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# ADVANCES AND PERSPECTIVES OF PORPHYRIN SYNTHESIS

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Abstract - A review of the methods of porphyrin synthesis is given. The synthesis of linear polypyrrolic compounds, their transformations into porphyrins and side reaction have been considered.

## INTRODUCTION

The natural tetrapyrrolic macrocycles, including corrins, chlorins and porphyrins, (Fig. 1) are of central biological importance.

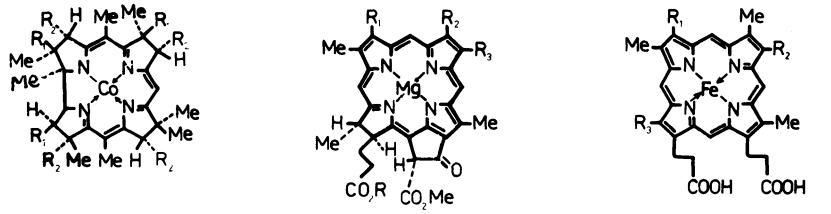



Fig. 1. The natural tetrapyrrolic macrocycles

Extensive studies of biological systems at the molecular level are connected with physico-chemical investigations of porphyrin containing proteins (hemoglobin, myoglobin and cytochromes). Metalloporphyrins, involved in the protein active site, take part in oxygen and electron transport. The advance in hemoprotein study is associated with development of porphyrin chemistry. Systematic investigations of porphyrins were started one hundred years ago, when F.Hoppe-Seyler prepared phylloporphyrin from chlorophyll and established structural similarity to heme (Ref. 1). Since the structure of natural porphyrins was determined and their syntheses have been accomplished. Much research on porphyrins and related compounds has been concentrated in elucidating their biological roles and photosynthesis. There has also been investigated the biosynthesis of natural tetrapyrrolic macrocycles. As it is now quite clear, protoheme, chlorophyll and cobyrinic acid, the precursor of vitamin $B_{12}$, are all derived from uroporphyrinogen III (Ref. 2). The important role of porphyrins in the development of geochemistry is well recognized (Ref. 3). Porphyrins have been utilized as biological markers for characterization the fossil porphyrins. They are detected in the meteorites (Ref. 4). Vanadyl and nickel porphyrins are found in crude oils and bitumens. The composition and the distribution of petroporphyrins are illustrative of the action and geochemical processes occurring in the geosphere (Ref. 5). Metalloporphyrins are also being studied for the search of new semiconductors, superconductors (Ref. 6), drugs (Ref. 7), catalysts (Ref. 8 & 9), solar energy transducers and dye laser materials. These data, taken as a whole, indicate that porphyrin syntheses have discovered possibilities in solving some important problems.
The first synthesis of porphyrins has been completed by Hans Fischer in 1920's (Ref. 10-12). Culminating in this research has been the total synthesis

of hemin, which confirmed the Kuster structure for porphyrins. The brilliant total syntheses of chlorophyll (Ref. 13 & 14) and vitamin $B_{12}$ (Ref. 15) accomplished by R.B.Woodward and colleagues are the greatest success in synthetic organic chemistry. At the same time the general methods of porphyrin synthesis have been developed. It became possible to prepare numerous porphyrins for physico-chemical study and practical application. A great number of research of porphyrins are summarized in fundamental monographs (Ref. 10-12, 16 & 17).

## GENERAL METHODS OF PORPHYRIN SYNTHESIS

There are several ways of cyclic porphyrin system formation (Fig. 2) from monopyrroles, dipyrrolic and tetrapyrrolic intermediates.

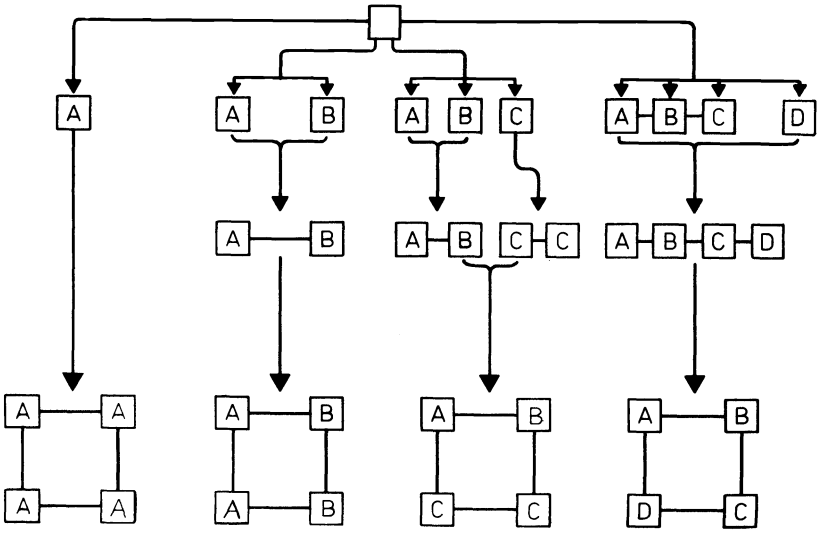



Fig. 2. Schematic diagram of porphyrin synthesis

The simplest route is a one-step synthesis of porphyrins from monopyrroles. This method has however not been used for the preparation of porphyrins with numerous various substituents. In addition a mixture of isomers may be obtained. On the other hand, this method has been very successful in the preparation of meso-substituted porphyrins (Ref. 18 & 19) (Fig. 3).

