New Tetrapyrrolic Macrocycles. 18 and 20 π Electron Homoporphyrins

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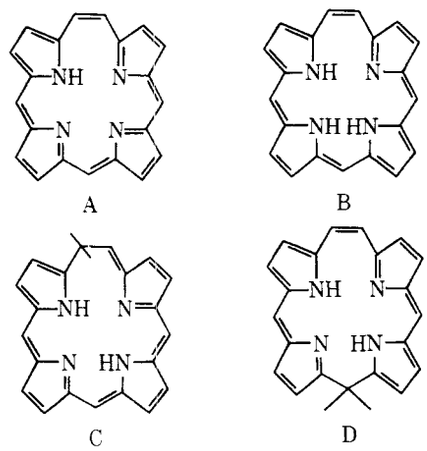
We describe the preparation and properties of a series of homoporphyrin derivatives, either as nickel(II) complex or as free bases. The π system may be fully unsaturated (18 or 20 π electrons) or interrupted by a sp^3 carbon at C_{21} or C_{10}. The nonplanar (helicoidal or rooflike) conformation of homoporphyrins is demonstrated.

Homoporphyrin derivatives have only recently been characterized.[1,2] Typical representatives of this new class of unsaturated tetrapyrrolic macrocycles may be based on the ring systems A, B, C, and D (Scheme I). Fully conjugated systems

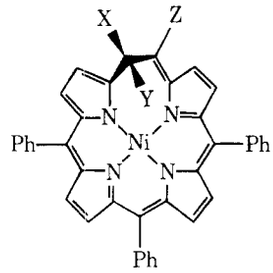
Scheme I



A B C D

A and B are formally aza analogues of 18 π and 20 π annulenes, whereas conjugation is interrupted in the case of C and D.

In an earlier study,[1,2] we reported the preparation of a series of type C homoporphyrins, namely esters **1–4**, via nickel-catalyzed rearrangement of N-substituted porphyrins. We now describe the isolation of several derivatives of type A, B, and D systems.[3]

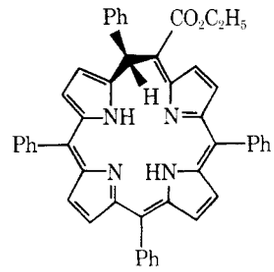


1, X = CO_2Et; Y = H; Z = Ph
2, X = H; Y = CO_2Et; Z = Ph
3, X = Ph; Y = H; Z = CO_2Et
4, X = H; Y = Ph; Z = CO_2Et

Results

Mild acid treatment of ester **2** (3×10^{-2} M CF_3COOH in CH_2Cl_2) yielded an equilibrium mixture of all four isomers **1, 2, 3,** and **4.** More drastic conditions (1 M CF_3COOH, or concentrated HCl) led to rapid demetalation and isolation of two isomeric bases **5** and **6** (20:80, prototropic equilibrium mixture).

The structure of base **5** was confirmed by its spectral properties and its remetalation [$Ni(OAc)_2 \cdot 4H_2O$] to form the nickel complex **3.** The ^{13}C NMR spectrum of base **6** demonstrated the presence of the fully unsaturated system B. This was confirmed by its IR spectrum (conjugated ester). Moreover, its visible spectrum (λ_{max} 472 and 692 nm, ε 38 000 and 13 400) was quite different from that of esters **1–5,** and had no common feature with the spectrum of a porphyrin. Typical also was the occurrence of pyrrolic protons signals in the δ 6–7 ppm range. Base **6** was very unstable and decomposed slowly even at 0 °C in the solid state, yielding a multitude of polar products. This observation could fit the formal "antiaromaticity" of base **6** (this point and the possible conformation of **6** will be discussed further).



