Rearrangement of N-Substituted Porphyrins. Preparation and Structure of Homoporphyrins

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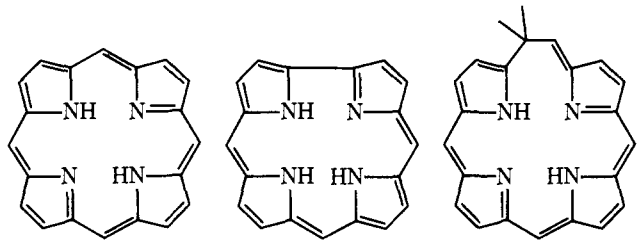
Abstract: The preparation of "homoporphyrin" derivatives—porphyrins possessing a two-carbon meso bridge—is reported. These new tetrapyrrolic macrocycles were obtained from N-CH_2CO_2Et-porphyrins via nickel(II) salt catalyzed rearrangement. The reaction involves formation of intermediate nickel(II) cationic complex and cyclization to an aziridine fused to a pyrrole, followed by migration of a C-C bond to the meso position and electrocyclic ring-opening of the resultant cyclopropanic intermediate. The stereospecificity of this rearrangement is high. These homoporphyrins derivatives show a ring inversion at 110° with a barrier of *ca.* 30 kcal mol^{-1}.

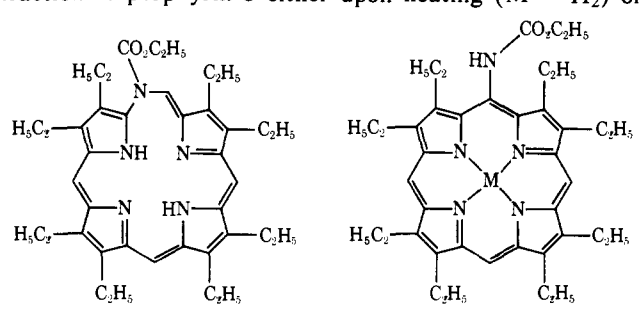
The aromaticity of the porphin nucleus **1** has been well established both by its chemical and physical properties.[1-3] The macrocyclic conjugated system can thus be considered in some ways as homologous to benzene, as are [4*n* + 2] annulenes.[4]

The idea of comparing porphyrins lacking a bridge carbon, namely corroles (derivatives of **2**), with cyclopentadiene has been well illustrated by the ease of formation of anions from corroles or metallocorroles.[1,5,6] In order to complete the comparison, it only remained to prepare and study the chemical behavior of the "homoporphyrin" system **3**. This new tetrapyrrolic macrocycle should display



1 **2** **3**

chemical properties related, to a certain extent, to those of cycloheptatriene and the corresponding heterocyclic systems, as azepine. At the time we obtained our results on homoporphyrins chemistry, the only known compounds possessing the required skeleton was the azahomoporphyrin **4** prepared by Grigg.[7] Although well characterized, Grigg's compound was found to be unstable, undergoing ring contraction to porphyrin **5** either upon heating (M = H_2) or



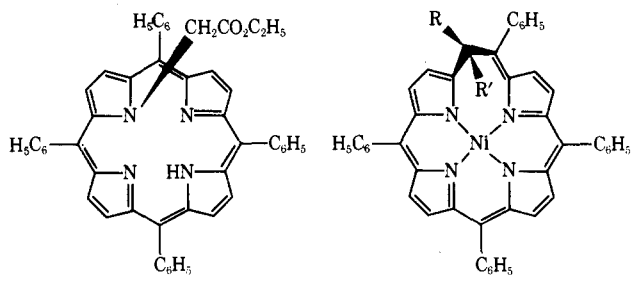
4 **5**, M = H_2, Zn, Cu

treatment with a divalent cation (M = Zn, Cu). This reaction is similar to the ring contraction of *N*-carbethoxyazepine.[8]

We found that the nickel(II) promoted rearrangement of N-substituted porphyrins led to homoporphyrin derivatives in good yield, and therefore we undertook a study of the mechanistic details of that new reaction and of the thermal behavior of homoporphyrins.[9]

Results

Synthesis of Homoporphyrins 7 and 8. The substituted porphyrin **6** was prepared according to the literature procedure[10] and treated with a mixture of Ni(II) bis(acetyl)acetonate and Ni(II) carbonate in 1,2-dichloroethane. The resultant mixture consisted of three major compounds: homoporphyrins **7** (57%) and **8** (4%) in addition to the known tetraphenylporphinatonickel(II) (NiTPP) (8%). Compounds **7** and **8** were very similar (infrared, mass spectra,