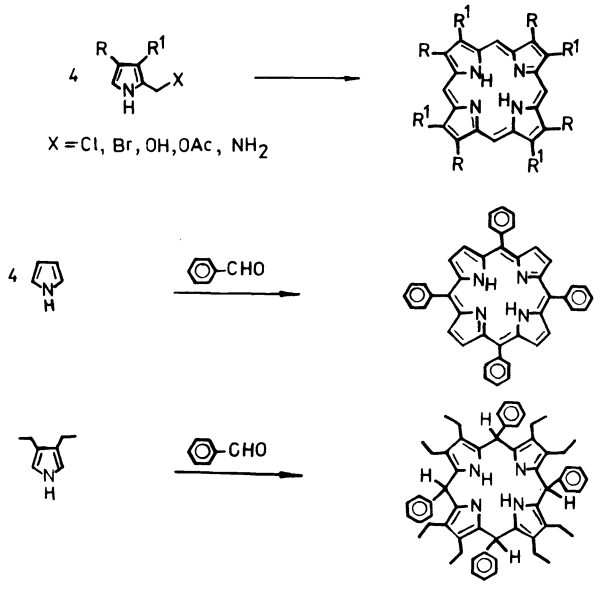



Fig. 3. Synthesis of porphyrins from monopyrroles

Another way supposes the formation of porphyrins from dipyrrolic intermediates (pyrromethanes, pyrromethenes and pyrroketones). The first synthesis of natural porphyrin was accomplished by H.Fischer(Ref. 11 & 12) from pyrromethenes (Fig. 4). The resulting yields were 0.2 or 20% .

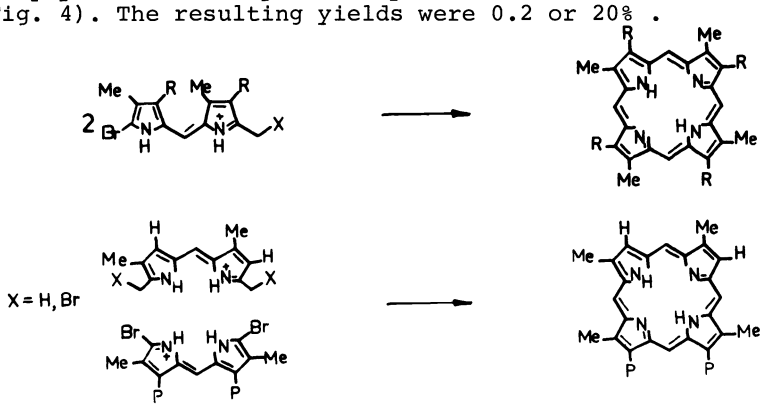



Fig. 4. Synthesis of porphyrins from pyrromethenes

The use of pyrromethanes as intermediates gave good results. Special mention should be made of the "dialdehyde synthesis", which was developed independently by R.Woodward (Ref. 13 & 14) and S.MacDonald (Ref. 20). The yields are high, up to 60%. This method is represented in Fig. 5.

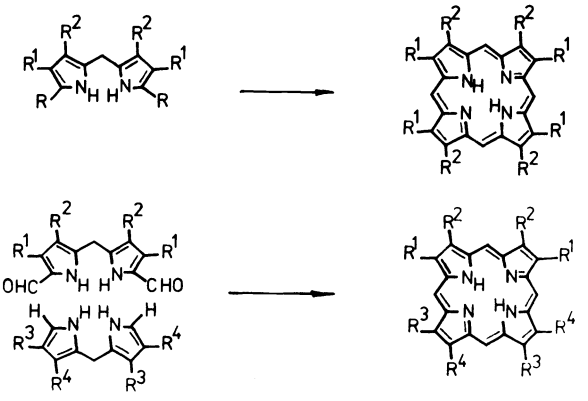


Fig. 5. Synthesis of porphyrins from pyrromethanes

Furthermore, the routes of porphyrin synthesis from tetrapyrrolic intermediates were proposed (Fig. 6). Linear tetrapyrroles were obtained by condensation of dipyrrole intermediates. Several specialized syntheses of porphyrins from bilanes (Ref. 21), oxobilanes (Ref. 22 & 23), bilenes (Ref. 24), biladienes (Ref. 25-28) have been devised. This route gave high yields of porphyrins with alkyl or substituted alkyl groups, however, the presence of electron-withdrawing substituents imposes certain difficulties.
The route of stepwise addition of the four pyrrole subunits with isolating tripyrrene and biladiene has been an important achievement. This method gave high yields and it is free of all symmetry restraints. We developed this method for the synthesis of porphyrins with electron-donating and electron-withdrawing substituents, as well as for the porphyrins of natural origin such as the protoporphyrin IX and the substituted cytodeuteroporphyrins.