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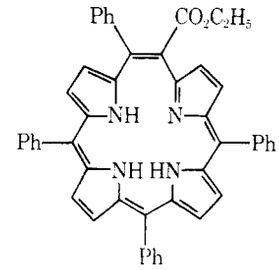
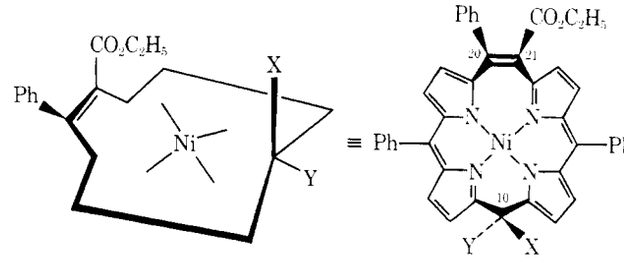


6

Metalation of **6,** under an inert atmosphere (purified N_2; $Ni(OAc)_2 \cdot 4H_2O$, AcOH, 25 °C), gave a 15% yield of ester **1.** The low yield of **1** is most likely due to the poor stability of **6** under the reaction conditions. The mixture of esters **1–4** (30%), which was obtained upon reaction at 60 °C, is undoubtedly the consequence of an acid-catalyzed equilibrium.

On the other hand, in the presence of oxygen, nucleophilic solvents, and base (CH_3OH or H_2O, K_2CO_3) metalation of **6** rapidly yielded type **7** compounds (X = OCH_3 or OH), which on heating in refluxing toluene gave quantitatively type **8** products (Y = OCH_3 or OH).

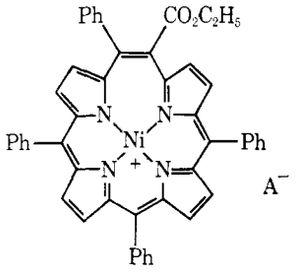


7a, X = OCH_3; Y = Ph
b, X = OH; Y = Ph
8a, X = Ph; Y = OCH_3
b, X = Ph; Y = OH

The structural determination by x-ray analysis of alcohol **8b** has been achieved.[4] It showed a large, rooflike folding of the macrocycle along the C_{10}–Ni axis, thus differentiating the two substituents on C_{10}. This deformation explained the formation of the kinetically favored **7** (X in axial configuration) and its transformation into the thermodynamically favored **8** (equatorial Y). Furthermore, the large C_{20}–C_{21} bridge and carbon C_{10} are placed in a "chimneylike" position, thus avoiding any conjugation with the neighboring pyrrole rings. Buchler et al.[5] observed a very similar deformation on studying a series of 5,15-dihydro-5,15-dimethylporphyrins,

in which the axial methyl substituents are located in the chimney position of the roof. The visible spectra of **7** and **8** (complex pattern between 400 and 500 nm, ϵ ca. 30 000) were of the dipyrromethene type, confirming the lack of conjugation through the C_{20}–C_{21} bridge. The low extinction coefficient agrees well with the structural data which indicate the presence of two nonplanar dipyrromethene units. The NMR data allow series **7** to be distinguished from series **8**. The pyrrolic protons of **8** (phenyl group axial) give rise to a 1:1:6 pattern (from high to low field), located between δ 6.0 and 7.0 ppm. The same protons in **7** exhibit a 3:4:1 pattern, thus illustrating the shielding of the neighboring protons due to the equatorial phenyl group of type **7** compounds. Although a ring inversion could explain the **7** → **8** isomerization, the expected stabilization of a cation at C_{10} suggests a different mechanism, one which proceeds via C–O heterolysis followed by equatorial addition of the resulting anion (CH_3O^- or HO^-). Kinetic measurements, which show a 77-fold increase in rate in going from benzene to CH_3CN, strongly support this hypothesis.

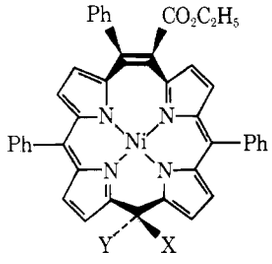
The intermediate cation **9** was isolated on acid treatment (CF_3COOH) of either **7** or **8**.