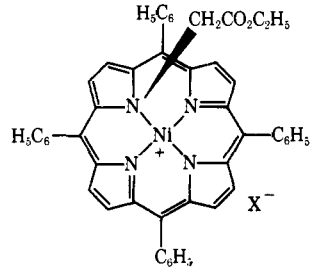
6

7, R = H; R′ = $CO_2C_2H_5$ (endo)
8, R = $CO_2C_2H_5$; R′ = H (exo)

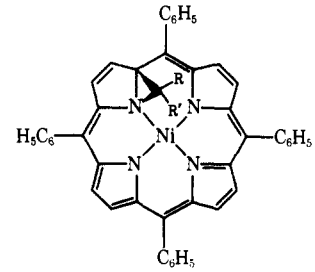
visible spectra) except for the ^1H NMR and chromatographic data. Visible spectra of both isomers were compared with those of unsaturated tetrapyrrolic derivatives whose conjugation has been interrupted, e.g., azahomoporphyrins,[7] bilatrienes,[11] and phlorins.[12] The presence of two major absorption bands at ca. 450 and 680 nm could be related to a certain amount of deformation of the macrocycle.[13] The ^1H NMR data allowed us to attribute the endo and exo configuration to **7** and **8**.[14] The large differences in chemical shifts for the ester signals (ca. 1 ppm) and that of the adjacent proton (ca. 5 ppm) particularly demonstrate the proximity of the strongly shielding conjugated system and the endo substituent. The ^{13}C magnetic resonance spectrum of the ester **7** confirmed the hypothesis of the structure, showing only the expected high-field signals due to the ethyl ester and only one saturated carbon, in addition to a complex multiplet due to the remaining carbon nuclei. The X-ray structural determination[15] of the ester **7** confirmed our hypothesis and demonstrated the large deformation of the whole conjugated system.

Stepwise Conversion of Porphyrin 6 into Esters 7 and 8. When treated at lower temperature with an excess nickel(II) acetate in chloroform-methanol mixture, N-substituted porphyrin **6** gave the nickel(II) salt **9** (X = CH_3COO^-). Addition of aqueous sodium chloride to a methanolic solution of **9** (X = CH_3COO^-) precipitated the corresponding chloride (X = Cl^-). This salt was found to be paramagnetic.[16] Measurement of the magnetic moment using the para-

magnetic shift of $Si(CH_3)_4$ in chloroformic **9** ($X = Cl^-$) against a $Si(CH_3)_4$ external reference led to a value μ_{eff} = 1.8 μ_B. Treatment of **9** ($X = Cl^-$) in dichloromethane with an excess of triethylamine led to the isolation of a unique[17] aziridine **10** (45%). This compound proved to be stable at



9

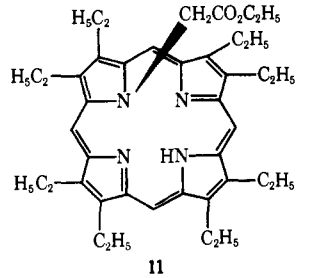


10, R = R' = H or $CO_2C_2H_5$

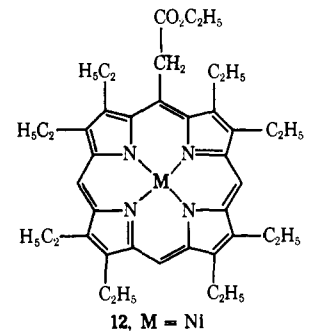
room temperature, although refluxing in benzene converted aziridine ***10*** almost quantitatively to homoporphyrin **7** (TLC revealed the presence of a trace of homoporphyrin **8**). We are not able, at the present time, to specify the stereochemistry of **10**. The visible spectrum of this compound was of the same type as that of **7** and **8**. ^1H NMR data showed the signals due to an isolated proton and an ethyl ester group, both strongly shielded, as expected for the substituent of a three-membered ring which should be approximately at right angles to the macrocycle.

