spectra were obtained on a Bruker WM 250 spectrometer operating at 49.964 MHz; shifts are reported relative to tetramethylsilane and positive shifts are to high frequency.

Synthesis of 4-(Trimethylsilyl)diphenylmethane. 4-Chlorobenzophenone (22 g, 0.1 mol) dissolved in anhydrous ether was added to $LiAlH_4$ (6.6 g, 0.18 mol) and $AlCl_3$ (48 g, 0.36 mol) in 100 mL of ether, and the mixture was heated under reflux for 1.5 h according to the method of Blackwell and Hickinbottom.[20] Excess of the reagent was destroyed by adding ethyl acetate, and the mixture was poured into 20% aqueous H_2SO_4. Ether extraction, solvent evaporation, and vacuum distillation (160 °C/11 torr) gave 4-chlorodiphenylmethane (18 g, 0.089 mol; 89%). This latter product (8 g, 0.04 mol) was stirred with magnesium (3.6 g, 0.15 mol) in THF at 50 °C over a 12-h period. Chlorotrimethylsilane (15 g, 0.138 mol) was added and the mixture heated at 90 °C for 48 h. Addition to water, ether extraction, and removal of solvent in vacuo gave 4-(trimethylsilyl)diphenylmethane (9.5 g) as a pale yellow, slightly viscous liquid, which was not further purified. This product gave a ^{29}Si NMR peak at −5.2 ppm.

Syntheses of the (Diphenylmethane)tricarbonylchromium(0) Complexes. (Diphenylmethane)bis(tricarbonylchromium(0)) was prepared as described previously.[21,22] 4-(Trimethylsilyl)diphenylmethane (3 g, 12.5 mmol), $Cr(CO)_6$ (2.2 g, 10 mmol), dibutyl ether (100 mL), and THF (10 mL) were heated under reflux in a nitrogen atmosphere for 24 h. After filtration and evaporation of the solvent, the residual oil was chromatographed on a silica gel column by using ether/petroleum ether (1:10) as eluent. The first product was recrystallized from ether/petroleum ether to give yellow crystals of (4-(trimethylsilyl)diphenylmethane)tricarbonylchromium(0) (700 mg, 1.86 mmol; 19%), mp 80 °C. Anal. Calcd for $C_{19}H_{20}CrO_3Si$: C, 60.6; H, 5.3. Found: C, 60.9; H, 5.4.

The second product eluted was recrystallized from ether/petroleum ether to give yellow crystals of (4'-(trimethylsilyl)diphenylmethane)tricarbonylchromium(0) (150 mg, 0.4 mmol; 4%), mp 123 °C. Anal. Calcd for $C_{19}H_{20}CrO_3Si$: C, 60.6; H, 5.3. Found: C, 60.4; H, 5.4.

4-(Trimethylsilyl)diphenylmethane (1.7 g, 7.1 mmol), $Cr(CO)_6$ (4.4 g, 20 mmol), dibutyl ether (100 mL), and THF (10 mL) were heated under reflux in a nitrogen atmosphere for 48 h. After filtration the solution was cooled in a refrigerator overnight. Yellow crystals precipitated and were recrystallized from ether/petroleum ether to give (4-(trimethylsilyl)diphenylmethane)bis(tricarbonylchromium(0)) (2 g, 3.9 mmol; 55%), mp 144 °C. Anal. Calcd for $C_{22}H_{20}Cr_2O_6Si$: C, 51.6; H, 3.9. Found: C, 51.5; H, 4.1.

Synthesis of (α-(Trimethylsilyl)diphenylmethane)bis(tricarbonylchromium(0)). (Diphenylmethane)bis(tricarbonylchromium(0)) (220 mg, 0.5 mmol) was dissolved in THF (4 mL) and was treated with potassium *tert*-butoxide (280 mg, 2.5 mmol) at 0 °C. After 5 min the solution was filtered and treated with anhydrous hexane to precipitate the anion 4. After decantation and removal of liquid by using a syringe, the anion was redissolved in THF (6 mL). Immediately, chlorotrimethylsilane (1 mL) was added and the initially orange solution gradually became yellow. After 30 min the reaction was quenched with water. After ether extraction and removal of solvent in vacuo, the crude residue was chromatographed on a silica gel column and was eluted with ether/petroleum ether (3:2) to give yellow crystals of (α-(trimethylsilyl)-diphenylmethane)bis(tricarbonylchromium(0)) (30 mg, 0.06 mmol), mp 168 °C. Anal. Calcd for $C_{22}H_{20}Cr_2O_6Si$: C, 51.6; H, 3.9. Found: C, 51.8; H, 3.8. Some starting material, viz. $(PhCH_2Ph)[Cr(CO)_3]_2$, was also recovered (80 mg); the global yield of the α-silylated complex was thus 19%.

Generation of the Anions for the NMR Study. Freshly distilled THF was added to a mixture of the appropriate complex and a 5-fold quantity of potassium *tert*-butoxide at 0 °C. (For the two monocomplexed compounds this was done at −30 °C since their anions are thermally sensitive.) After stirring for 5 min the anion was filtered directly into the NMR tube and sealed in vacuo. The anions were kept frozen in liquid nitrogen until required for the NMR studies. The data pertaining to the anions listed in Table I were obtained at −40 °C except where stated.

Acknowledgment. We thank Dr. R. E. Lenkinski, Southwest Ontario Regional NMR Center, Guelph, Ontario, for recording the high-field ^{13}C spectra. Financial support from the CNRS (France) and NSERC (Canada) is greatly appreciated. G.J. and S.T. thank the France-Canada Scientific Exchange Program for Visiting Fellowships.

Registry No. 4, 32823-67-9; **4**$^-$, 75983-29-8; **6**, 86969-84-8; **6**$^-$, 86969-78-0; **7**, 86969-82-6; **7**$^-$, 86969-79-1; **8**, 86969-83-7; **8**$^-$, 86969-80-4; **9**, 86969-85-9; **9**$^-$, 86969-81-5; 4-chlorobenzophenone, 134-85-0; 4-chlorodiphenylmethane, 831-81-2; 4-(trimethylsilyl)diphenylmethane, 17964-29-3.

(20) Blackwell, J.; Hickinbottom, W. J. *J. Chem. Soc.* **1961**, 1405.
(21) Mahaffey, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1975**, *19*, 154.
(22) Top, S.; Jaouen, G. *J. Organomet. Chem.* **1979**, *182*, 381.