9

Acidic solutions of **9** were stable but pure crystals (A = ClO_4 or BPh_4) could not be obtained completely free of hydrolysis products. The spectral properties of cation **9** differed markedly from those of porphyrins. The pyrrolic protons resonance occurred at higher field (δ 7.3–8.1 ppm) as compared to *meso*-tetraphenylporphine (9 ppm). Its visible spectrum (λ_{max} 457, 594, and 796 nm; ϵ 55 000, 6800, and 10 600) was similar to those of systems where the cyclic conjugation has been interrupted. Methanolysis of **9** at room temperature gave exclusively **7** (X = OMe). Zinc–acetic acid reduction of **9** yielded, in addition to a small amount of esters **1** and **2**, an isomeric homoporphyrin **10**, belonging to the same series as **7** and **8**.

On refluxing in *o*-dichlorobenzene **10** gave isomer **11**. The structure of **10** and **11** was assigned from their NMR data: H_{10}

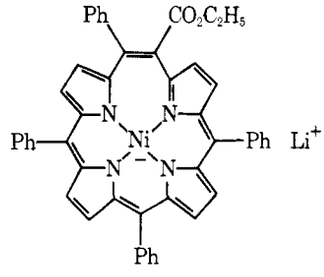


10, X = H; Y = C_6H_5
11, X = C_6H_5; Y = H

has an axial configuration in ester **10** and an equatorial configuration in ester **11**. This follows from the very similar pattern exhibited by the signals of the pyrrolic protons of **7** and **10**, and of **8** and **11**.

In the presence of a base (NEt_3), ester **10** isomerized within a few minutes to form ester **1** while, under the same conditions, **11** remained unchanged for more than a day. This observation allows us to postulate a thermal ring inversion for the **10** → **11** isomerization, thus ruling out the possibility of a base-catalyzed epimerization. Again we observed a large enhancement of the axial vs. equatorial reactivity, as in compounds **7** and **8**.

A study, which is still in progress, showed the formation of anion **12** from either **1** or **2** (*i*-Pr_2NLi, THF). Its protonation gave, depending on the conditions (H_2O or AcOH), a satisfactory yield of a mixture consisting of **1**, **2**, and **10**.



12

Discussion

The reactions described above allowed us to study a series of compounds possessing, in addition to the general homoporphyrin skeleton, the cyclic or interrupted π systems A (cation **9**), B (base **6**), C (esters **1–5**), and D (esters **7**, **8**, **10**, and **11**). Anion **12**, still under study, is another example of system B.

Only two of these reactions differ from simple metalation, demetalation, or prototropy, namely **6** → **7** and **9** → **10**. The former reaction required first metalation of **6** to yield anion **12** whose rapid oxidation in the presence of oxygen (solutions of **12** are highly oxygen sensitive and upon hydrolysis in the presence of air gave **7b** as the major identified product) gave cation **9**, which upon methanolysis or hydrolysis yielded **7** (X = OCH_3 or OH). Similar oxidation of metal complexes of tetrapyrrolic macrocycles have been described by Johnson.[6] On the other hand, the zinc reduction of cation **9** yielded anion **12** whose immediate protonation in acetic acid gave the same products, **1** + **2** + **10**, as did the quenching with acetic acid of a solution of **12** prepared from **1** or **2** and base.

The conformation of macrocycles **1–12** remains the major point to be discussed. Actually our observations indicate that, in the case of **6** and **9**, the overcrowding of the C_{20}–C_{21} bridge is determining, rather than the nature of the cyclic conjugated system (B or A). This point is well illustrated by the x-ray structural determination of **8** (Y = OH): when unsaturated, the large C_{20}–C_{21} bridge is unable to conjugate with the neighboring pyrrole rings, and its "expulsion" from the mean plane of the molecule introduces large deformations. The C_{20}–C_{21} olefinic bond is not conjugated and its length (1.43 Å) is close to that of an isolated double bond. This is also true for compounds **6–12**, whereas **1–5** exhibit a different conformation.[7] These facts explain the absence of aromatic character (e.g., NMR deshielding and porphinlike absorption spectra) of cation **9**, and the a priori unpredictable similarity of its visible spectrum with that of **6**. If the resulting U-shaped conjugated system is further interrupted at C_{10}, the molecule adopts a rooflike conformation leading to a dipyrromethene-like absorption (**7**, **8**, **10**, and **11**). Although possessing the same carbon skeleton, compounds **1–5** exhibit a helicoidal conformation and a Z-shaped C_{20}–C_{21} bridge. The better local planarity observed[7] compares well with the higher extinctions measured.[1,2]

