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# Acid Catalyzed Isomerization and Thermal Rearrangement of Nickel Homoporphyrins

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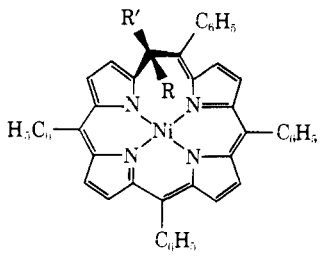
**Abstract:** Homoporphyrin derivatives possessing a two-carbon meso bridge lead, in acidic solution, to an equilibrium mixture via a reversible protonation-deprotonation of the meso carbons. The pair of homoporphyrins thus formed also show ring inversion. On heating in an inert solvent, homoporphyrins undergo rearrangement to cyclopropanic chlorines via electrocyclic ring closure followed by successive [1.17] C-C bond shifts. This behavior is similar to the cyclopropane migration known in the norcaradiene series.

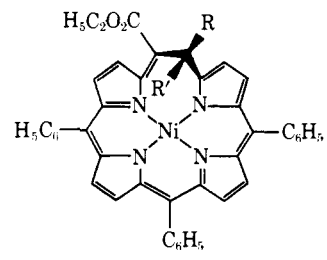
The preceding publication[1] described the synthesis and characterization of the new tetrapyrrolic macrocycle "homoporphyrin". We now report the isomerizations and skeletal rearrangements displayed by these compounds under the influence of dilute acid and heat.

## Results

When heated in an inert solvent, homoporphyrin derivatives **1** and **2** first led to the 6:4 equilibrium mixture described earlier.[1] On further heating, at temperatures greater than 160° in purified 1,2-dichlorobenzene, we observed the formation of esters **3** and **4** (relative proportions 41:29:23:7). The new homoporphyrins **3** and **4** could be separated at room temperature but reverted to the **1** to **4** mixture on heating in 1,2-dichlorobenzene.



1, (endo), R = $CO_2Et$; R′ = H
2, (exo), R = H; R′ = $CO_2Et$

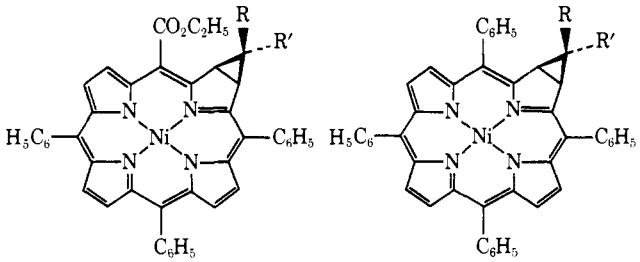


3, (endo), R = H; R′ = $C_6H_5$
4, (exo), R = $C_6H_5$; R′ = H

We later found that the same mixture was obtained on acid treatment at room temperature ($3 \times 10^{-2}$ *M* trifluoroacetic acid in dichloromethane).[2] The ratio of compounds **1**, **2**, **3**, and **4**, as determined by neutralization, isolation, and spectrophotometric measurements was found to be ca. 60:25:10:5, starting from any of the esters **1** to **4**. Reinvestigation of the reaction in boiling dichlorobenzene demonstrated the influence of the purity of the solvent. Compounds **3** and **4** were similar to **1** and **2** with regard to their visible spectra. They substantially differed in their infrared spectra (presence of a strongly conjugated ester) and NMR spectra; the phenyl group on the saturated carbon was considerably shielded for ester **3** (endo configuration) as was the corresponding endo proton of ester **4**. Mass spectra of **3** and **4** showed an important molecular ion (100%) and a relatively small amount of ester cleavage (29 and 47%). It is interesting to note that the opposite was observed for esters **1** and **2**[1] (loss of $CO_2Et$ amounts for 100% and molecular ion for 52 and 70%, respectively). These findings were in agreement with the preferential cleavage of a allylically activated C-C bond in **1** or **2**. Compounds **3** and **4** were stable at room temperature, although, when heated at ca. 80° in benzene, both led to the same equilibrium mixture (75:25 in favor of endo ester **3**). Kinetic measurements permitted an

inversion barrier to be measured (26.8 ± 0.2 kcal mol$^{-1}$). The height of this barrier was significantly lower (3 kcal mol$^{-1}$) than for the inversion **1** ⇄ **2**.