Sapphyrins: Novel Aromatic Pentapyrrolic Macrocycles

Victor J. Bauer,[†] Derrick L. J. Clive,[‡] David Dolphin,*[§] John B. Paine III,[§] Francis L. Harris,*[∥] Michael M. King,[⊥] John Loder,[⊗] Shen-Wei Chien Wang,[▽] and Robert Burns Woodward[&]

Contribution from the Departments of Chemistry, Harvard University, Cambridge, Massachusetts 02138, and University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6. *Received August 10, 1982*

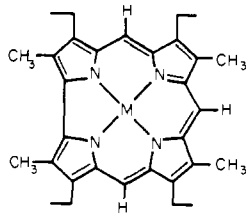
Abstract: Sapphyrins are pentapyrrolic macrocycles containing one direct link and four bridging methine groups between the five pyrrolic subunits. The syntheses of decamethylsapphyrin, other peripherally alkylated derivatives, and metal complexes are described. The physical and chemical properties of sapphyrins show them to be aromatic like porphyrins and corroles. This aromaticity is reflected in the large shielding of the methine and deshielding of the NH protons in the NMR spectra and by their optical spectra, which exhibit Soret and visible bands similar to porphyrins but all bathochromically shifted.

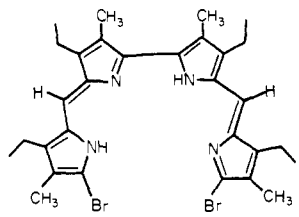
The chemistry described here was performed under the guidance and encouragement of the late R. B. Woodward and began two decades ago following a report by Johnson and Price[1] claiming the synthesis of metallocorroles (**1**). These complexes were supposedly prepared by treating the palladium complex of 5,5″-bi(5′-bromo-3,3′-diethyl-4,4′-dimethyldipyrromethene) (**2**), originally prepared by Fischer and Stachel,[2] with formaldehyde and hydrochloric acid in refluxing ethanol. However, it was shown that this reaction gave the metallooxocorroles (**3**) instead.[3] Since the original claim for a corrole synthesis had not been fulfilled, Woodward and Bauer directed their efforts toward such a synthesis

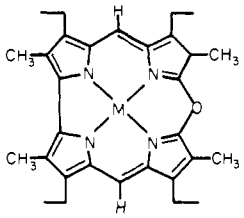
[†] Hoechst-Roussel Pharmaceuticals Inc., Somerville, NJ 08876.
[‡] University of Alberta, Edmonton, Alberta, Canada T6G 2G2.
[§] University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6.
[∥] California State University, Northridge, CA 91330.
[⊥] The George Washington University, Washington, DC 20052.
[⊗] CSIRO, Melbourne 3001, Australia.
[▽] The Henkel Co., Hawthorne, CA 90250.
[&] Deceased.

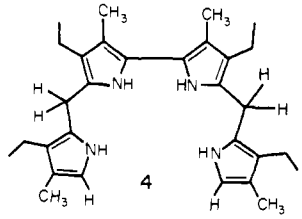
(1) Johnson, A. W.; Price, R. *J. Chem. Soc.* **1960**, 1649.
(2) Fischer, H.; Stachel, A. *Hoppe-Seyler's Z. Physiol. Chem.* **1939**, *258*, 121.
(3) Johnson, A. W.; Kay, I. T. *Proc. Chem. Soc., London* **1961**, 168.

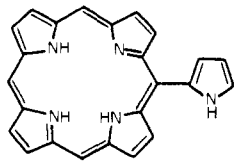
0002-7863/83/1505-6429$01.50/0 © 1983 American Chemical Society

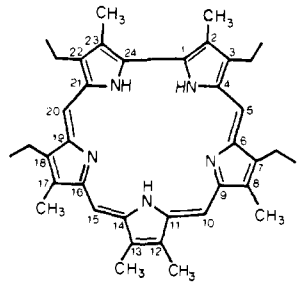

1


2


3

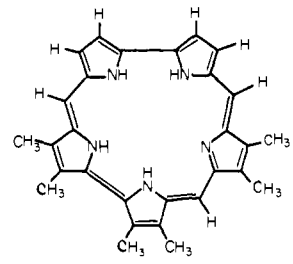

4

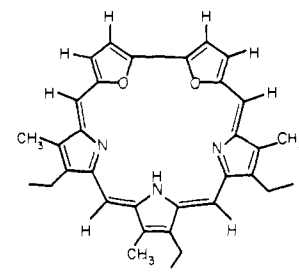

5

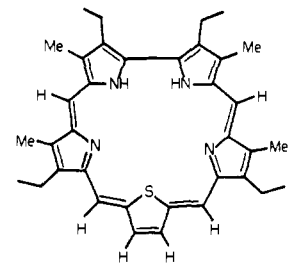

6

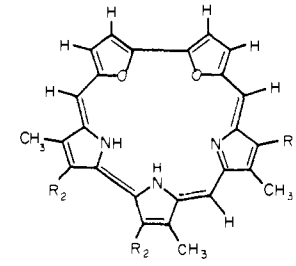
from linear tetrapyrrolic intermediates. Catalytic hydrogenation of the free base bi(dipyrromethene) (**2**) with platinum oxide in tetrahydrofuran gave the dehalogenated tetrahydro derivative **4**. This crude material was treated with formic and hydrobromic acid, in order to cyclize the tetrapyrrole by the insertion of carbon between the two termini, followed by iodine to oxidize the reduced macrocycle. The product, a blue glass isolated in low yield, exhibited an intense "Soret" band in the visible spectrum at 458 nm. This suggested that cyclization to the corrole **1**, M = H, H, might have occurred since an intense "Soret" band is indicative of polypyrrolic aromatic macrocycles. However, Johnson and Kay[4] had by now prepared authentic samples of corroles by the photochemical cyclization of 1,19-dideoxybiladienes-*ac*. The electronic spectra the of corroles[5] showed a Soret band at ~400 nm clearly different from the Harvard material, for which the name sapphyrin was proposed.