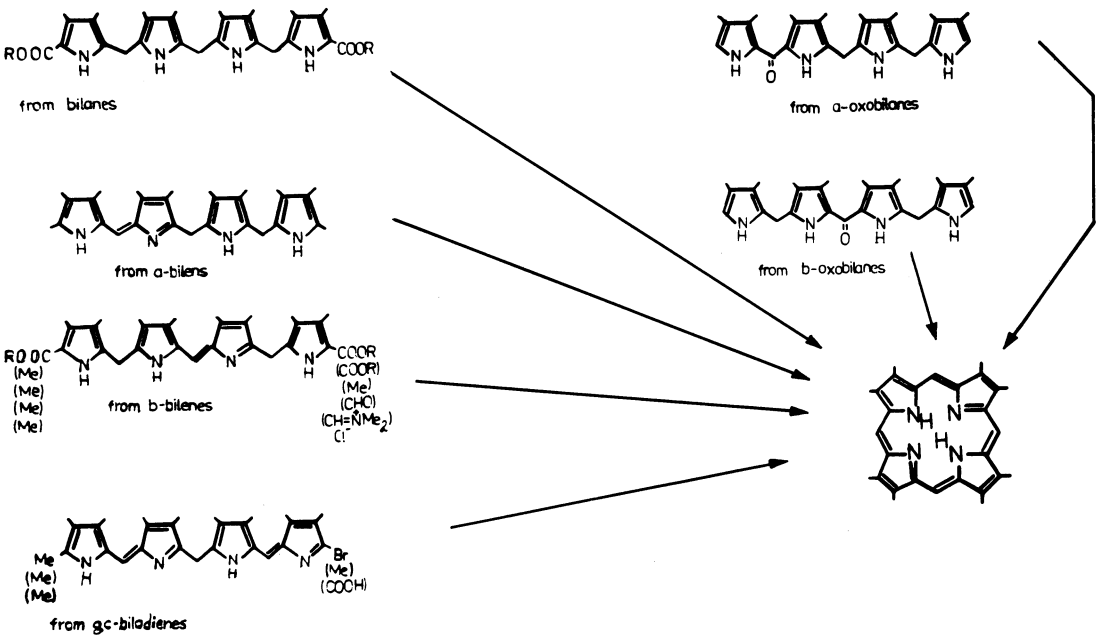



Fig. 6. Synthesis of porphyrins from linear tetrapyrrolic intermediates

## SYNTHESIS OF PROTOPORPHYRIN IX

Since protoporphyrin IX contains one "synthetic symmetry" element in the C and D rings, we could use in this case a facile variant of tripyrrene route (Ref. 29) from α,α'-diunsubstituted pyrromethane (Ref. 30) and substituted pyrrole bearing 2-bromoethyl group at the 3-position, which is to be transformed into vinyl group at a later stage (Ref. 31) (Fig. 7).

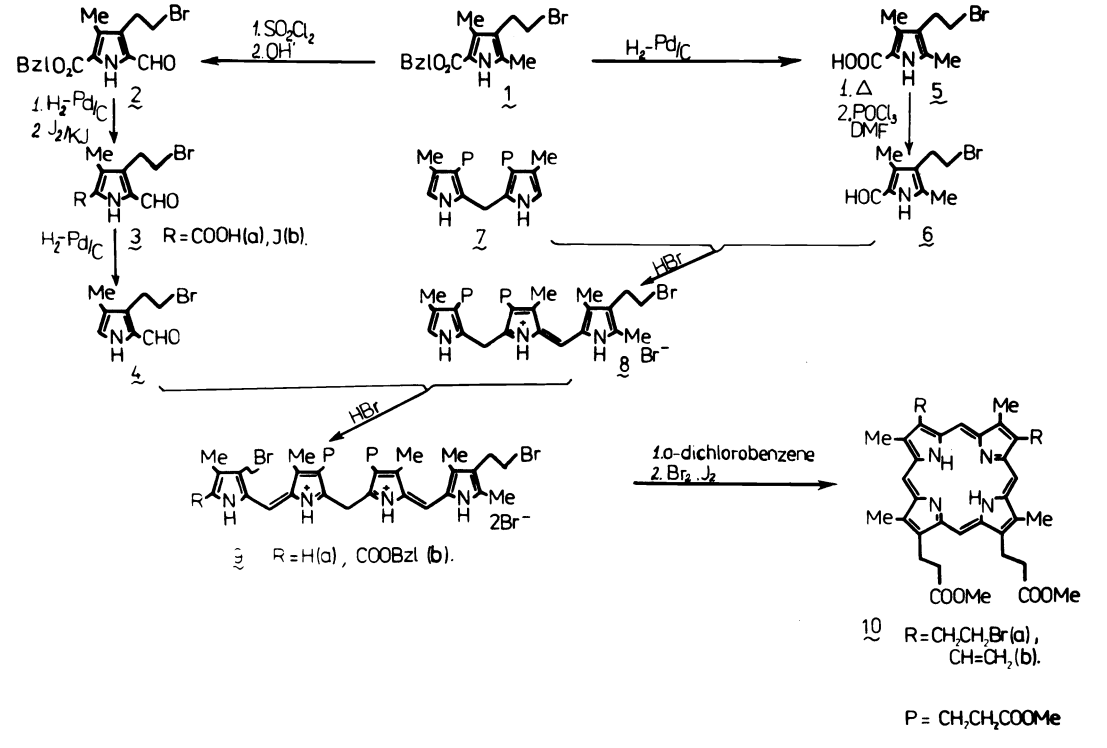
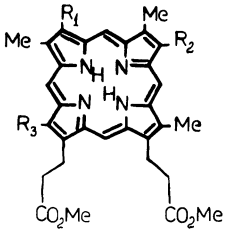


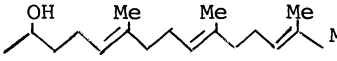

Fig. 7. Synthesis of protoporphyrin IX

α-Formylpyrrole (6) was prepared from pyrrole (1) by hydrogenolysis over palladized charcoal followed by Vilsmeier-Haack formylation of pyrrole (5). Pyrrole (1) was also converted into pyrrole (4). For this purpose pyrrole (1) was treated with sulfuryl chloride. Upon hydrolyzing α-formylpyrrole (2) was obtained, which was then hydrogenated over palladized charcoal to cleave the benzyl ester and to yield α-carboxy - pyrrole. The carboxy group was substituted for the iodine. α-Unsubstituted α-formylpyrrole (4) was prepared by the catalytic deiodination over palladium on charcoal. Condensation of α-formylpyrrole (6) and of α,α'-diunsubstituted pyrromethane (7) using a calculated amount of hydrogen bromide yielded tripyrrene (8) isolated as the hydrobromide in 90% yield. Subsequent treatment with α-formylpyrrole (4) gave the biladienes-*ac* dihydrobromide (9) in 88% yield. The oxidative cyclization of biladiene (9) in the presence of bromine and iodine in o-chlorobenzene gave porphyrin (10a) in 63% yield. Finally double dehydrobromination with aqueous alkali in pyridine gave porphyrin (10b). The crystalline protoporphyrin IX dimethyl ester was isolated in 92% yield. This compound was identical in all respects with the sample prepared from hemin. Thus, the overall yield from the pyrromethane is 46%.

## SYNTHESES OF SUBSTITUTED CYTODEUTEROPORPHYRINS

The advantage of the stepwise route may be demonstrated by the synthesis of porphyrins with a number of labile groups. Porphyrin a (1a) the prosthetic group of cytochrome oxidase, is such a compound.