When heated to 213° (refluxing 1,2,4-trichlorobenzene), the equilibrium mixture of esters **1**, **2**, **3**, and **4** was transformed into a mixture of four components **5**, **6**, **7**, and **8**



**5**, (exo), R = H; R′ = $C_6H_5$; **6**, (endo), R = $C_6H_5$; R′ = H



**7**, (exo), R = H; R′ = $CO_2Et$; **8**, (endo), R = $CO_2Et$; R′ = H

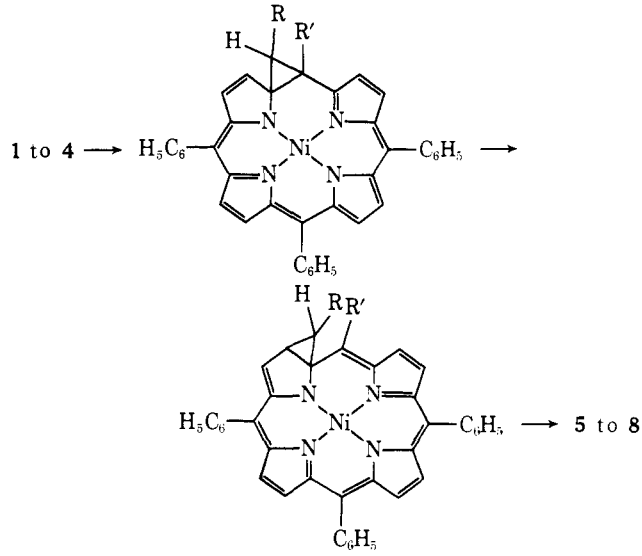
(ratio ca. 65:15:15:5). Identification of those cyclopropyl chlorines was made easier by comparing with the known compounds obtained from the reaction of ZnTPP with carbethoxycarbene.[3] We synthesized esters **7** and **8** by replacing zinc with nickel (acid catalyzed demetalation followed by treatment with nickel(II) acetylacetonate).

Esters **5** and **6** presented a conjugated ester (1705 cm$^{-1}$; KBr), and the NMR data were in agreement with the presence of a phenyl moiety on an $sp_3$ carbon atom. Chemical shifts and coupling constants of the cyclopropyl protons, as well as the large upfield shifts observed for the endo substituents (H or $C_6H_5$), confirmed the stereochemical attributions. The precise position of the ester of compounds **5** and **6** was demonstrated by the downfield shift of one cyclopropyl proton (at ring junction) and one pyrrolic proton nearest to the ester group (doublet at δ 8.78 and 8.68). Saponification of ester **5** in ethanolic KOH followed by thermal decarboxylation caused the latter signal to disappear in the aromatic multiplet and the cyclopropyl proton signal to almost collapse with that of the other ring junction proton.

## Discussion

The occurrence of an equilibrium between the two pairs of homoporphyrins **1**, **2**, and **3**, **4** in acidic solution at room temperature is explained by a reversible protonation of the two-carbon meso bridge. From each homoporphyrin the two possible protonated intermediates can be deprotonated to both isomers of the other pair and/or revert to the starting material. The appearance of an equilibrium was demonstrated by the fact that the same ratio of isomers from **1**, **2**, **3**, or **4** was always found. We do not envisage a ring inversion of the intermediate at room temperature since a barrier similar to that known for homoporphyrins (27 to 30 kcal mol$^{-1}$) would be expected for that inversion. At higher temperatures we envisage a catalytic effect of the glass to account for the slow formation of isomers **3** and **4** from **1** and **2**. The rate of formation of **3** and **4** was found to be strongly dependent on the purity of the solvent (distillation, storage over basic drying agents). We cannot completely exclude the earlier suggested [1.19] hydrogen shift[4] which is favored by the geometry of the molecule as determined by X-ray crystallography.[5] In view of the facile acid-catalyzed reaction, it is thought that the latter reaction could not be completely inhibited and would lead to a randomization of label in any double-labeling experiment.