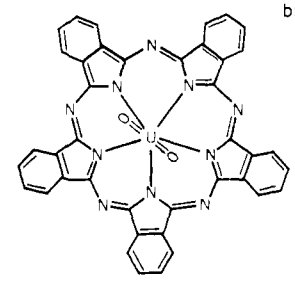
These observations led to a renewed effort when the Harvard group found that their material formed a diperchlorate salt, whereas corroles only underwent mono-*N*-protonation. Combustion analysis on the diperchlorate salt gave an empirical formula of $C_{39}H_{51}N_5Cl_2O_9$, which was consistent with a monohydrate diperchlorate salt containing *five* pyrrolic units. Of the two likely structures the pyrrolyl-substituted porphyrin **5** was clearly much less intriguing than the larger macrocycle **6**, which had in fact been formed. The considerable interest in the potential aromaticity of Hückel systems has prompted syntheses of 22 π-electron hydrocarbons[7] and a number of other macrocycles containing heteroatoms. The first member of the heteroatom series was the sapphyrin alluded to above. Its formation was rationalized as proceeding through the condensation of two molecules of **4** with formic acid followed by α-protonation and bond cleavage to give a pentapyrrolic unit that cyclized to give a sapphyrin. That any sapphyrin was formed at all attests to the inherent stability of the pentapyrrolic superstructure. Since this initial observation, additional sapphyrin-like macrocycles have been prepared, such as the 25,29-dioxasapphyrin[8] (**8**), and the 27-thiasapphyrin[9] (**9**). A


7


8


9


10 a: R_1 = H, R_2 = CH_3
b: R_1 = R_2 = C_2H_5


11

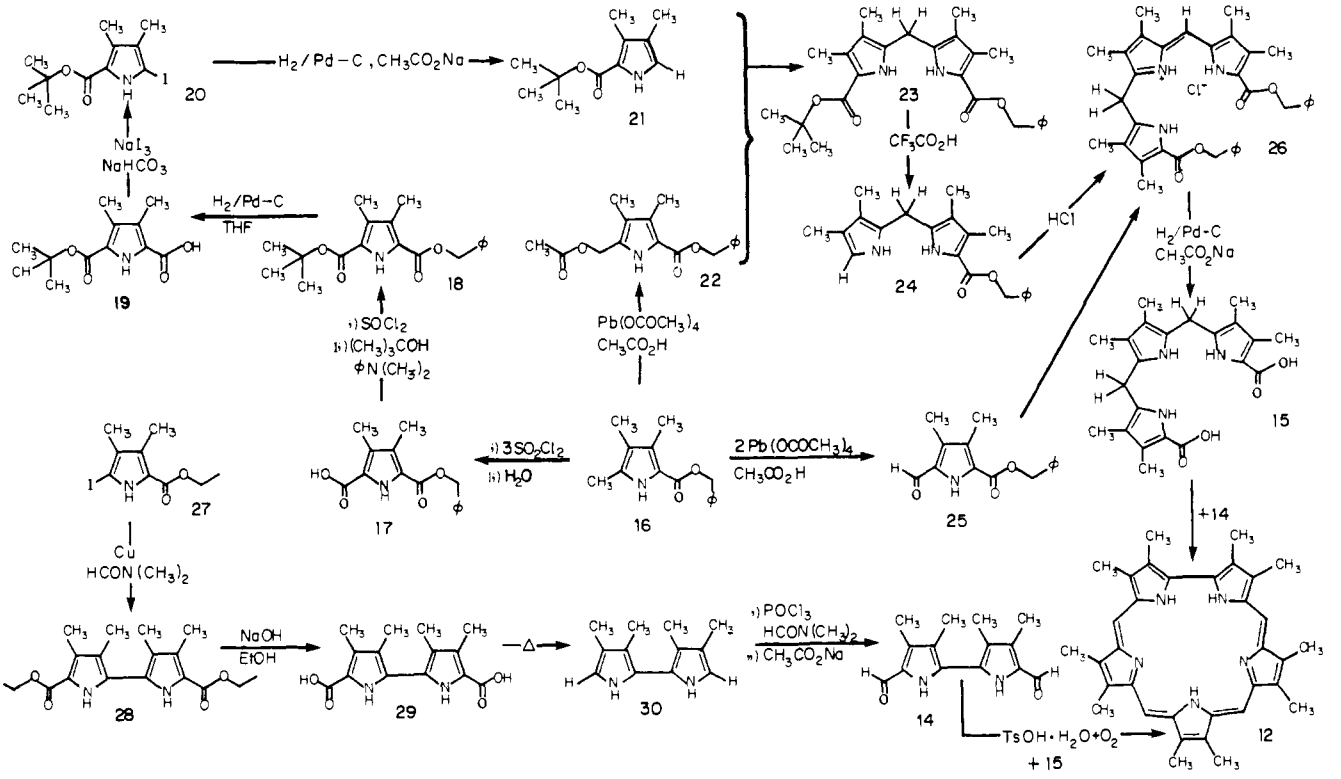
variation on this theme is compound **7** synthesized by King and Woodward,[6] named a smaragdyrin (*smaragdus*: emerald), which bears the same relationship to sapphyrin as corrole does to porphine. Johnson and co-workers[9] also attempted to synthesize this system, which they called norsapphyrin; they did in fact succeed in the syntheses of the dioxanorsapphyrins (or dioxasmaragdyrins) (**10a,b**).[9] A series of heteroatom-bridged annulenes containing furan and thiophene rings has also been synthesized,[10] as has "superphthalocyanine" as a uranyl complex (**11**).[11] The synthesis of a pentaethylpentamethylsapphyrin has been described,[9] and we report here the synthesis and physical and chemical properties of 3,7,18,22-tetraethyl-2,8,12,13,17,23-hexamethylsapphyrin (**6**), 2,3,7,8,12,13,17,18,22,23-decamethylsapphyrin (**12**, Scheme I) and 7,8,12,13,17,18-hexamethylsapphyrin (**31**).

Results and Discussion

In addition to the surprising initial discovery of the sapphyrin system described above, the formation of this ring system is also observed, in small amounts, from the reaction of a bipyrroledicarboxaldehyde with a dipyrromethanedicarboxylic acid, as well as in the reaction of 3,4-dimethylpyrrole with 2,5-diformyl-3,4-dimethylpyrrole, both reactions being carried out in the presence of HBr while open to the air. Rational syntheses of the sapphyrin chromophore from pyrrolic precursors logically involve either 4 + 1 or 3 + 2 condensations in analogy to the MacDonald[12] and

(4) Johnson, A. W.; Kay, I. T. *Proc. Chem. Soc., London* **1964**, 89.
(5) Johnson, A. W.; Kay, I. T. *J. Chem. Soc.* **1965**, 1620.
(6) King, M. M. Ph.D. Dissertation, Harvard University, Cambridge, MA, 1970.
(7) Sondheimer, F. *Acc. Chem. Res.* **1972**, *5*, 81, Sondheimer, F. *Proc. R. Soc. London, Ser. A* **1967**, *297*, 173.
(8) Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1124.
(9) Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2111.
(10) Vollhardt, K. P. C. *Synthesis* **1975**, *12*, 765.
(11) Marks, T. J.; Stojakovic, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 1695.