The only known route to homoporphyrins requires the presence of bulky C_{20} and C_{21} substituents. It is obvious that homoporphyrins which are unsubstituted at these positions may adopt a more planar conformation. But it must be kept in mind that the effect of the metal itself, although difficult to measure, can lead to deformations by imposing given metal-N bond lengths.

Experimental Section[8]

Demetalation of Ester 1. To a solution of 1 (500 mg) in $CHCl_3$ (150 mL) was added concentrated HCl (2.5 mL). After stirring for 2 h at 25 °C, the mixture was neutralized (10% aqueous ammonium carbonate), washed with H_2O, dried (Na_2SO_4), and evaporated. Chromatography (alumina, 300 g) using toluene–cyclohexane (1:1) as eluent gave **5** (crystallized from CH_2Cl_2–MeOH, 84 mg, 18%). Further elution using toluene–EtOAc gave **6** (crystallized from CH_2Cl_2–hexane, 250 mg, 54%). The same products were obtained when treating **2, 3,** or **4** under the same conditions. Treatment of either **5** or **6,** in $CHCl_3$ solution, with concentrated HCl gave the same 20:80 equilibrium mixture as demonstrated by visible spectrophotometry, after neutralization and rapid isolation of the products (TLC).

Base **5:** IR ν_{max} (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (t, 3, CH_3, J = 7 Hz), 1.92 (s, 1, H-20), 4.21 (q, 2, CH_2, J = 7 Hz), 6.97 (d, 1, pyrrole H, J = 5 Hz), 7.15 (s, 5, C-20 phenyl), 7.6 (m, 20, 15 phenyl + 5 pyrrole H), 7.90 (d, 1, pyrrole H, J = 4.5 Hz), 8.55 (d, 1, pyrrole H-2, J = 5.5 Hz); visible (C_6H_6) λ_{max} 668 nm (ϵ 10 000), 619 (11 400), 577 (7800), 532 (6000), 433 (75 000); no mass spectrum (decomposition). Anal. Calcd for $C_{48}H_{36}N_4O_2$: C, 82.27; H, 5.18; N, 7.99. Found: C, 82.42; H, 5.29; N, 8.11.

Base **6:** IR ν_{max} (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.71 (t, 3, CH_3, J = 7 Hz), 3.76 (q, 2, CH_2, J = 7 Hz), 4.0 (broad, 3, NH), 6.19 and 6.31 (2 d, 2, 2 pyrrole H, AB, J = 4 Hz), 6.59 and 6.73 (2 d, 2, 2 pyrrole H, AB, J = 4 Hz), 7.5 (m, 24, phenyl + 4 pyrrole H); ^{13}C NMR 12.3 (CH_3), 60.7 (CH_2), 110.5–159.2 (aromatic C), 167.1 (carbonyl); visible (C_6H_6) λ_{max} 692 nm (ϵ 13 400), 472 (38 000); no mass spectrum (decomposition). Anal. Calcd for $C_{48}H_{36}N_4O_2$: C, 82.27; H, 5.18; N, 7.99. Found: C, 79,96; H, 5.35; N, 6.53. The rapid decomposition of base **6** may explain the poor analytical result. All spectra were run on freshly crystallized samples.

Metalation of 5. A solution of base **5** (7 mg) and $Ni(OAc)_2 \cdot 4H_2O$ (20 mg) in CH_3OH (15 mL) was stirred for 2 h at 25 °C. Evaporation followed by alumina TLC gave ester **3** (5 mg, 67%, from CH_2Cl_2–MeOH).