The formation of the cyclopropanic chlorines **5** to **8** can be rationalized in term of successive [1.17] carbon–carbon bond migrations.[6] It is necessary to involve, in the first step, an electrocyclic ring closure of the starting homoporphyrin to the cyclopropanic isomers followed by [1.17] migration of a C–C bond to the nearest pyrrolic β carbon, then again a [1.17] migration to the next pyrrolic carbon. These migrations resemble the known cyclopropyl migration, reported in the norcaradiene series,[7] the whole process being thus homologous to the isomerization of cycloheptatrienes via norcaradienes. The major difference is that the homoporphyrin rearrangement stops at a cyclopropanic stage, the aromaticity of the porphyrin nucleus being rebuilt in the chlorines thus formed. If one assumes that the same mecha-



nism applies to both migrations, the stereochemistry of each of the cyclopropanic esters obtained should be identical with that of the starting homoporphyrin (endo → endo, exo → exo). Since starting homoporphyrins are in equilibrium, the observed distribution of products should reflect the relative velocity of migration of substituted epimeric carbons:

starting equilibrium

endo:exo = 64:36; (**1** + **2**):(**3** + **4**) = 70:30

products

endo:exo = 20:80; (**7** + **8**):(**5** + **6**) = 20:80

If the original assumption is correct, the reaction is therefore more rapid when the migrating carbon bears an exo substituent, and when the substituent is a phenyl rather than an ester group.

At this stage, it is interesting to go back to the comparison of corrole with cyclopentadiene and homoporphyrin with cycloheptatriene.[1] In our opinion, our results confirm the validity of the hypotheses: as cycloheptatrienes, homoporphyrins are nonplanar, flexible compounds; as cycloheptatrienes, they display skeletal rearrangements—formation of cyclopropanic isomers, homologous to norcaradienes, leading to ring contraction to the porphyrin series (in the case of the unstable octaalkylhomoporphyrins), or cyclopropane migration (in the case of bridge-disubstituted homoporphyrins). Preliminary results[8] indicate that the formation of stable cationic species, homologous to tropylium cation, is also possible.

## Experimental Section[9]

**Equilibrium between Esters 1, 2, 3, and 4.** (a) A solution of ester **1** or **2** in dichlorobenzene (distilled and stored over potassium carbonate) was heated to 180° for 0.5 hr. At this stage, the NMR spectrum showed the presence of esters **1**, **2**, **3**, and **4** (ratio 41:29:23:7). The same mixture could be obtained from **3** or **4**. Chromatographic separation of the components could be achieved using 100 g of silica gel for 100 mg of product and a gradient of benzene in cyclohexane. Esters **3** and **4** were crystallized from dichloromethane–methanol.

(b) Ester **1**, **2**, **3**, or **4** (20 mg) was added to a solution of trifluoroacetic acid ($3 \times 10^{-2}$ *M*) in dichloromethane (10 ml). The equilibrium was reached within ca. 6 hr. The solution was neutralized ($K_2CO_3$) and the product analyzed (alumina TLC separation, eluent toluene, absorptions measured in dichloromethane solution).

Ester **3** showed: mp 148–151°; ir $\nu_{max}$(KBr) 1685 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 1.11 (s, 1, exo H), 1.58 (t, 3, ester $CH_3$, 7 Hz), 4.70 (q, 2, ester $CH_2$, 7 Hz), 5.15 and 6.0 (2 m, 5, endo phenyl), 7.3–8.1 (m, 22, 3 phenyl + 7 pyrrolic H), 8.74 (d, 1, pyrrolic H, 5.5 Hz); visible ($CH_2Cl_2$) $\lambda_{max}$ 695 ($\epsilon$ 13,600), 600 (sh), 452 (68,000); mass spectrum *m/e* (%) 756 (100), 727 (6), 683 (29), 670 (17), 666 (10), 621 (5), 605 (17), 594 (8). Anal. ($C_{48}H_{34}N_4O_2Ni$) C, H, N.