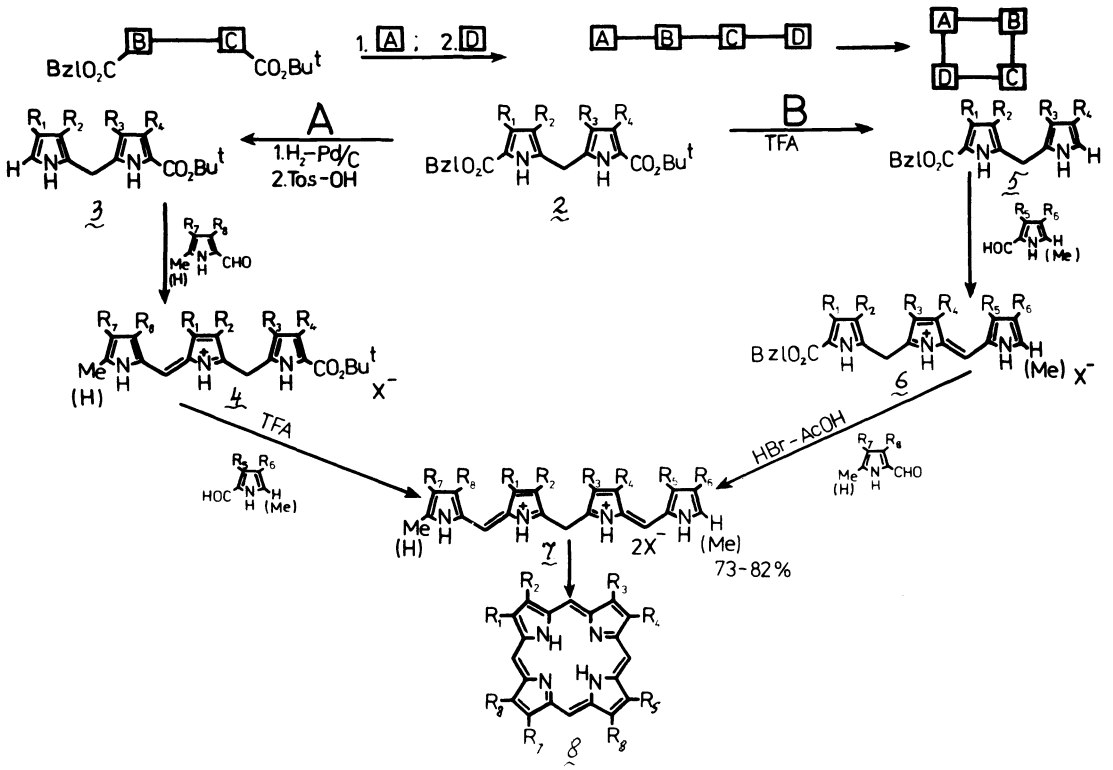

(1a) $R_1$ =  Me; $R_2$=-CH-$CH_2$; $R_3$=-CHO



(1b) $R_1$=$CO_2R$; $R_2$=$CH_2CH_2X$; $R_3$=H

R=Et, Bzl, Cl; X=Cl, Br, J, OAc, $N(C_2H_5)_2$

The presence of labile functional groups attached directly to the periphery of porphyrin ring system, such as vinyl, formyl and unsaturated terpenoid side chain, posed many problems. To avoid the difficulties it is necessary to introduce these functions in the form of a suitable precursor. Thus the porphyrin (1b) appeared to be a suitable intermediate. Based on the previous investigations (Ref. 32-42) we developed pathways of syntheses of a number of such porphyrins. The general scheme (Fig. 8) suggests utilizing the intermediates of pyrromethanes (2), including pyrroles B and C. Pyrromethane has at position 5 and 5' selective deprotecting groups: *tert*-butoxycarbonyl and benzyloxycarbonyl ones. Benzyl ester may be cleaved by hydrogenolysis, while *tert*-butyl ester is saponified with acid. There are two alternative ways (A and B) for the subsequent addition of formylpyrrole. In the first case (A) pyrromethane (2) was hydrogenated over palladized charcoal and the resulting pyrromethanecarboxylic acid was decarboxylated in the presence of p-toluene sulphonic acid. The α-unsubstituted pyrromethane was condensed with formylpyrrole to give the tripyrrene (4) isolated as the hydrobromide. Tripyrrene (4) was treated with trifluoroacetic acid followed by formylpyrrole. The biladiene-*ac* was obtained as the dihydrobromide. In the second case (B) pyrromethane (2) was saponified and decarboxylated by dissolution in trifluoroacetic acid. Condensation of α-unsubstituted pyrromethane (5) with formylpyrrole led to tripyrren hydrobromide (6). The removal of the benzyl protecting group was carried out by treating hydrogen bromide in acetic acid. Condensation of unprotecting tripyrren with formylpyrrole gave biladiene-*ac* (7). The yields of tripyrrenes and biladienes-*ac* are higher in the last case. Oxidative cyclization of biladiene-*ac* into porphyrins (8) was accomplished in o-dichlorobenzene or in dinitrobenzene in the presence bromine and iodine. The subsequents $R_2$, $R_4$ and $R_8$ were transformed into substituents of natural type.