Metalation of 6. 1. Under Nitrogen at 25 °C. Through a solution of $Ni(OAc)_2 \cdot 4H_2O$ (100 mg) in acetic acid (20 mL) was bubbled purified N_2 for 1 h. Solid **6** was then added and the solution was stirred for 36 h under N_2. After vacuum evaporation of the solvent and alumina chromatography ester **1** was isolated (6 mg, 15%) along with traces of **2, 3,** and **4.**

2. Under Nitrogen at 60 °C. The same procedure was used, except that the reaction mixture was heated at 60 °C for 0.5 h. The same workup led to the isolation of a mixture of esters **1, 2, 3,** and **4** (ratio 25:50:5:20; total yield 30%).

3. In the Presence of Air. A solution of $Ni(OAc)_2 \cdot 4H_2O$ (100 mg) in MeOH (2 mL) was added to base **6** (30 mg) in CH_2Cl_2 (5 mL), in the presence of K_2CO_3 (100 mg). The mixture was stirred at 25 °C for 1 h, then extracted (CH_2Cl_2), washed with water, dried (Na_2SO_4), and vacuum evaporated at 25 °C. Product **7a** was purified on TLC using benzene–cyclohexane (1:1) as eluent and crystallized from CH_2Cl_2–MeOH (8 mg, 24%). In the absence of K_2CO_3, in wet MeOH, a limited amount of alcohol **7b** was also obtained, although the yield was difficult to reproduce. A better procedure is the following: to a solution of **2** (170 mg) in tetrahydrofuran (35 mL) was added saturated aqueous Na_2CO_3 (5 mL). The mixture was stirred at 25 °C for 2.5 h and extracted ($CHCl_3$). Chromatography of the solution on alumina (100 g) using $CHCl_3$ as eluent gave **7b** (36 mg, 21%), contaminated with traces of **8b.**

Ether 8a from Isomer 7a. A solution of ether **7a** in toluene was boiled for 10 h. Evaporation of the solvent and crystallization from CH_2Cl_2–MeOH gave a quantitative yield of ether **8a.** Kinetic data were obtained from heating **7a** (2 mg) in benzene or acetonitrile (5 mL) at 80 °C. The products were separated on alumina TLC and the visible absorption measured in CH_2Cl_2 solution: $k_{C_6H_6} = (0.15 \pm 0.01) \times 10^{-4}$ s^{-1}; $k_{CH_3CN} = (11.6 \pm 1.0) \times 10^{-4}$ s^{-1}; ratio 1:77.

Ether 7a from Isomer 8a. To a solution of **8a** (32 mg) in $CHCl_3$ (10 mL) was added CF_3COOH (1 mL). The red-brown solution turned yellow green, and was immediately evaporated. The residue was dissolved in CH_3OH (10 mL). On addition of solid K_2CO_3 the solution turned red brown. It was then evaporated and the residue filtered through a short column (alumina, CH_2Cl_2). The product was crystallized from CH_2Cl_2–MeOH to yield **7a** (28 mg, 88%).

Ether 7a: mp >290 °C; IR ν_{max} (KBr) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (t, 3, CH_3, J = 7 Hz). 3.37 (s, 3, OCH_3), 3.89 (q, 2, CH_2, J = 7 Hz), 6.2 (m, 3, pyrrole H), 6.8 (m, 4, pyrrole), 7.3–7.9 (m, 21, phenyl + 1 pyrrole H); visible (CH_2Cl_2) $\lambda_{shoulder}$ 605 nm (ϵ 4860), 500 (26 000), 465 (27 400), λ_{max} 425 (32 800); mass spectrum *m/e* (%) 756 (3), 700 (8), 684 (22), 670 (70), 607 (9), 594 (100).

Anal. Calcd for $C_{49}H_{36}N_4O_3Ni$: C, 74.72; H, 4.60; N, 7.12. Found: C, 74.30; H, 4.70; N, 7.39.

