of monooxacorroles, by acid-catalyzed condensation of furylpyrromethanes and dipyrromethanes [65]. Monooxacorroles (**56**) with one *meso*-free carbon has been prepared by acid-catalyzed [3+1] condensation, (Fig. 19) [35]. The presence of the free *meso* position is susceptible to

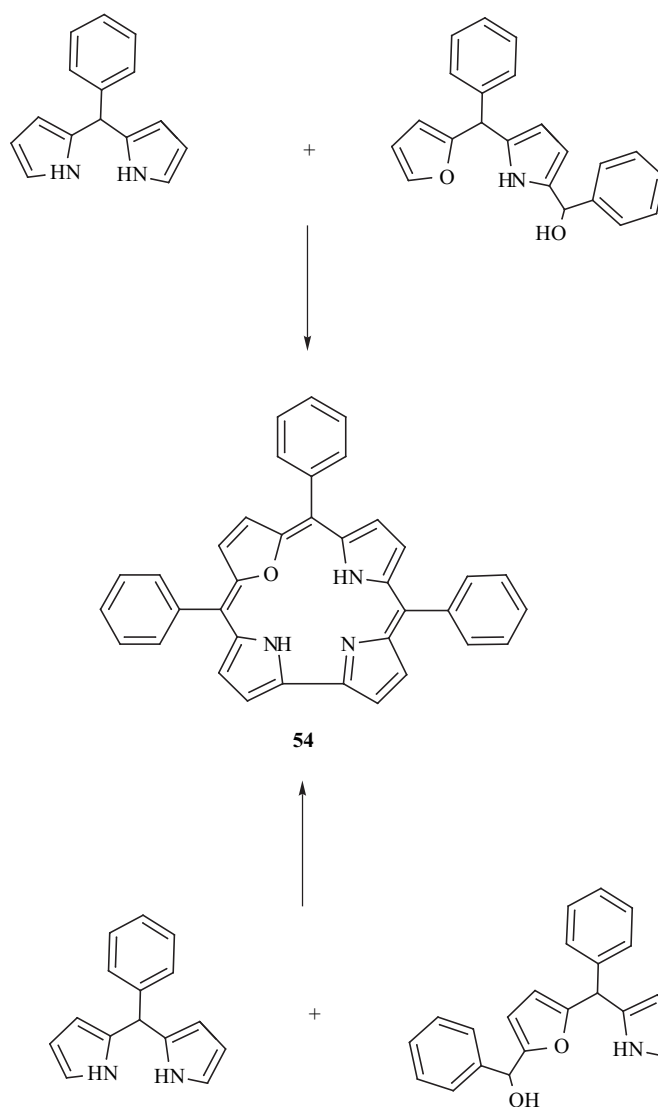


Fig. (18).

undergo further functionalization, owing to the high reactivity of such position.

Homo- and Heterobinuclear Corroles

Binuclear corroles are regarded as potential precursors of catalysts for the four-electron reduction of molecular oxygen. In this area, dicobalt cofacial bisporphyrins [66] have been found to be the most active species in the electrocatalyzed conversion of dioxygen to water. In particular, a very high affinity toward molecular oxygen was featured in mixed-valence Co(II)Co(III) bis-macrocycles. Face-to-face porphyrin-corrole systems, as well as its mixed-valence Co(II)Co(III) derivative, have been prepared by Guilard and co-workers [67] and spectroscopically characterised. Preliminary electrochemistry showed a different behaviour of the complex with respect to the monomeric Co(II)porphyrin and Co(III)corrole counterparts, indicating a promising influence between the linked macrocycles. Noteworthy, a related biscobalt μ -superoxo derivative has been prepared and characterized by electrochemistry, spectroelectrochemistry, and ESR spectroscopy [68]. The title complex has been

found to be exceptionally stable toward the replacement of the co-ordinated dioxygen by external ligands. Face-to-face, anthracenyl bridged, biscorrole have been prepared, as well as the related porphyrin-corrole dyad. These bismacrocycles present a peculiar reactivity upon metal insertion with Ni(II) salts. Two nickel bisoxocorrole, *cis* and *trans* isomers, are formed in the presence of air. In the hetero-dyad, only the corrole ring is oxidated. Conversely, in the case of biphenylene spacers homo- and hetero-dyads, only the expected bisnickel bisradical species are formed. No traces of oxoderivatives are detected. The different reactivity has been inferred to the longer distance of the macrocycles in the anthracenyl dyad (i.e. 4.9 vs 3.8 Å), which hinders the “electronic communication” between the two radical rings. More recently the preparation of these porphyrin-corrole and bis-corrole systems has been further improved by Guilard and co-workers [69].