Thermal Interconversion of 7 and 8. Heating esters **7** or **8** in toluene at 110° led to the same equilibrium mixture (**7**, 58%; **8**, 42%). The thermodynamic parameters for this inversion were determined either by NMR or chromatographic isolation of the products, followed by spectrophotometric measurement. At 110 ± 1°, the inversion barrier ΔF^* was found to be 30.0 ± 0.2 kcal mol^{-1} (**7** → **8**) or 29.8 ± 0.2 kcal mol^{-1} (**8** → **7**). Kinetic measurements made at different temperatures (80, 90, 100, 110, 120, and 130° in xylene) led to a $\Delta S^{\ddagger}$ value of −3 ± 5 eu. The height of the barrier and the expected low activation entropy found for the homoporphyrin inversion are in good agreement with literature data compiled for various polybenzocycloheptatrienes.[18]

Rearrangement of the Corresponding N-Substituted Octaethylporphyrin.[19] The starting material **11** was prepared in 50% yield by treatment of zinc(II) octaethylporphyrin (ZnOEP) with ethyl diazoacetate at elevated temperature in bromobenzene, followed by HCl catalyzed demetalation. The same compound was obtained by direct alkylation of octaethylporphyrin with ethyl bromoacetate or from the corresponding cobalt(III) complex and ethyl diazoacetate followed by concentrated H_2SO_4 catalyzed demetalation.[20,21] Treatment of porphyrin **11** with nickel(II) acetylacetonate + nickel(II) carbonate mixture in refluxing 1,2-dichloroethane gave NiOEP (16%) and a major rearranged product **12** (39%). This compound **12** was demetalated in concentrated sulfuric acid to give the free base **13**. The same base was prepared from CuOEP and ethyl diazoacetate, followed by acid demetalation, although in low yield.[22] It is of importance to note that, during the rearrangement of **11** to **12**, a transient green color developed (λ_{max} 428 and 680 nm in benzene). Attempts to isolate an intermediate homoporphyrin derivative, likely to be responsible for this absorption, were unsuccessful, even when using basic chromatographic materials (alumina or calcium carbonate).



11



12, M = Ni

13, M = H_2

Discussion

The first step of the described reaction sequence involved the insertion of a nickel(II) cation into the substrate. The precise structure of the resultant salt requires comment, due to its significant paramagnetism (1.8 μ_B). The infrared spectrum did not reveal any interaction between the ester carbonyl and the metal and, since the product possessed the properties of a typical salt, we inferred that we were dealing with a four-coordinated nickel species. A deviation from a square-planar coordination, imposed by the deformed macrocycle[21,23,24] may account for the observed paramagnetism.

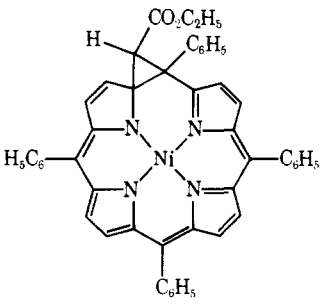
The second step cyclization to the aziridine required the presence of a base to attack a proton α to the ester group.[25] We found that nickel(II) acetylacetonate alone gave a low yield (ca. 15%) of homoporphyrins, the presence of added nickel(II) carbonate increasing the yield to ca. 60%. The utility of the acetylacetonate for bringing the nickel salt into solution could be demonstrated by the inertness of **6** in the presence of insoluble nickel(II) carbonate alone.

The corresponding copper(II) and zinc(II) derivatives of **6** did not react under the cyclization conditions. The only reaction so far described for these complexes is cleavage of the acetic chain, at considerably higher temperatures, followed by a secondary C-alkylation reaction.[10] We do not yet have a clear explanation for the marked specificity of nickel to initiate the cyclization. The strong requirement for nickel, as opposed to zinc for example, to be in a square-planar arrangement in tetrapyrrolic macrocycles[26] may explain this.

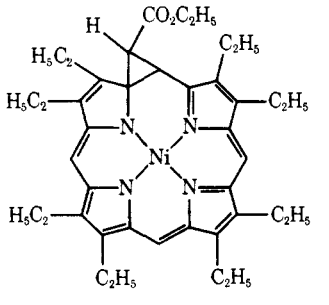
The stereochemistry of aziridine **10** is still to be determined, but the isolation of only one of the two possible isomers and the rearrangement to ester **7** (endo configuration) is of importance. This implies an almost total stereospecificity for both cyclization and rearrangement reactions.