Alcohol 7b. This compound could not be obtained free of traces of isomer **8b.** It showed IR ν_{max} (KBr) 1715 cm^{-1}; ^1H NMR δ 0.82 (t, 3, CH_3, J = 7 Hz), 1.55 (s, 1, OH), 3.89 (q, 2, CH_2, J = 7 Hz), 6.2 (m, 3, pyrrole H), 6.8 (m, 4, pyrrole H), 7.5 (m, 1 pyrrole + 18 phenyl H), 8.0 (m, 2 phenyl H); visible (CH_2Cl_2) $\lambda_{shoulder}$ 610 nm (ϵ 4700), λ_{max} 480 (28 950), 420 (35 200).

Ether **8a:** mp >300 °C; IR ν_{max} (KBr) 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, 3, CH_3, J = 7 Hz), 3.37 (s, 3, OCH_3), 3.83 (q, 2, CH_2, J = 7 Hz), 6.02 and 6.52 (2 d, 2, pyrrole H, AB, J = 4.5 Hz), 6.75–7.1 (m, 6, pyrrole H), 7.3–7.5 (m, 20, phenyl); visible (CH_2Cl_2) $\lambda_{shoulder}$ 610 nm (ϵ 3390), λ_{max} 498 (26 700), 422 (27 600); mass spectrum *m/e* (%) 728 (M^+·, 28), 756 (100), 683 (13), 581 (64).

Anal. Calcd for $C_{49}H_{36}N_4O_3Ni$: C, 74.73; H, 4.60; N, 7.12. Found: C, 74.58; H, 4.72; N, 7.72.

Alcohol **8b:** mp 294–297 °C; IR ν_{max} (KBr) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, 3, CH_3, J = 7 Hz), 2.87 (s, 1, OH), 3.86 (q, 2, CH_2, J = 7 Hz), 6.01 and 6.56 (2 d, 2, pyrrole H, AB, J = 4.7 Hz), 6.94–7.04 (m, 6, pyrrole H), 7.3–7.5 (m, 18, phenyl H), 7.9–8.05 (m, 2 phenyl H); visible (CH_2Cl_2) $\lambda_{shoulder}$ 605 nm (ϵ 3700), λ_{max} 499 (28 100), 424 (29 200); mass spectrum *m/e* (%) 772 (M^+·, 48), 756 (39), 683 (24), 667 (100), 621 (16), 593 (48), 582 (39).

Anal. Calcd for $C_{48}H_{34}N_4O_3Ni$: C, 74.53; H, 4.43; N, 7.25. Found: C, 74.59; H, 4.52; N, 7.95.

Cation 9. All spectra were run on acidified solutions of **8** (Y = OH). ^1H NMR ($CDCl_3$) δ 0.94 (t, 3, CH_3, J = 7 Hz), 4.12 (q, 2, CH_2, J = 7 Hz), 7.3–8.1 (m, 28, pyrrole + phenyl H); visible (CH_2Cl_2) λ_{max} 786 nm (ϵ 10 600), 594 (6800), 457 (55 000). Addition of aqueous $LiB(C_6H_5)_4$ to methanolic **9** precipited crystals but slow hydrolysis to **7** (X = OH) occurred leading to impure material.

Reduction of Cation 9. Alcohol **8** (2 mg) was dissolved in CH_2Cl_2 (3 mL) containing ca. 10% CF_3COOH. The solvent was evaporated, the residue dissolved in 1:1 benzene–acetic acid (1 mL), and zinc powder (50 mg) added. The mixture was stirred at 25 °C under argon for 2 h, diluted with water, extracted with CH_2Cl_2, dried (Na_2SO_4), and separated (alumina TLC). Visible spectrophotometry indicated a 6:12:82 ratio for isomers **1, 2,** and **10** (total yield 96%). Comparison of chromatographic data with samples of **1, 2,** and **10** confirmed the identity of the products.