Spirocorrole

A novel and intriguing example of dicorrole species (57) has been recently reported by Vogel and co-workers [70]. In

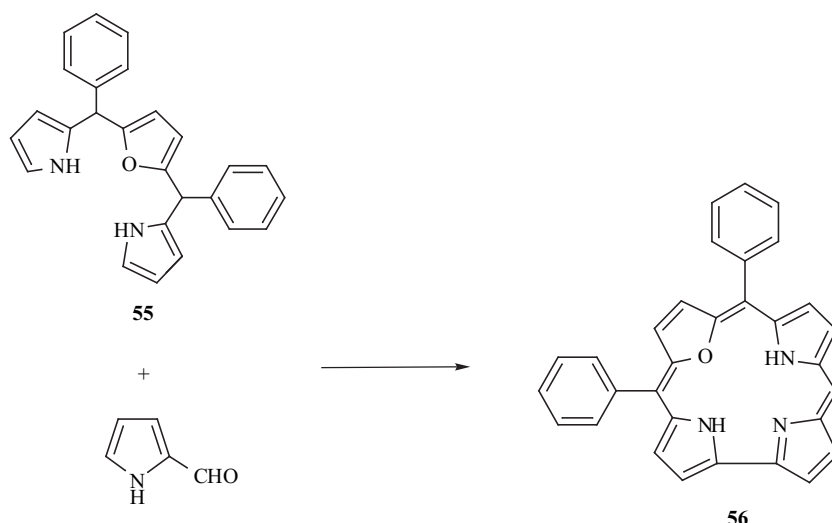
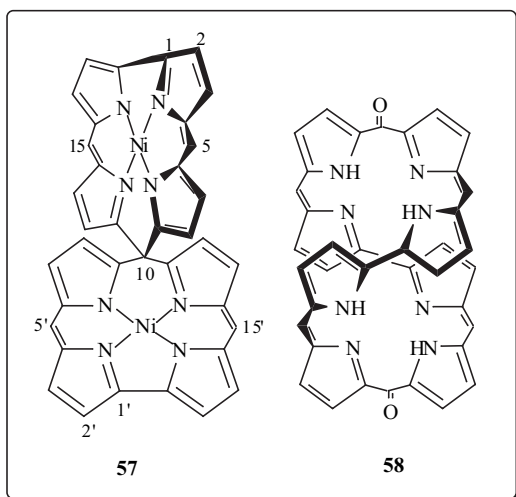


Fig. (19).

this so-called spirodicorrole the two macrocyclic moieties are linked through a spiro center at the 10 position and consequently they are present as isoforms. This species was firstly obtained as Ni complex by reaction of the figure-eight cyclooctapyrrole (**58**) with Ni(II) acetate in DMF. The exact route for the formation of (**57**) has not been completely elucidated, but it needs the elimination of a carbon dioxide unit.



Compound (**57**) is particularly appealing, because it might exhibit spiroconjugation [71]. To further study the effect of spiroconjugation on the spectroscopic properties of (**57**), Vogel and co-workers were also successful in the preparation of the Ni(II) complex of the isocorrole (**59**), the first of this kind of isomeric form of corrole, prepared by the

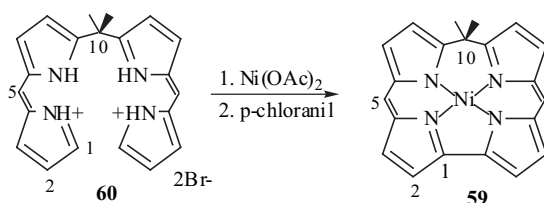


Fig. (20).

oxidative cyclization of the Ni complex of a,c-biladiene (**60**), (Fig. **20**) [72]. The comparison of the electronic spectra of (**57**) and (**59**) revealed bathochromic shifts and changes in the relative spectral intensities of the absorption bands, which can be attributed to the presence of spiroconjugation.

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