Scheme I



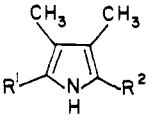
Woodward[13] porphyrin syntheses and require "formylpyrroles" as the electrophilic component of the synthesis. In addition, the other linear tri- or tetrapyrrolic unit must be at the dipyrromethane level of oxidation since dipyrromethenes would be protonated under acidic coupling conditions and thus effectively nonnucleophilic.

3,7,18,22-Tetraethyl-2,8,12,13,17,23-hexamethylsapphyrin (**6**) was prepared by the catalytic reduction of **2** to give **4** followed by reaction with 2,5-diformyl-3,4-dimethylpyrrole (**13**) in methanol–formic acid and aerial oxidation. However, the sequence depicted in Scheme I proved to be more efficient for the synthesis of decamethylsapphyrin (**12**). This could be produced through coupling of the bipyrroledicarboxaldehyde **14** with the tripyrrane diacid **15** by the agency of *p*-toluenesulfonic acid in oxygenated ethanol. **12** gave a parent ion in the mass spectrum at *m/e* 515 and a characteristic Soret band in the electronic absorption spectrum (vide infra). In a similar procedure, 7,8,12,13,17,18-hexamethylsapphyrin (**31**) was prepared from 5,5′diformyl-2,2′-bipyrrole (**32**) and tripyrrane (**15**) in excellent yield.

The bipyrroledicarboxaldehyde **14** was prepared from 3,3′,4,4′-tetramethylbipyrrole (**30**)[14] by treatment with ethoxydichloromethane–phosphorus oxychloride[43] in the presence of stannic chloride or by Vilsmeier–Haack formylation. This latter reaction was found to produce good yields of **14** despite the fact that previous attempts[14] had provided primarily the monoformyl derivative. Compound **32** was prepared in good yield by the Vilsmeier formylation of 2,2′-bipyrrole.[15]

Although the transformations described in Scheme I are those that were used when this work was initiated, some considerable improvement in technique and strategy have been made in the intervening years and are included here. Whereas in the original synthesis decamethylsapphyrin was derived entirely from a single *pyrrolic* starting material (2-((benzyloxy)carbonyl)-3,4,5-trimethylpyrrole (**16**)), in fact it is more convenient to diverge from a common precursor at the slightly earlier (*acyclic*) stage. This common precursor is 3-methyl-2,4-pentanedione (**34**). At the time this work was largely done this diketone was prepared by Johnson's[16] method, from 2,4-pentanedione and methyl iodide. The method leads to a product with variable contamination of starting material (which subsequently reacts with the ethyl oximinoacetoacetate to give a pyrrolic impurity with a 4-acetyl group, instead of the 4-methyl) and dialkylated ketone (which does not interfere although it represents a waste of iodomethane). We have recently come to appreciate the use of boron trifluoride in diketone synthesis[17-19] whereby the action of BF_3 upon a mixture of 2-butanone and acetic anhydride leads, after an exothermic reaction and subsequent aqueous dilution, to the crystalline difluoroboryl complex of 3-methyl-2,4-pentanedione (**33**), which we find contains no detectable isomers or other impurities. A convenient and expeditious hydrolysis by KOH (unlike the tedious steam distillations recommended earlier[19]) leads to high-purity diketone **34** in good yield.

Reaction of **34** with *tert*-butyl (hydroxyimino)acetoacetate (**35**) leads directly to the desired pyrrole *tert*-butyl ester (**36**), in a



36, $R^1 = CO_2$-*t*-Bu; $R^2 = CH_2$
37, $R^1 = CO_2$-*t*-Bu; $R^2 = CH_2OAc$
39, $R^1 = CO_2Et$; $R^2 = CH_3$
41, $R^1 = CO_2Et$; $R^2 = CO_2H$
42, $R^1 = CO_2Et$; $R^2 = H$
43, $R^1 = CO_2CH_2Ph$; $R^2 = H$
44, $R^1 = H$; $R^2 = CH_3$
45, $R^1 = CHO$; $R^2 = CH_3$
46, $R^1 = CH_3$; $R^2 = CH{=}C(CN)CO_2CH_3$
47, $R^1 = CHO$; $R^2 = CH{=}C(CN)CO_2CH_3$

(12) Arsenault, G. P.; Bullock, E.; MacDonald, S. F. *J. Am. Chem. Soc.* **1960**, *82*, 4384.
(13) Woodward, R. B.; Ayer, W. A.; Beaton, J. M.; Bickelhaupt, F.; Bonnett, R.; Buchschacher, P.; Closs, G. L.; Dutler, H. Hannah, J.; Hauck, F. P.; Ito, S.; Langemann, A.; LeGoff, E.; Leimgruber, W.; Lwowski, W.; Sauer, J.; Valenta, Z.; Volz, H. *J. Am. Chem. Soc.* **1960**, *82*, 3800.
(14) Grigg, R.; Johnson, A. W.; Wasley, J. W. F. *J. Chem. Soc.* **1963**, 359.
(15) Rapoport, H.; Castagnoli, N., Jr., *J. Am. Chem. Soc.* **1962**, *84*, 2178.
(16) Johnson, A. W.; Markham, E.; Price, R. Organic Syntheses"; Wiley: New York **1973**; Collect. Vol. V, p 785.
(17) Hauser, C. R.; Adams, J. T. *J. Am. Chem. Soc.* **1944**, *66*, 345.
(18) Sagredos, A. N. *Liebigs Ann. Chem.* **1966**, *700*, 29.
(19) Wang, C. B.; Chang, C. K. *Synthesis* **1979**, 548.