$R_1=R_3=R_5=CH_3$; $R_6=R_7=CH_2CH_2COOCH_3$

(8a) $R_2=CO_2Bzl$; $R_4=CH_2CH_2Cl$; $R_8=H$

(8b) $R_2=CO_2Et$; $R_4=CH_2CH_2Br$; $R_8=H$

(8c) $R_2=CO_2Me$; $R_4=CH=CH_2$; $R_8=H$

(8d) $R_2=COCH_2CO_2C_2H_5$; $R_4=CH_2CH_2Br$; $R_8=H$

(8e) $R_2=CO_2Et$; $R_4=CH_2CH_2OAc$; $R_8=H$

(8f) $R_2=CO_2Et$; $R_4=CH_2CH_2N(C_2H_5)$; $R_8=H$

(8g) $R_2=CO_2Et$; $R_4=CH_2CH_2Br$; $R_8=CHO$

Fig. 8. Synthesis of unsymmetric porphyrins

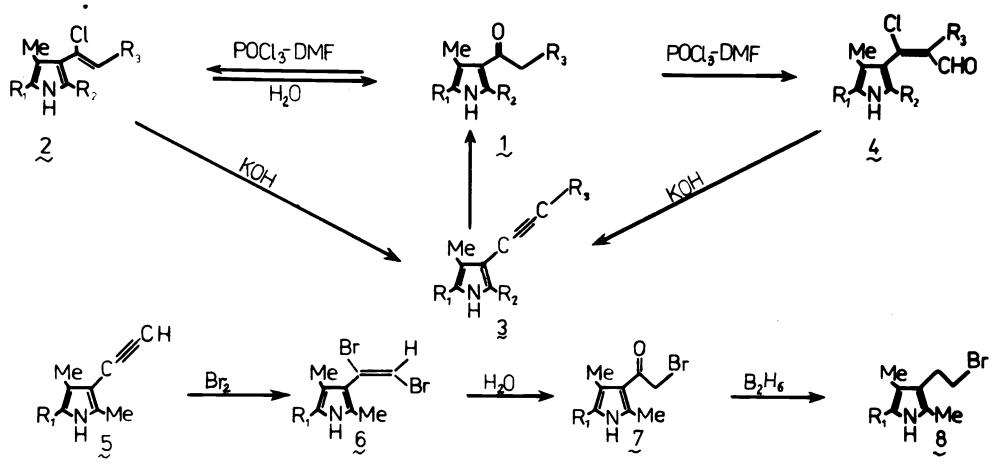
In the course of porphyrin synthesis and the transformation of substituents were found several previously unknown conversions which are of independent interest. Some of these reactions will be considered below.

## SYNTHESES OF PYRROLYLACETYLENES AND ETHYNYLPORPHYRINS

An unusual conversion of 3-acylpyrroles (1) into 3-pyrrolylacetylenes (3) (Ref. 43) takes place under the conditions of the Vilsmeier-Haack reaction (Fig. 9). At first the formation of 3(α-chloroalkenyl)-pyrroles (2) occurs, then those are dehydrochlorinated with aqueous alkali resulting in pyrrolylacetylene. In cases of 3-acyl-2,4-dimethyl-5-ethoxycarbonylpyrroles (1a-c, e) the yields are almost quantitative (Ref. 44-46) the presence of the ester group at the C-2-position (1d), however, slightly decreases the yield. The present reaction seems to be general for alkyl pyrrolyl ketones. Owing to the availability of the acylpyrroles (1) this reaction allows the preparation of pyrrolylacetylenes (3) of varying structures. The other side reaction encountered in the formylation of acylpyrroles led to α-chloro-β-formylvinylpyrroles (4). This reaction proceeds easily in the case of acetylpyrroles, more difficult with benzylpyrrylketone and is absent with long chained acylpyrroles. α-Chloro-β-formylpyrroles are converted into pyrrolylacetylenes by heating with aqueous alkali.

The bromination of pyrrolacetylene (5) resulted in dibromoderivative (6), which is easily hydrolyzed into bromoketones (7). The diborane reduction of (7) gave bromoethylpyrrole (8), which was used in the synthesis of vinyl-

porphyrins.




| 1–4 | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| a | H | H | H |
| b | CHO | H | H |
| c | H | Me | H |
| d | CHO | Me | H |
| e | Me | H | H |
| f | Me | CHO | H |
| g | $CO_2Et$ | Me | H |

| 1–4 | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| i | Me | $CO_2Et$ | H |
| j | $CO_2Et$ | Me | Me |
| k | $CO_2Et$ | Me | $C_4H_9$ |
| l | $CO_2Et$ | Me | $C_6H_{13}$ |
| m | $CO_2Et$ | Me | $[CH_2CH_2CH(CH_3)CH_2]_2H$ |
| n | $CO_2Et$ | Me | $C_6H_5$ |

Fig. 9. Synthesis of pyrrolylacetylenes

Pyrrolylacetylenes and dibromovinylpyrroles were utilized for porphyrin synthesis by tripyrrene route (Fig. 10).

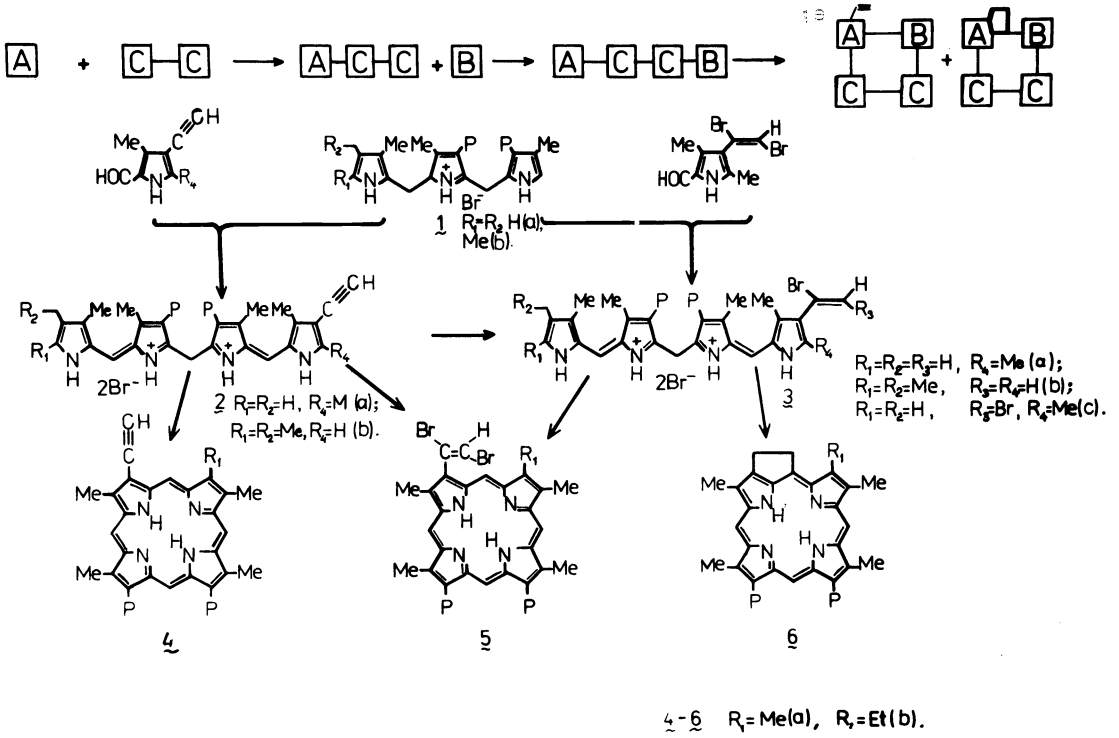



Fig. 10. Synthesis of ethynylporphyrins

Tripyrrene (1) converted into biladienes-*ac* (2 and 3) by treating suitable formylpyrrole. Porphyrins with ethynyl (4) and dibromovinyl (5) substituents al-