Ester **4** showed: mp 188–190°; ir $\nu_{max}$(KBr) 1690 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 0.31 (s, 1, endo H); 1.06 (t, 3, ester $CH_3$, 7 Hz), 4.23 (q, 2, ester $CH_2$, 7 Hz), 7.10 (s, 5, exo phenyl), 7.5 (m, 19, 3 phenyl + 4 pyrrolic H), 8.08 (s, 2, pyrrolic H), 8.12 (d, 1, pyrrolic H, 4.5 Hz), 8.62 (d, 1, pyrrolic H, 5.5 Hz); visible ($CH_2Cl_2$) $\lambda_{max}$ 688 ($\epsilon$ 13,800), 595 (sh), 450 (72,400); mass spectrum *m/e* (%) 756 (100), 727 (6), 683 (47), 666 (12), 621 (4), 605 (22), 594 (6), 582 (5). Anal. ($C_{48}H_{34}N_4O_2Ni$) C, H, N.

**Preparation of Esters 5, 6, 7, and 8.** Ester **1** (or **2**, **3**, and **4**) was dissolved in 1,2,4-trichlorobenzene (ca. $5 \times 10^{-3}$ *M*) and the solution refluxed under nitrogen for 10 hr. The solvent was distilled under vacuum and the residue filtered through a silica gel column using benzene as eluent. Evaporation of the solvent gave a mixture of esters **5** to **8** (60%). At this stage, the ratio of the products was found by NMR to be ca. 65:15:15:5. Chromatography of the mixture (TLC silica gel, 0.5 atm of pressure, cyclohexane–benzene 1:1) gave **5** + **6** + **7** followed by pure **8**, crystallized from dichloromethane–methanol.

Chromatography of **5** + **6** + **7** (same conditions but benzene as eluent) gave pure **5** (crystallized from dichloromethane–methanol) followed by **6** + **7**.

Separation of the latter mixture was achieved using TLC alumina and benzene as eluent. Both esters were crystallized from dichloromethane–methanol.

Ester **5** showed: mp 167–169°; ir $\nu_{max}$(KBr) 1705 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 1.25 (t, 3, ester $CH_3$, 7 Hz), 1.84 (t, 1, endo H, 3 Hz), 4.02 (dd, 1, cyclopropyl H, 3 and 6 Hz), 4.51 (q, 2, ester $CH_2$, 7 Hz), 4.75 (dd, 1, cyclopropyl H, 3 and 6 Hz), 7.25 (s, 5, exo phenyl), 7.40–8.0 (m, 18, 3 phenyl + 3 pyrrolic H), 8.20 (d, 1, pyrrolic H, 5.5 Hz), 8.29 (d, 1, pyrrolic H, 5.5 Hz), 8.78 (d, 1, pyrrolic H, 5.0 Hz); visible ($CH_2Cl_2$) $\lambda_{max}$ 624 ($\epsilon$ 21,400), 585 (7400), 507 (6600), 418 (150,000); mass spectrum *m/e* (%) 756 (100), 727 (5), 710 (3), 683 (28), 668 (2), 651 (2), 621 (5), 605 (18), 594 (7); mol wt (calcd for $C_{48}H_{34}N_4O_2Ni$, 756.2035) 756.2044.