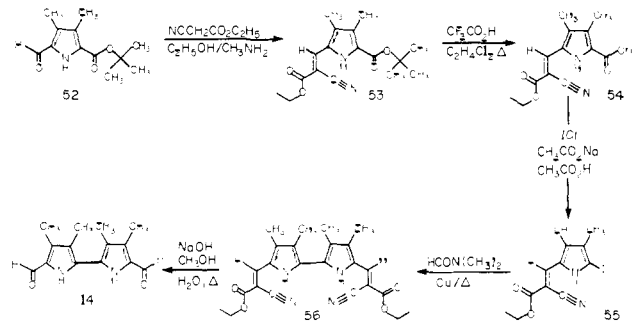
typical Knorr yield of around 45%.[20] Lead tetraacetate in glacial acetic acid–acetic anhydride gives the desired acetoxymethylpyrrole **37** in about 80% yield.[20,21] The same diketone,[22] with diethyl aminomalonate (**38**) leads to 2-(ethoxycarbonyl)-3,4,5-trimethylpyrrole (**39**) in 85–93% yield (the acetoacetate route[20] gives yields of only 45–55%). Rapid, high-temperature transbenzylation of **39** produces the benzyl ester **16** in 80–90% yield, for an overall production of the benzyl ester much in excess of the 45% obtaind from the "direct" Knorr synthesis using benzyl (hydroxyimino)acetoacetate[23] (**40**), a compound itself the result of a transbenzylation (from ethyl acetoacetate).

The traditional[24] trichlorination of the ethyl ester **39** was performed in dichloromethane, and hydrolysis in aqueous acetone converted the intermediary (trichloromethyl)pyrrole to the carboxylic acid **41** without competitive formation of pyrrocoll.[25] The yield was 65–73% at best. Two-phase iodination (1,2-dichloroethane, water) gave **27**. Subsequent acidic deiodination (HI–H_3PO_2–CH_3CO_2H) gave **42**. This procedure is more convenient, on a large scale, than catalytic deiodination; the usual high-temperature transbenzylation gave the other required reagent, 2-((benzyloxy)carbonyl)-3,4-dimethylpyrrole (**43**). This product, and the aforementioned *tert*-butyl ester of the acetoxymethylpyrrole **37**, afforded the desired unsymmetrical dipyrromethane **23** under a variety of conditions, sodium acetate-buffered hot glacial acetic acid giving yields comparable to that from the procedure described above but considerably inferior in yield and purity to that produced by the procedure discovered subsequently by Gossauer and co-workers.[26] The procedure using catalytic amounts of *p*-toluenesulfonic acid suspended in dichloromethane produces little discoloration, debutylation, or symmetrical pyrromethane byproduct. The above sequence is far more expeditious and amenable to large-scale work.

The sapphyrin synthesis further demonstrates the versatility of the cyanoacrylate functionality for protection of pyrrolic aldehydes.[27] Fischer's[24] synthesis of 2,5-diformyl-3,4-dimethylpyrrole (**13**) was wastefully long, in that *both* of the α-carbon substituents of the ubiquitous starting material, 2-(ethoxycarbonyl)-3,4,5-trimethylpyrrole (**39**),[20] were degraded away, only to be replaced at a different oxidation level. For technical reasons,[28] the transformation of a pyrrolic α-ester to the corresponding α-aldehyde is most efficiently performed indirectly by saponification, decarboxylation, and Vilsmeier formylation rather than by direct reduction. The α-methyl substituent, however, can be easily oxidized to the aldehyde level. To that end, 2-formyl-3,4,5-trimethylpyrrole (**45**) prepared earlier by Gattermann or Vilsmeier formylation[24] was protected as its cyanoacrylate (**46**) and oxidized (sulfuryl chloride or lead tetraacetate) to the desired aldehyde, **47**.

Further, the suitability of cyanoacrylate-protected pyrroles for bipyrrole synthesis was investigated. After some effort, optimal procedures were devised to synthesize 5-iodo-2-pyrrolylcyanoacrylates (e.g., **55**, Scheme II).[27] Copper bronze in refluxing dimethylformamide[14] proved to convert these to the desired bipyrrole (**56**) in about 35% yield. This yield is low, but not much lower than those for coupling 5-iodopyrrole 2-monoesters,[14] whose bipyrrolic products are tediously purified and even more tediously converted to dialdehyde. Initial attempts to deprotect the bipyrrole adduct **56** were complicated by incomplete knowledge of the

Scheme II



behavior of the reaction; when oxygen was excluded, and the temperature allowed to reach 100 °C by distilling off the alcoholic solvents employed in the initial stages of the hydrolysis, the deprotection proceeded quite cleanly, and product crystallized directly from the hydrolysis solution in better than 90% yield.

Aromaticity. An upper limit of aromaticity of [4*n* + 2]-annulenes has been predicted at the 22 π-electron system.[29,30] Indeed [30]annulene,[31] two dehydro[30]annulenes,[32] and a tridehydro[26]annulene[33] have been synthesized and found to be nonaromatic. Sapphyrins and related systems can be regarded as heteroatom-bridged [22]annulenes, just as porphyrins are 18 π-electron systems, and interest has centered on their aromaticity.[34] In most respects the physical and chemical properties of the sapphyrins parallel those of the porphyrins and corroles. The optical spectra of porphyrins, which are dominated by the intense Soret absorption band at ~400 nm, have been interpreted as evidence of the aromatic character of these tetrapyrrolic systems.[35]

The sapphyrins described here and elsewhere[9] all exhibit very intense Soret bands in the 450–460 nm region for the free base and the mono- and dicationic forms (vide infra). For example, the dihydrochloride salt of decamethylsapphyrin has a Soret absorption at 456.5 nm (ϵ 594000). This is at a longer wavelength and is more intense than that of the corresponding transition of octamethylporphyrin dihydrochloride in chloroform (414 nm, ϵ 266700).[5] Nevertheless, the general features of the optical spectra of the free bases of octamethylporphyrin and decamethylsapphyrin and the "simplification" of these spectra upon protonation when the symmetry is increased establish the close similarity in the electronic structure of these two macrocyclic systems (Figure 1).