so with isocycle (6) were obtained. The yields were 46-48%.

## SYNTHESIS AND PROPERTIES OF 6(H)-PYRROLO[3,2f]INDOLIZINES

During the synthesis of 3-acetylpyrromethane (1), we found that the intramolecular condensation had taken place, which led to the pyrroloindolizine (2) (Ref. 47 & 48). The reaction proceeds well in such solvents as dimethylformamide, chloroform, benzene and alcohol. We further undertook a systematic study of these compounds (Ref. 49 & 50). A number of pyrroloindolizine was synthesized for this purpose (Fig. 11).

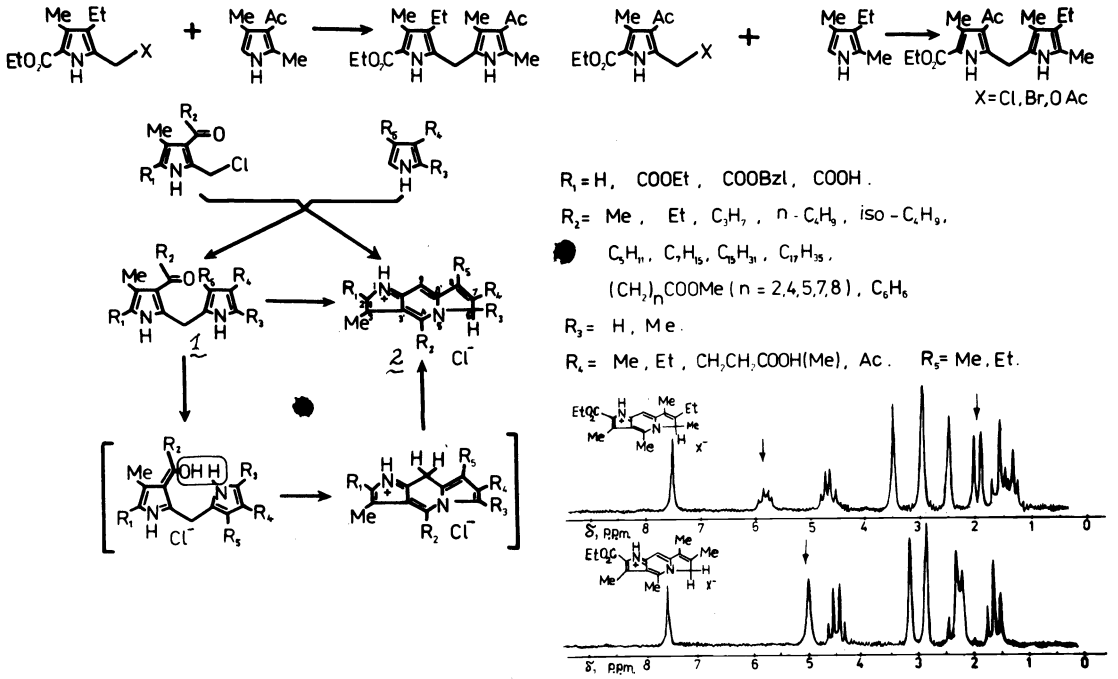



Fig. 11. Pyrroloindolizine and their proton NMR spectra at 60 MHz in $CDCl_3$

The yields of pyrroloindolizines depend on the type of the substituent and are 40-76%. It was established by means proton NMR spectra, that these compounds are 6(H)-pyrrolo[3,2f]indolizines (2). There were typical doublet with intensity of three proton units at 1.5-1.8 ppm and quartet of one proton unit at 5.3-5.6 ppm in proton NMR spectra. These signals absent in spectrum of compound with two atoms hydrogen at 6-position. The X-ray diffraction analysis of 3,6,7,8-tetramethyl-4-isobutyl-6(H)pyrrolo[3,2f]indolizine hydrochloride confirmed the suggested structure and showed that there are centre symmetric dimers with a system of hydrogen bonds including two anions of chlorine and two molecules water (Fig. 12).
The pyrroloindolizine base was isolated by the treatment of salt with alkali (Fig. 13). In proton NMR spectrum of the base (3) the signal of $N_{(1)}$-H disappeared and the signal $C_{(6)}$-H was displaced into the higher field. The base (3) was reconverted into salt by acidification. However, the free base is not stable and is converted into form (4). The rearrangement is easily detected by means of NMR spectrum. The doublet at 1.5-1.8 ppm and quartet at 5.3-5.7 ppm disappear and the $C_{(6)}$-Me singlet at 1.7-1.8 ppm and signal NH appear. Based on these data were arrived at the conclusion that proton transfer from $C_{(6)}$ to $N_{(1)}$ takes place. Compounds (4) is not reconverted into salt. The sodium boron hydride reduction of (2) gave the compound (5).
To elucidate the structure of pyrroloindolizine obtained from pyrromethene, for which the Australian scientists proposed the structure (9) (Ref. 51), we have carried out a synthesis of the compound (6). The conversion of (6)

into (2) and (5) and NMR data show that $CH_2$-group is at C-6.