The migration of the ester bearing carbon from nitrogen to bridge carbon can be described as a [1.17] shift. If one assumes that [1.17] shifts homologous to [1.5] shifts[27] have the same stereochemical requirements (i.e., retention of configuration), one should infer, from the known stereochemistry of **7**, that the ester group of **10** should point toward the "outside" the macrocycle. Thus the stereochemistry of the cyclization step is determined by a preferred conformation for the acetic chain of salt **9**, the very conformation that minimizes steric interactions between the bulky ester substituent and ortho hydrogens of the phenyl groups. The above assumptions correlate with the known stereochemistry of cyclopropane migrations[28] found in the norcaradiene series but are contradictory to the recent studies of Klärner[29] supporting inversion of the migratory carbon through the "least-motion" process.

The X-ray structural determination of ester **7** allowed us to rule out a cyclopropanic structure such as **14** in the solid state. If one considers an equilibrium **7** ⇄ **14** in solutions, the concentration of **14** is too low to enable characterization, as demonstrated by the ^{13}C NMR data. When considering the octaethylporphyrin series, it is necessary to as-



14



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sume the presence of a certain amount of isomer **15** to explain the observed ring contraction of an intermediate homoporphyrin. This latter reaction recalls the known instability of azahomoporphyrins.[7] The thermal behavior of esters **7** and **8** will be presented in the following paper in this issue.

Experimental Section[30]

Rearrangement of 21-Ethoxycarbonylmethyl-5,10,15,20-tetraphenylporphine. To a refluxing solution of **6** (0.5 g, 0.7 mmol) in 1,2-dichloroethane was added nickel(II) acetylacetonate (275 mg, 1.07 mmol) and $NiCO_3 \cdot 6H_2O$ (1.0 g, 4.4 mmol). The solution was stirred for 1.5 hr. The solvent was concentrated to dryness under reduced pressure and the residue chromatographed on alumina (250 g) packed in cyclohexane–benzene (1:1). Elution with the latter solvent mixture gave NiTPP (40 mg, crystallized from $CHCl_3$–MeOH), followed by ester **8** (19 mg, crystallized from CH_2Cl_2–MeOH). The material showed: mp 238–239°; ir ν_{max}(KBr) 1745 cm^{-1}; ^1H NMR ($CDCl_3$) 0.16 (s, 1, endo H), 1.0 (t, 3, CH_3, 7 Hz), 3.92 (q, 2, CH_2, 7 Hz), 7.5–8.0 (m, 25, phenyl + pyrrolic H), 8.09 (s, 2, pyrrole), 8.23 (d, 1, pyrrole, 5 Hz); visible (CH_2Cl_2) λ_{max} 675 (ε 14,700), 579 (6760), 449 (86,700); mass spectrum *m/e* (%) 756 (70), 683 (100), 670 (24), 605 (9), 582 (15). Anal. ($C_{48}H_{34}N_4O_2Ni$) C, H, N.

Elution with benzene gave ester **7** (309 mg; crystallized from CH_2Cl_2–MeOH). The material showed: mp 243–245°; ir ν_{max}(KBr) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) −0.12 (t, 3, CH_3, 7 Hz), 2.71 and 2.83 (2 q, 2, CH_2, 7 Hz), 5.14 (s, 1, exo H), 7.3–8.0 (m, 27, phenyl + 7 pyrrolic H), 8.2 (d, 1, pyrrole, 5 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si; Varian XL-100) 12.4 (CH_3), 47.1 (CH), 60.6 (CH_2), 167.6 (CO); visible (CH_2Cl_2) λ_{max} 688 (ε 17,300), 584 (6350), 453 (87,000); mass spectrum *m/e* (%) 756 (52), 683 (100), 670 (42), 605 (10), 581 (18). Anal. ($C_{48}H_{34}N_4O_2Ni$) C, H, N.