The NMR spectrum of decamethylsapphyrin provides confirmation of its structure (**12**) and attests to its aromaticity. The bis(hydrotrifluoroacetate) in $CDCl_3$ (100 MHz) exhibited two resonances of equal intensity at δ 11.51 and 11.70 corresponding to the two sets of meso protons. The ten methyl groups gave signals in the ratio of 1:2:1:1 at δ 4.04, 4.08, 4.19, and 4.22 while the NH groups exhibited broader resonances at δ −5.46, −5.0, and −4.84 in the ratio of 2:1:2. The same general characteristics are exhibited in the NMR spectrum of octamethylporphyrin bis(hydrotrifluoroacetate) (δ 10.98, 3.78, −4.82)[36] for meso, methyl, and NH protons, respectively. These distinctive spectra clearly show the presence of a strong ring current that reflects their aromatic character.[37]

In the mass spectrometer decamethylsapphyrin exhibits an intense parent peak at *m/e* 515 (calculated for $C_{34}H_{37}N_5$) with a P + 1 of the expected 40% intensity. However, the P + 2 is

(20) Bullock, E.; Johnson, A. W.; Markham, E.; Shaw, K. B. *J. Chem. Soc.* **1958**, 1430.
(21) Badger, G. M.; Harris, R. L. N.; Jones, R. A.; Sasse, J. M. *J. Chem. Soc.* **1962**, 4329.
(22) Paine, J. B., III; Dolphin, D., manuscript in preparation.
(23) Johnson, A. W.; Markham, E.; Price, R.; Shaw, K. B. *J. Chem. Soc.* **1958**, 4254.
(24) Fischer, H.; Höfelmann, H. *Liebigs Ann. Chem.* **1938**, *533*, 216.
(25) Cavaleiro, J. A. S.; Rocha Gonsalves, A. M. d'A.; Kenner, G. W.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2471.
(26) Engel, J.; Gossauer, A. *J. Chem. Soc., Chem. Commun.* **1975**, 570.
(27) Paine, J. B., III; Woodward, R. B.; Dolphin, D. *J. Org. Chem.* **1976**, *41*, 2826.
(28) Paine, J. B., III. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 1, pp 101–234.
(29) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685.
(30) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1959**, *251*, 172.
(31) Coulson, C. A.; Dixon, W. T. *Tetrahedron* **1962**, *17*, 215.
(32) Sondheimer, F. "Proceedings of the Robert A. Welch Foundation Conference on Chemical Research", XII, Organic Synthesis, Milligan, W. O., Ed., Houston, TX, 1969.
(33) Leznoff, C. C.; Sondheimer, F. *J. Am. Chem. Soc.* **1967**, *89*, 4247.
(34) George, P. *Chem. Rev.* **1975**, *75*, 85.
(35) Gouterman, M. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, pp 1–165.
(36) Dolphin, D.; Paine, J. B., III, unpublished results.
(37) Janson, T. R.; Katz, J. J. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 1–59.

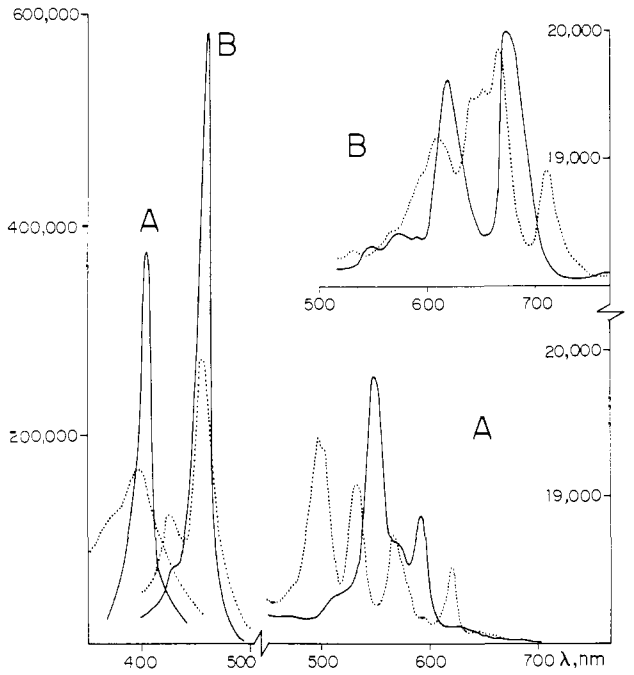


Figure 1. Optical spectra (CH_2Cl_2) of: (A) octamethylporphyrin (---) free base, (—) dication in the presence of trifluoroacetic acid; (B) decamethylsapphyrin (**12**) (---) free base, (—) dication in the presence of trifluoroacetic acid.

always more intense than the calculated 14%. Intensities ranging between 19% and 68% have been observed (even with the same sample) reflecting the basicity of the sapphyrin chromophore and protonation within the mass spectrometer.[38] As with all aromatic polypyrrolic macrocycles, including porphyrins and corroles, the next most intense peak in the MS of decamethylsapphyrin was the *m/2e* at 257.5, which had an intensity 10% that of the parent peak.

Chemical Properties. The dioxasapphyrins have been reported to be unusually basic while the dioxanorsapphyrins seem to be markedly less so.[7] Dioxasapphyrin could not be obtained analytically pure, and solutions of the free base soon revert to monocation. The sapphyrins are also basic. On silica gel they are protonated, which allows for their ready separation and purification, and in the presence of acid they readily protonate to give the dication (Figure 1). In fact the free base when dissolved in chloroform is partially protonated by the acid derived from the breakdown of chloroform and only in rigorously purified acid-free solvents can the free base be seen. Monoprotonated sapphyrins, as with porphyrins, are difficult to observe. In the case of porphyrins the second protonation is normally easier than the first, and only under special conditions can the monocation be observed.[39] The optical spectrum of the monocation of decamethylsapphyrin has, however, been accidentally measured. Thus when decamethylsapphyrin was dissolved in chloroform the spectrum of a new species was observed (Figure 2) that upon treatment with trifluoroacetic acid gave the dication, while in the presence of triethylamine the free base was generated. Since the new species is between that of the free base and the dication, we presume that it is the monocation.

Chlorins[40] and corroles[4] undergo rapid electrophilic substitution with D^+ at the meso positions when treated with CF_3CO_2D, whereas several weeks are required, even at 100 °C, to exchange the meso protons of porphyrins.[41] After decamethylsapphyrin was allowed to stand at room temperature overnight in CF_3CO_2D the meso protons were no longer observable in the NMR spectrum.