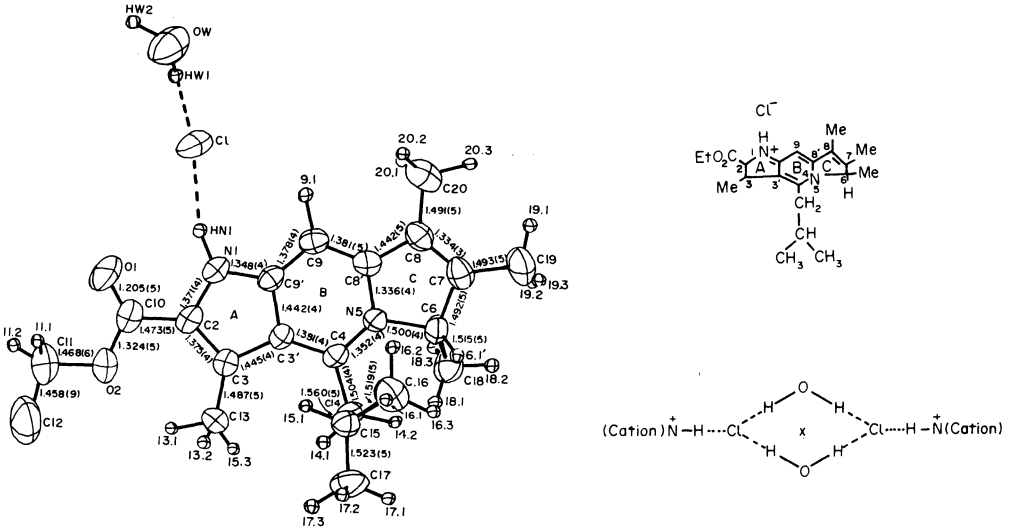


Fig. 12. X-Ray crystal structure of 3,6,7,8-tetramethyl-4-isobutyl-6(H)-pyrrolo[3,2f]indolizine hydrochloride

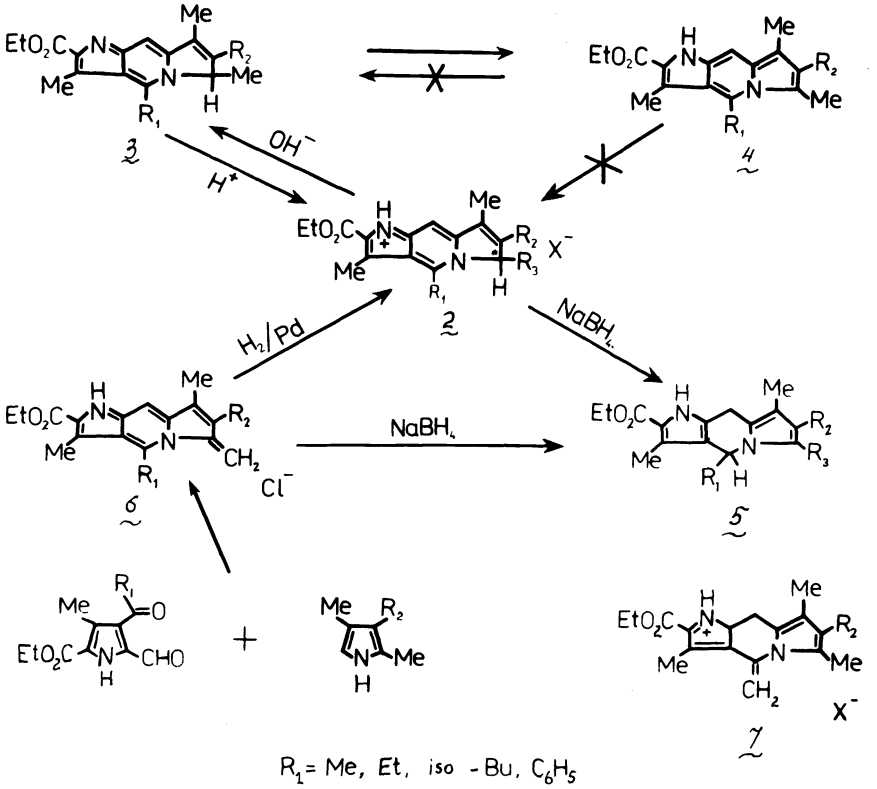
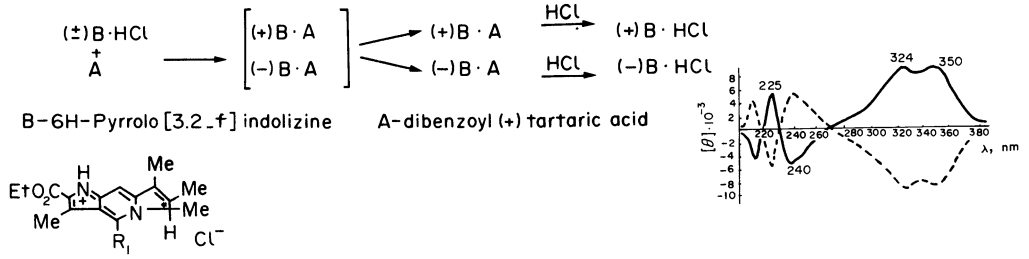



Fig. 13. Chemical conversion of pyrroloindolizines

We resolved four (±)-pyrroloindolizines into the enantiomers by dibenzoyl (+)-tartaric acid (Ref. 52). The CD spectra of the enantiomers show in Fig. 14.




| N° | Racemate | | Diastereoisomers | | Solvent | Enantiomers | |
|---|---|---|---|---|---|---|---|
| | $R_1$ | M.p. °C | M.p. °C | $[\alpha]_D^{20°}$ (C1, $CH_3OH$) | | M.p. °C | $[\alpha]_D^{20°}$ (C1, $CH_3OH$) |
| 1 | Me | 253 | 178-80<br>168-70 | −58°<br>−36 | $CH_3OH$<br>$HCON(CH_3)_2$ | 225<br>224-6 | +107°<br>−105° |
| 2 | $n-C_4H_9$ | 175 | 137<br>– | +9°<br>– | $CH_3OH$<br>$CH_3OH-(C_2H_5)_2O$ | 202<br>199-200 | +126°<br>−125° |
| 3 | $iso-C_4H_9$ | 215-7 | 148-9<br>141 | −95°<br>−91° | $CH_3OH$<br>$CH_3OH-(C_2H_5)_2O$ | 231-3<br>232 | +53.5°<br>−54° |
| 4 | $C_6H_5$ | 278-9 | 145-6<br>142-3 | +45°<br>−46° | $CH_3OH$<br>$CH_3OH-(C_2H_5)_2O$ | 284-6<br>285 | +136°<br>−135° |