Ester **6** showed: mp 160–163°; ir $\nu_{max}$(KBr) 1705 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 1.50 (t, 3, ester $CH_3$, 7 Hz), 3.04 (t, 1, exo H, 8 Hz), 4.30 (dd, 1, cyclopropyl H, 6 and 8 Hz), 4.68 (q, 2, ester $CH_2$, 7 Hz), 5.04 (dd, 1, cyclopropyl H, 6 and 8 Hz), 6.35 and 6.65 (2m, 2 + 1, endo phenyl), 7.6–8.3 (m, 22, phenyl + 5 pyrrolic H), 8.68 (d, 1, pyrrolic H, 5.0 Hz); visible ($CH_2Cl_2$) $\lambda_{max}$ 618 ($\epsilon$ 17,800), 580 (5600), 505 (4600), 416 (120,000); mass spectrum *m/e* (%) 756 (100), 727 (5), 710 (3), 683 (28), 651 (3), 621 (4), 605 (15), 594 (5); mol wt (calcd for $C_{48}H_{34}N_4O_2Ni$, 756.2035) 756.2050.

Ester **7** showed: mp 287–288°; ir $\nu_{max}$(KBr) 1720 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 1.18 (t, 1, endo H, 2.5 Hz), 1.24 (t, 3, ester $CH_3$, 7 Hz), 4.20 (q, 2, ester $CH_2$, 7 Hz), 4.36 (d, 2, cyclopropyl H, 2.5 Hz), 7.7–8.10 (m, 20, phenyl), 8.12 (d, 2, pyrrolic H, 5 Hz), 8.29 (s, 2, pyrrolic H), 8.41 (d, 2, pyrrolic H, 5 Hz); visible ($CH_2Cl_2$) $\lambda_{max}$ 610 ($\epsilon$ 29,200), 575 (7900), 505 (6750), 417 (194,000); mass spectrum *m/e* (%) 756 (100), 728 (2), 683 (48), 605 (19); mol wt (calcd for $C_{48}H_{34}N_4O_2Ni$, 756.2035) 756.2050.

Ester **8** showed: mp 297–298°; ir $\nu_{max}$(KBr) 1730 $cm^{-1}$; $^1H$ ($CDCl_3$) 0.0 (t, 3, ester $CH_3$, 7 Hz), 2.41 (t, 1, exo H, 8 Hz), 3.20 (q, 2, ester $CH_2$, 7 Hz), 4.25 (d, 2, cyclopropyl H, 8 Hz), 7.5–7.9 (m, 20, phenyl), 8.08 (d, 2, pyrrolic H, 5 Hz), 8.24 (s, 2, pyrrolic H), 8.35 (d, 2, pyrrolic H, 5 Hz); visible ($CH_2Cl_2$) $\lambda_{max}$ 610 ($\epsilon$ 28,400), 573 (7900), 505 (6650), 416 (184,000); mass spectrum *m/e* (%) 756 (100), 728 (2), 683 (83), 605 (22); mol wt (calcd for $C_{48}H_{34}N_4O_2Ni$, 756.2035) 756.2051.

**Preparation of Esters 7 and 8.** The corresponding zinc complexes were prepared according to ref 3. Treatment of a dichloromethane solution of these complexes with concentrated HCl followed by neutralization with aqueous ammonium carbonate gave the endo and exo free bases which were crystallized from dichloromethane–methanol (melting points are >300°).

Endo base showed: ir $\nu_{max}$(KBr) 1735 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 0.02 (t, 3, ester $CH_3$, 7 Hz), 2.70 (t, 1, exo H, 8 Hz), 3.08 (q, 2, ester $CH_2$, 7 Hz), 4.36 (d, 2, cyclopropyl H, 8 Hz), 7.7–8.15 (m, 20, phenyl), 8.38 (d, 2, pyrrolic H, 5 Hz), 8.45 (s, 2, pyrrolic H), 8.63 (d, 2, pyrrolic H, 5 Hz); visible ($C_6H_6$) $\lambda_{max}$ 655 ($\epsilon$ 27,500), 600 (6200), 548 (12,400), 519 (16,800), 420 (211,000); mass spectrum *m/e* (%) 700 (76), 681 (9), 627 (100). Anal. ($C_{48}H_{36}N_4O_2$) C, H, N.