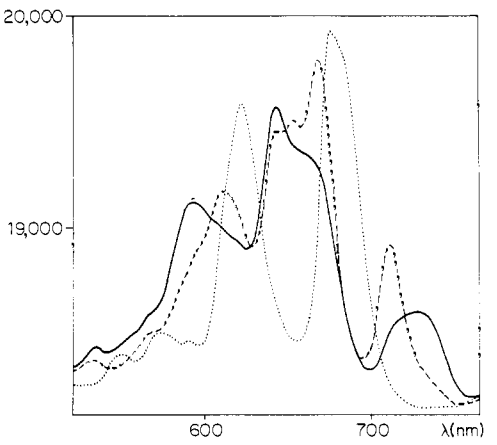
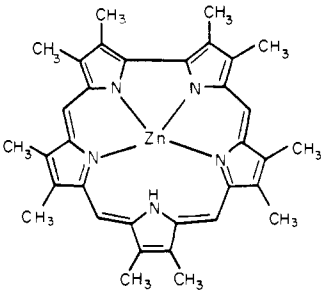


Figure 2. Optical spectra ($CHCl_3$) of decamethylsapphyrin (12) (---) free base in the presence of triethylamine, (—) monocation, (···) dication in the presence of trifluoroacetic acid.

Mass spectral analysis showed that indeed all four of the meso positions had been exchanged for deuterium indicating the ease of electrophilic attack on the sapphyrin nucleus. However, attempts to nitrate or brominate decamethylsapphyrin gave intractable products.

The 25,29-dioxanorsapphyrins do not appear to form metal complexes. We had originally supposed that the large "hole" in the center of the ring and the planar pentadentate array of nitrogens might make the sapphyrins good ligands for groups such as UO_2^{2+} that are known to form pentagonal bipyramids.[42] However, we have been unable to make complexes between UO_2^{2+} (or Pb^{2+}, which also has a large ionic radius) and decamethylsapphyrin. On the other hand, when a methanolic solution of decamethylsapphyrin and the acetate salts of Ni^{2+}, Fe^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, and Zn^{2+} were heated in the presence of sodium acetate, spectral changes indicated that metal complexes were formed and the Co^{2+} and Zn^{2+} complexes have been isolated as crystalline solids (**57** and **58**). The mass spectrum of the zinc



57

complex showed as the parent peak a signal at *m/e* 577.2120. The calculated value for decamethylsapphyrin + Zn^{++} − 2H is 577.2183. Thus when zinc coordinates to sapphyrin only two of the three NH protons are lost. Presumably the resulting neutral complex has only four of the five nitrogen atoms coordinated to zinc while the other nitrogen remains protonated. The symmetric complex **57** accounts for the observed facts.

While the parent peak is observed for zinc decamethylsapphyrin, the base peak is at *m/e* 484, the mass of zinc octamethylporphyrin. Thus in the mass spectrometer the sapphyrin nucleus apparently rearranges to the porphyrin nucleus with the loss of a monopyrrolic fragment. The cobalt complex, in analogy to the zinc complex, contains an NH group and also rearranges to give cobalt octamethylporphyrin in the mass spectrometer.

Experimental Section

Melting points are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark, at the Woodward Research Institute, Basel, and at the University of British

(38) Budzikiwicz, H. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, pp 395–461.
(39) Falk, J. E. "Porphyrins and Metalloporphyrins"; Elsevier: New York, 1964.
(40) Woodward, R. B.; Skaric, V. *J. Am. Chem. Soc.* **1961**, *83*, 4676.
(41) Paine, J. B., III; Dolphin, D. *J. Am. Chem. Soc.* **1971**, *93*, 4080.
(42) Muetterties, E. L.; Wright, C. M. *Quant. Rev.* **1967**, *21*, 109.

Columbia. NMR spectra were measured on Varian Associates Models A-60, T-60, and HA-100 spectrometers using Me_4Si as an internal standard. Mass spectra were recorded on an AEI MS-9 using a direct inlet probe and 70 eV.

3,7,18,22-Tetraethyl-2,8,12,13,17,23-hexamethylsapphyrin (6). To a solution of 5,5″-bi(5′-bromo-3,3′-diethyl-4,4′-dimethyldipyrromethene) (**2**)[2] (41 mg) in tetrahydrofuran (35 mL) containing triethylamine (10 drops) was added platinum oxide (50 mg), and the mixture was hydrogenated under pressure (1200 psi). Thereafter the reaction mixture was protected at all times by a blanket of argon. The magenta-colored solution was filtered into a round-bottomed flask, and the clear filtrate was taken to dryness in vacuo at ca. 25 °C while protected from light. The mauve residue was covered with argon and the flask was closed with a serum cap. Deaerated methanol (4 mL) was introduced, and brief swirling effected complete dissolution of the residue. This solution was added over ca. 45 s to a stirred solution, kept under argon, of 2,5-diformyl-3,4-dimethylpyrrole (**13**)[24] (21 mg) in 88% formic acid (3.5 mL). Immediately after the addition the mixture was exposed to air and within a few seconds a green color developed. Stirring at room temperature was continued overnight with protection from light. The mixture was then poured into chloroform and washed first with an excess of ammonium hydroxide (2 N) and then with hydrochloric acid (1 N). The chloroform layer was dried and evaporated in vacuo below 40 °C.

A chloroform solution of the total product was washed with ammonium hydroxide (2 N), dried, and evaporated in vacuo at room temperature. The residue was chromatographed on neutral alumina (Woelm, grade 3). A dark-green band was eluted with chloroform containing increasing proportions of ethyl acetate (up to chloroform/ethyl acetate 20:3 v/v). The green eluate was collected, washed with hydrochloric acid (1 N), and dried. Evaporation in vacuo below 40 °C left the sapphyrin dihydrochloride as a crystalline residue (9.5 mg).

Recrystallization from acetonitrile (dissolution effected at ca. 100 °C in a sealed tube) gave blue crystals: MS, *m/e* 573, 571, 286.5, 285.5.

2,3,7,8,12,13,17,18,22,23-Decamethylsapphyrin (12). The bipyrroledialdehyde (**14**) (488 mg, 2.00 mmol) in absolute ethanol (2 L) was heated at reflux for 3 h with stirring to dissolve all solids. The solution was cooled to room temperature, and the ethanolic solution of the tripyrromethanedicarboxylic acid **15** (vide infra) was added. The color of the solution changed from green to red. *p*-Toluenesulfonic acid dihydrate (1.7 g, 8.0 mmol) was added to yield a dark red solution. Oxygen was bubbled through the solution for 18 h. Ethanol was removed at reduced pressure, and the residue was dissolved in chloroform and chromatographed over 150 g of neutral alumina (Woelm activity 1) with chloroform as the eluent. The first fraction (blue) and the second fraction (brown) were discarded. The third fraction (green) was collected and evaporated to dryness. The residue was heated in chloroform (75 mL) for 30 min, and the resulting green solution was allowed to stand in a desiccator containing petroleum ether. After 1 day, small needles were observed in the solution. The crystals were collected after 6 days: yield 484 mg (47% based on **26**); mp >350 °C; IR (KBR) 1590 cm^{-1}; MS, *m/e* (relative intensity) 517 (30), 516 (43), 515 (M^+, 100), 257.5 (10); vis, see above.