Reaction of 1 (or 2) with Base. Solid **1** (100 mg) and *i*-Pr_2NLi (in THF, slight excess) were successively added to THF (10 mL, freshly distilled over $LiAlH_4$), kept at 0 °C under a flow of purified nitrogen. The initial green solution of **1** turned orange brown. After stirring for 0.2 h, acetic acid (0.1 mL) was slowly added. The solution was diluted with water, extracted with CH_2Cl_2, dried (Na_2SO_4), and evaporated. Chromatographic separation (silica gel, toluene–cyclohexane, 1:1) gave isomers **1** (35 mg, 35%) and **10** (25 mg, 25%, crystallized from CH_2Cl_2–CH_3OH). In a smaller scale experiment (20 mg of **1**) rapid quenching of the solution with a larger amount of acetic acid (3 mL) gave **1** + **2** + **10** (ratio 43:28:29, total yield 70% as determined spectrophotometrically). Opening of the reaction vessel before the addition of acid gave **7b** (50%), accompanied by a smaller amount of **1** and **2** (40%, 40:60 ratio).

Ester 10: mp 224–225 °C; IR ν_{max} (KBr) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, 3, CH_3, J = 7 Hz), 3.96 (q, 2, CH_2, J = 7 Hz), 5.39 (s, 1, H-10), 5.9–6.1 (m, 3, pyrrole H), 6.5–6.75 (m, 4, pyrrole H), 7.07 (d, 1, pyrrole H, J = 4.4 Hz), 7.4 (m, 10, phenyl H); visible (CH_2Cl_2) $\lambda_{shoulder}$ 610 nm (ϵ 4200), λ_{max} 462 (32 800), 420 (34 000); mass spectrum *m/e* (%) 756 (M^+·, 91), 683 (38), 679 (25), 670 (95), 582 (100), 545 (45).

Anal. Calcd for $C_{48}H_{34}N_4O_2Ni$: C, 76.10; H, 4.53; N, 7.40. Found: C, 76.05; H, 4.60; N, 7.20.

Ester 11 from Ester 10. Ester **10** (10 mg) was dissolved in *o*-dichlorobenzene)5 mL) and the solution refluxed for 4 h. The solvent was evaporated and the residue crystallized from CH_2Cl_2–MeOH (7 mg, 70%).

Ester 11: mp 216–218 °C; IR ν_{max} (KBr) 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, 3, CH_3, J = 7 Hz), 3.94 (q, 2, CH_2, J = 7 Hz), 5.27 (s, 1, H-10), 6.01 (d, 1, pyrrole H, J = 4.5 Hz), 6.4–7.2 (m, 6, pyrrole H), 7.4–7.6 (2 m, 19, pyrrole H + 19 phenyl H), 8.55 (d, 1, phenyl H, J = 8 Hz); visible (CH_2Cl_2) $\lambda_{shoulder}$ 605 nm (3700), λ_{max} 495 (30 700), 422 (29 000); mass spectrum *m/e* (%) 756 (M^+·, 88), 683 (15), 679 (27), 670 (8), 605 (8), 582 (100).

Anal. Calcd for $C_{48}H_{34}N_4O_2Ni$: C, 76.10; H, 4.53; N, 7.40. Found: C, 75.70; H, 4.34; N, 7.23.

Treatment of 10 or 11 with Base. A solution of **10** (0.265 mg) in CH_2Cl_2 (10 mL) was transfered into a UV cell and flushed with argon. Triethylamine (0.04 mL) was added and the reaction followed at 675 nm. Transformation into **1** was complete within 12 min. Using the same conditions **11** remained unchanged over a day.

Registry No.—1, 55820-93-4; **2**, 55820-92-3; **5**, 57766-46-8; **6**, 57766-47-9; **7a**, 57811-82-2; **7b**, 57808-62-5; **8a**, 61664-37-7; **8b**, 58165-65-4; **9**, 61587-64-2; **10**, 61664-38-8; **11**, 57781-98-3.