Nickel(II) Salt 9 (X = Cl^-). A mixture of porphyrin **6** (27 mg) and nickel(II) acetate (50 mg) was refluxed for 0.25 hr in chloroform–methanol 50:50 (20 ml). The reaction mixture was evaporated to dryness under vacuum and the residue dissolved in methanol. Addition of aqueous sodium chloride precipitated the chloride. After filtration of the crystals, the procedure (MeOH, aqueous NaCl) is repeated and the product washed with distilled water, air dried, and crystallized from methylene chloride–hexane. The salt (21 mg) showed: ir ν_{max}(KBr) 1740 cm^{-1}; ^1H NMR shifted very broad signals due to paramagnetism. The shift of an internal Me_4Si signal vs. an external reference sample was measured: 5 and 10.5 Hz at 0.035 and 0.07 mol/l. A known procedure[31] allowed us to determine μ_{eff} = 1.8 mass spectrum *m/e* 756 (5, HCl), 670 (100), 592 (12); visible (CH_2Cl_2) λ_{max} 666 (ε 5000), 606 (10,000), 556 (9000), 451 (130,000). Anal. Calcd for $C_{48}H_{35}O_2N_4NiCl$: C, 72.61; H, 4.45; N, 7.05; Cl, 4.47. Found: C, 70.74; H, 4.56; N, 7.03; Cl, 5.00. Replacing aqueous NaCl by aqueous $NaClO_4$ gave the corresponding perchlorate **9** (X = ClO_4). Anal. ($C_{48}H_{35}O_6N_4ClNi$) C, H, N.

Aziridine 10. A mixture of the salt **9** (X = Cl) (146 mg) and triethylamine (25 ml) and dichloromethane (25 ml) was stirred for 22 hr. After washing with water (five times) and drying with Na_2SO_4, the solution was evaporated to dryness at room temperature under vacuum. The residue was chromatographed on alumina (70 g, packed in benzene–cyclohexane 50:50). The latter solvent eluted a trace of NiTPP (8 mg) followed by a minor brown component (17 mg) and aziridine **10** (green eluates; 63 mg, crystallized from dichloromethane–methanol).

Compound **10** showed: ir ν_{max}(KBr) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) −0.36 (s, 1); 0.08 (t, 3, CH_3, 7 Hz), 2.73 and 2.78 (2 q, 2, CH_2, 7 Hz), 7.1–8.5 (m, 28, phenyl + pyrrolic H); visible (CH_2Cl_2) λ_{max} 639 (ε 11,400), 443 (66,700). Anal. ($C_{48}H_{34}N_4O_2Ni$) C, H, N.

Conversion of Aziridine 10 to Ester 7. A solution (10^{-3} mol/l.) of **10** in benzene was heated under reflux. Samples were taken at different times and the products separated on alumina TLC. The relative amounts of **10** and **7** were determined spectrophotometrically. A plot of these data vs. time allowed us to determine the activation energy of the process $\Delta F^{\ddagger}_{80°} = 26.1 \pm 0.2$ kcal mol^{-1}.

Thermal Interconversion of Esters 7 and 8. We used the same procedure as above (concentration 10^{-3} mol/l. in refluxing toluene) or measured the relative amounts of products by NMR (concentration 10^{-1} mol/l. in chlorobenzene at 110°). A plot of the data gave identical values for the inversion barrier (see Results).

Alkylation of ZnOEP. A refluxing (155°) solution of ZnOEP (340 mg) in bromobenzene (10 ml) was treated dropwise with ethyl diazoacetate (0.7 ml) over 0.2 hr and heated under reflux for a further 0.5 hr. The solvent was evaporated under vacuum and the residue dissolved in dichloromethane (40 ml) and treated with concentrated aqueous HCl (4 ml). The solution was neutralized with aqueous ammonium carbonate, washed twice with distilled water, and evaporated. Chromatography on alumina (200 g packed in benzene–cyclohexane 50:50) gave some H_2OEP followed by base **11**. Crystallization from chloroform–methanol gave violet crystals (160 mg). The product showed: ir ν_{max}(KBr) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) −4.27 (s, 2, N–CH_2), −3.55 (b, 1, NH), 0.22 (t, 3, ester CH_3, 7 Hz), 1.43 (t, 6, CH_3 of ethyl groups of alkylated pyrrole, 7 Hz), 1.83, 1.86, 1.90 (3 t, 18, CH_3, 7 Hz), 2.72 (q, 2, ester CH_2, 7 Hz), 3.6–4.3 (m, 16, CH_2), 9.88 (s, 2, meso), 10.00 (s, 2, meso); visible λ_{max} 631 (ε 3200), 578 (5300), 540 (6400), 505 (13,500), 408 (149,000). Anal. (as the hydrochloride $C_{40}H_{53}N_4O_2Cl$) H, N; C: calcd, 73.08; found, 72.43.