Fig. 14. The scheme of resolution of pyrroloindolizine racemates into the enantiomers, their physical constants and CD spectra of enantiomers of (2)

## SYNTHESIS OF FORMYLPORPHYRINS

Formylporphyrins (4) were formed during oxidative cyclization of 2(18)-unsubstituted 1,19-dimethylbiladienes-*ac* (1 & 2), which proceeds in dimethylformamide in the presence of copper (II) chloride (Fig. 15) (Ref. 53).

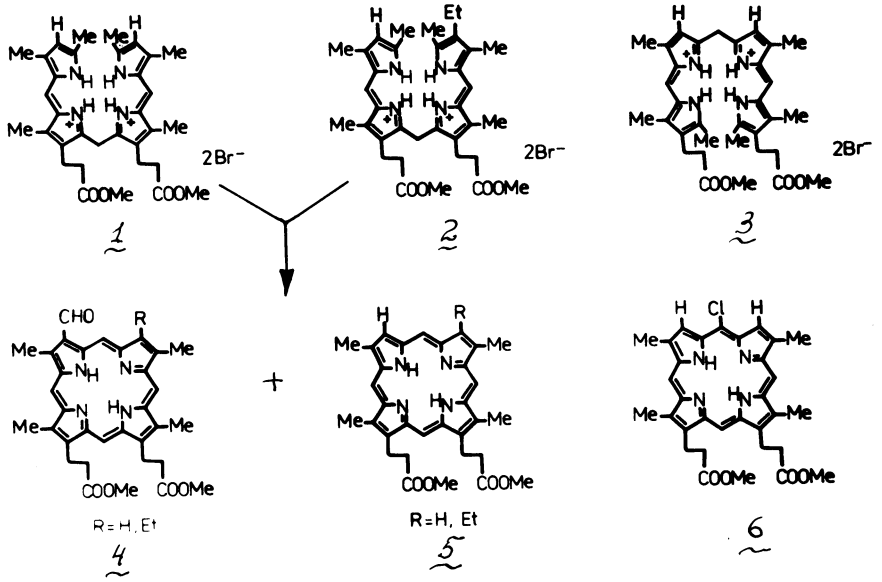
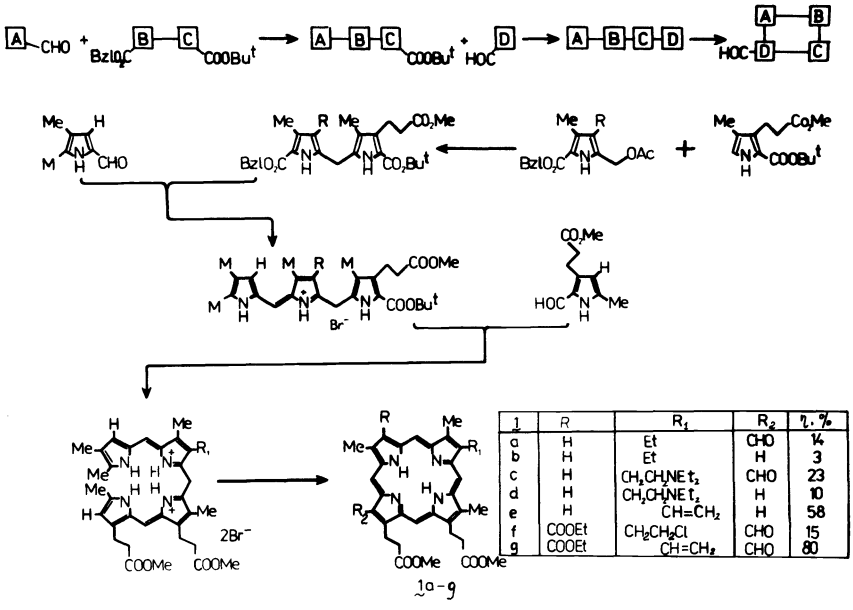



Fig. 15. Synthesis of formylporphyrins by oxidative cyclization of 1,19-dimethyl-2(18)-unsubstituted biladienes-*ac*

The formyl group may be formed from the biladiene methyl group as a result of oxidation and rearrangement or from dimethylformamide. To elucidate the real direction of this reaction we undertook the synthesis of biladiene-*ac* (3). Oxidative cyclization of (3) gave deuteroporphyrin III (5, R=H) and chloroporphyrin (6), formylporphyrin being absent. These data are in agreement with the first suggestion.
This reaction was used for the synthesis of 8-formylcytodeuteroporphyrins (Fig. 16).




| 1 | R | $R_1$ | $R_2$ | η, % |
|---|---|---|---|---|
| a | H | Et | CHO | 14 |
| b | H | Et | H | 3 |
| c | H | $CH_2CH_2NEt_2$ | CHO | 23 |
| d | H | $CH_2CH_2NEt_2$ | H | 10 |
| e | H | CH=$CH_2$ | H | 58 |
| f | COOEt | $CH_2CH_2Cl$ | CHO | 15 |
| g | COOEt | CH=$CH_2$ | CHO | 80 |

Fig. 16. Synthesis of formylcytodeuteroporphyrins

The synthesis was carried out by the same route. The yields of formylporphyrins are 14-23% (Ref. 40).

## CONCLUSION

From the above consideration it is evident that the most important problems of porphyrin synthesis have been solved.
Further research progress will be achieved on the route of using porphyrins as models of natural systems and their practical application.

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