Exo base: ir $\nu_{max}$(KBr) 1720 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 1.28 (t, 3, ester $CH_3$, 7 Hz), 1.59 (t, 1, endo, H, 2.5 Hz), 4.24 (q, 2, ester $CH_2$, 7 Hz), 4.45 (d, 2, cyclopropyl H, 2.5 Hz), 7.7–8.1 (m, 20, phenyl), 8.41 (d, 2, pyrrolic H, 5 Hz), 8.45 (s, 2, pyrrolic H), 8.65 (d, 2, pyrrolic H, 5 Hz); visible ($C_6H_6$) $\lambda_{max}$ 656 ($\epsilon$ 26,800), 602 (6200), 549 (10,500), 520 (17,200), 421 (225,000); mass spectrum *m/e* (%) 700 (76), 627 (100). Anal. ($C_{48}H_{36}N_4O_2$) H, N; C: calcd, 82.26; found, 81.74.

The corresponding nickel complexes were prepared by refluxing a solution of the base and nickel(II) acetylacetonate in dichloroethane for 48 hr. The solvent was removed and the residue eluted with benzene from a short silica gel column. The products were crystallized from dichloromethane–methanol and found to be identical with esters **7** and **8** ($^1H$ NMR, visible spectrum, chromatographic behavior).

**Cleavage of the Ester Group of Compound 5.** A solution of ester **5** (35 mg) in ethanol (10 ml) was treated with sodium hydroxide (200 mg) and refluxed for 5.5 hr. The solution was cooled, acidified with dilute aqueous HCl, and extracted with chloroform. The organic phase was washed four times with water, dried over sodium sulfate, and concentrated. The residue was crystallized from dichloromethane–methanol and washed with pentane. The crystals (32 mg) showed: ir $\nu_{max}$(KBr) 1655–1710 $cm^{-1}$ (broad); visible spectrum ($CH_2Cl_2$) $\lambda_{max}$ 626 ($\epsilon$ 20,400), 585 (sh, 7350), 508 (6800), 418 (153,000).

These crystals (28.5 mg) were heated to 200° for 0.6 hr. The product was chromatographed on alumina (20 g), eluted with cyclohexane–benzene 1:1, and crystallized from dichloromethane–methanol to yield violet crystals (20 mg) showing mp >300°; ir (KBr) no more C=O absorption; $^1H$ NMR ($CDCl_3$) 1.54 (t, 1, endo H, 2.5 Hz), 4.22 (m, 2, cyclopropyl H), 7.0–8.5 (m, 27, all pyrrolic and phenyl H); visible ($CH_2Cl_2$) $\lambda_{max}$ 615 ($\epsilon$ 28,400), 575 (7300), 502 (7300), 414 (175,000); mass spectrum *m/e* (%) 684 (100), 607 (24), 594 (8), 529 (7), 516 (3). Anal. ($C_{45}H_{30}N_4Ni$) C, H, N.

## References and Notes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(2) More acidic media led to demetalation of the nickel complexes. Work on the kinetic data for the isomerization and the characterization and reactions of the free bases is in progress.

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(6) We can exclude a dissociative mechanism involving a retrocarbenic reaction from a cyclopropanic intermediate, thus forming phenyl- or carbethoxycarbene. The low reactivity of metalloporphyrins toward carbene addition and the low concentration of the solution should allow us to isolate NiTPP in a substantial yield. This was not observed.

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(8) H. J. Callot, Th. Tschamber, and E. Schaeffer, work in progress.

(9) All melting points are uncorrected. Infrared and visible spectra were recorded on a Perkin-Elmer 457 and a Cary 118 spectrophotometers, respectively. $^1H$ NMR spectra were recorded on a Perkin-Elmer Model R 12. The chemical shifts are expressed in $\delta$ values (ppm) relative to tetramethylsilane internal standard and the coupling constants in hertz (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet). Mass spectra (70 eV) were recorded on a LKB 9000 mass spectrometer equipped with a direct inlet system and a Thompson-Houston THN 208 mass spectrometer (high resolution). Combustion analyses were performed by the Service Central de Microanalyse du CNRS, Division de Strasbourg. Separation and purification of the products were obtained using Merck silica gel 60 (70–230 mesh) or Merck standardized alumina (II–III).