Nickel Catalyzed Rearrangement of 11. A solution of base **11** (40 mg) in benzene (12 ml) was treated with Ni(II) acetylacetonate (120 mg) and heated under reflux for 12 hr. At that stage, the cooled, diluted, green solution showed λ_{max} 428 and 660 (ratio 10:2.2), in addition to minor absorptions due to NiOEP. The solvent was evaporated under vacuum and the residue chromatographed on alumina (or silica gel). Elution with benzene gave NiOEP (6 mg) followed by ester **12**. Crystallization from dichloromethane–methanol yielded violet crystals (17 mg). The compound showed: mp 207–208°; ir ν_{max}(KBr) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) 0.77 (t, 3, ester CH_3, 7 Hz), 1.5–2.0 (m, 24, CH_3), 3.69 (q, 2, ester CH_2, 7 Hz), 3.6–4.1 (m, 16, CH_2), 5.58 (s, 2, side chain CH_2), 9.33 (s, 3, meso); visible (C_6H_6) λ_{max} 573 (ε 14,000), 533 (8300), 407 (168,000); mass spectrum *m/e* (%) 676 (100), 603 (11). Anal. ($C_{40}H_{50}N_4O_2Ni$) C, H, N.

Demetalation of Nickel Complex 12. Ester **12** (20.5 mg) was dissolved in concentrated sulfuric acid (5 ml) and the solution kept at 20° for 0.2 hr and then poured in a large excess of aqueous ammonium carbonate. The solid was filtered, washed with water, and crystallized from benzene–methanol to yield violet crystals (15 mg). Free base **13** showed: mp 150–151°; ir ν_{max}(KBr) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) −2.8 (b, 2, NH), 1.09 (t, 3, ester CH_3, 7 Hz), 1.6–2.1 (m, 24, CH_3), 3.7–4.3 (m, 18, CH_2), 6.2 (s, 2, side chain CH_2), 9.87 (s, 1, meso), 10.1 (s, 2, meso); visible (C_6H_6) λ_{max} 631 (ε 3200), 578 (5300), 540 (6350), 505 (13,800), 408 (159,000); mass spectrum *m/e* (%) 620. Anal. ($C_{40}H_{50}N_4O_2Ni$) C, H, N.

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(25) Preliminary results in our laboratory indicated a relationship between the acidity of the α proton and the formation of homoporphyrins vs. cleavage of the substituent on nitrogen. Upon replacing CO_2Et by $CON(CH_3)_2$ or COC_6H_5, the yield of homoporphyrins decreased as did the acidity of the α protons: $COC_6H_5 > CO_2Et > CON(CH_3)_2$.
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(30) All melting points are uncorrected. Infrared and visible spectra were recorded on a Perkin-Elmer 457 and a Cary 118 spectrophotometer, respectively. Proton magnetic resonance (^1H NMR) and ^{13}C NMR spectra were recorded on Perkin-Elmer Model R 12 and Varian Model XLS-100, respectively. The chemical shift values are expressed in δ 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. Combustion analysis were performed by the Service Central de Microanalyses 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). We thank Pr. H. H. Inhoffen (Braunschweig, Germany) for a gift of octaethylporphin.
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Acid Catalyzed Isomerization and Thermal Rearrangement of Nickel Homoporphyrins

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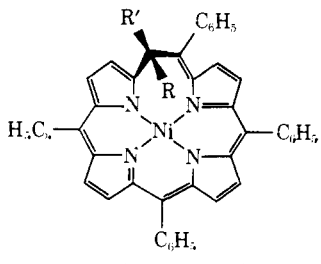
Abstract: Homoporphyrin derivatives possessing a two-carbon meso bridge lead, in acidic solution, to an equilibrium mixture via a reversible protonation-deprotonation of the meso carbons. The pair of homoporphyrins thus formed also show ring inversion. On heating in an inert solvent, homoporphyrins undergo 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.

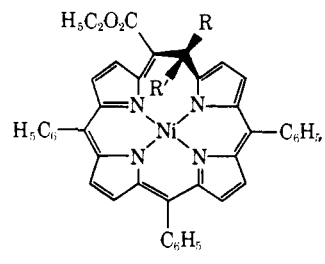
The preceding publication[1] described the synthesis and characterization of the new tetrapyrrolic macrocycle "homoporphyrin". We now report the isomerizations and skeletal rearrangements displayed by these compounds under the influence of dilute acid and heat.

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 (3×10^{-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