References and Notes

(1) H. J. Callot and T. Tschamber, *J. Am. Chem. Soc.*, **97**, 6175–6178 (1975).
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(8) 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 (^{1}H NMR) and ^{13}C NMR spectra were recorded on a Perkin-Elmer Model R-12 and a 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 C.N.R.S., 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).

Photolysis of Allyl Iodide in Aromatic Solvents

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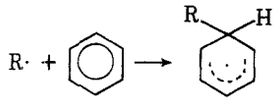
Photolysis of allyl iodide in aromatic solvents gives rise to allylated products. Isomer distribution and both total and partial rate factors determined for this reaction show a slightly electrophilic character of the substitution reaction. Total rate factors correlate well with the first ionization potentials of the aromatic substrates (slope −0.56, correlation coefficient 0.9966).

The first step in homolytic aromatic substitution in most of the cases investigated is a nonreversible exothermic addition of the attacking radical to the π system of the substrate, leading to a σ complex (**1**).



1

This reaction path is typical for highly reactive radicals like phenyl.[1] Positional selectivity and polar effects are normally low, if particular choice of highly polar solvents and substrates does not affect the original nonpolar character of the transition state.[2] The reaction may become reversible if the attacking species gives a relatively weak bond with the aromatic in the σ complex or if the stability of the attacking radical is increased; for instance, the homolytic aromatic thioarylation is very likely a reversible reaction, in which the aromatization step is of great importance in determining the products.[3,4] We wish now to report experiments in which a possible precursor of the stable π-delocalized allyl radical was decomposed in aromatic solvents.

Results

Photolysis of allyl iodide in aromatic substrates gives in almost every case investigated a good yield of isomeric allyl arenes (Scheme I); the presence of propene as a by-product was proved by mass spectrometry and no hydrogen iodide was observed in the reaction mixture. Low yields of high molecular weight iodinated by-products were detected in the reaction at very high reaction times; this does not seem, however, to affect isomer distribution of substitution products and relative reactivities between different substrates; reaction products are stable in the condition employed. In order to avoid any possible source of errors, in the quantitative experiments test analyses were carried out at different reaction times, but no variation of results was observed.

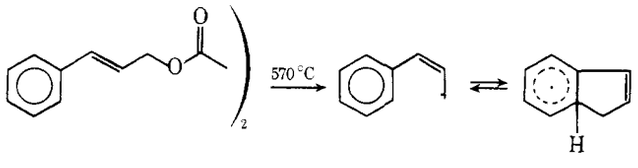
Scheme I

$$CH_2{=}CHCH_2I \xrightarrow[ArH]{h\nu} CH_2{=}CHCH_2Ar$$

$$+ I_2 + CH_2{=}CHCH_3 + (CH_2{=}CHCH_2)_2 \text{ (traces)}$$

No isotope effect on the products was found in the allylation of equimolecular benzene/benzene-d_6 mixtures. This result may be considered as indicative of the unimportance of the reverse reaction in the addition step at room temperature. Actually, a *reversible* intramolecular allylation reaction has been proposed by Trahanowsky and Ong[5] to explain an isotope effect k_H/k_D of 2.92 determined by analysis of the indene fraction obtained from pyrolysis of di-*trans*-*o*-deuteriocinnamyl oxalate at 570 °C (Scheme II).

Scheme II



Tables I and II report the reactivity data obtained from competitive experiments in which allyl iodide was photolyzed in a large excess of equimolecular solution of benzene and a substituted benzene or thiophene; total and partial rate factors were calculated in the usual way, assuming a reaction scheme in which products were formed by nonreversible parallel reactions of the same order, and the yield of conversion Ia → allyl arene not dependent on the particular isomer formed. This aromatization step is probably similar to that proposed by other workers[6] in the photolysis of CH_3HgI in aromatic solvents; iodine atoms are the oxidizing species, possibly through an addition–elimination process, and the so-formed hydrogen iodide then reduces the unreacted allyl iodide to propene. Product analysis is consistent with this mechanism.