For analytical purposes, decamethylsapphyrin dihydrochloride was prepared. A sample, purified by the procedure described above, was dissolved in chloroform and filtered through a sintered glass funnel. Gaseous hydrogen chloride was bubbled through the solution for 1 min; the color changed to light green. The solution was filtered, and the solid was collected and dissolved in chloroform. Gaseous hydrogen chloride was bubbled through the solution, which was filtered again. This procedure was repeated until no solid was left on the sintered glass funnel. All the filtrates were combined and put in a desiccator containing petroleum ether saturated with hydrogen chloride gas. After several days, the solid thus formed was collected. This material was found to be hygroscopic and to bind chloroform (from microanalysis data). The sample was dried at 100 °C on the diffusion pump for 2 days and subjected to microanalysis. Anal. Calcd for $C_{34}H_{39}Cl_2N_5$: C, 69.37; H, 6.68; N, 11.89; Cl, 12.05. Found: C, 69.11; H, 6.83; N, 11.83; Cl, 12.10. Spectral data are reported in the text.

2,5-Diformyl-3,4-dimethylpyrrole[24] (13). 2-(2-Cyano-2-(methoxycarbonyl)vinyl)-5-formyl-3,4-dimethylpyrrole[24] (**47**) (4.3 g, 0.02 mol), potassium hydroxide (32 g), ethanol (32 mL), and water (32 mL) were refluxed for 5 h (oil bath, 110 °C). The solution was chilled and acidified carefully with 6 N H_2SO_4. The crystallized mixture was extracted thoroughly with dichloromethane, and the extracts were evaporated. The crystalline residue was sublimed (120–130 °C (0.1 mm)) to afford pale yellow crystals (2.05 g).

The substance was recrystallized from 1,2-dichloroethane: mp 157–158 °C (lit. mp[24] 158 °C).

5,5′-Diformyl-3,3′,4,4′-tetramethyl-2,2′-bipyrrole (14). An ethoxydichloromethane–$POCl_3$ mixture[43] (190 mL) in a 1-L flask was cooled in an ice–salt bath. To this mixture was added a solution of 3,3′,4,4′-tetramethyl-2,2′-bipyrrole[14] (**30**, 2.78 g, 0.0148 mol) in anhydrous ether (60 mL). Stannic chloride (50 mL) was added dropwise with vigorous stirring; when addition was complete the bath was removed. The solution was stirred for 1 h at room temperature, then poured into water (1.5 L), and allowed to stand at room temperature overnight. The precipitate was collected, washed with aqueous $NaHCO_3$ and water, and dried. The resulting solid was sublimed (short path) at 220 °C (0.5 torr): mp 305–307 °C dec; yield 2.7 g (76%). A sample recrystallized from glacial acetic acid had mp 315 °C dec. Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.85; H, 6.64; N, 11.56. IR (KBr) 1621 cm^{-1}; MS, *m/e* 244.

2,5-Bis(5-carboxy-3,4-dimethylpyrrol-2-ylmethyl)-3,4-dimethylpyrrole (15). This compound decomposes readily and characterization proved to be impractical. Hydrogenation of **26** in methanol with added sodium acetate, followed by basic aqueous extraction and neutralization, has allowed isolation of an 81% yield of a red powder. Because of the instability of this substance, a second procedure described below proves to be more practicable.

The tripyrrene hydrochloride **26** (1.22 g, 2.00 mmol) was dissolved in tetrahydrofuran (500 mL) under nitrogen. Triethylamine (0.8 g, 8 mmol) and 5% Pd on charcoal (300 mg) were added, and the mixture was hydrogenated at atmospheric pressure and room temperature. Hydrogen uptake was nearly complete in 1 h. After 4 h, solids were removed by filtration and the filtrate was evaporated to dryness at reduced pressure and room temperature. The residue, which was again too unstable to characterize, was dissolved in absolute ethanol (20 mL) for use directly in the synthesis of **12** (vide supra).

2-((Benzyloxy)carbonyl)-3,4,5-trimethylpyrrole (16).[23] 2-(Ethoxycarbonyl)-3,4,5-trimethylpyrrole[20] (200 g, 1.1 mol) and benzyl alcohol (504 mL, distilled from K_2CO_3 at atmospheric pressure) were heated under nitrogen to reflux in an open Erlenmeyer flask (2 L). When any water had boiled off and the vapor temperature reached 200 °C a freshly prepared solution of sodium in dry benzyl alcohol was added cautiously in 1-mL portions until vigorous ethanol evolution started. Further portions were added periodically until the exchange was complete (as evidenced by a boiling point again above 200 °C, about 15 min).

The *hot* solution was cautiously poured into a stirred solution of methanol (1 L), water (500 mL), and acetic acid (25 mL). The slurry was chilled on ice; then the product was recovered by filtration and washed with aqueous ethanol (50% v/v) and finally with water. Main crop 229 g (85.2%); crude 2nd crop 21 g (7.7%); total 250 g (93%): mp 117–117.5 °C (lit. mp[23] 119–120 °C).

2-((Benzyloxy)carbonyl)-5-((*tert*-butyloxy)carbonyl)-3,4-dimethylpyrrole (18). A mixture of crude acid **17**[44] (44.1 g), distilled thionyl chloride (50 mL), and dry benzene (200 mL) was stirred at 40 °C for 1 h and then overnight at room temperature. All material had dissolved to provide a dark brown solution. Solvent was removed on the rotary evaporator, and the residual thionyl chloride was "chased" by adding and then stripping off two portions of dry benzene (ca. 150 mL each). To the residual brown solid was added a solution of *tert*-butyl alcohol (100 mL, about 7 mol) and redistilled *N,N*-dimethylaniline (80 mL, about 4 mol). The mixture was heated at 70 °C, and all the solid dissolved within a short time. Heating was maintained for 1 h, and then the solution was stirred at room temperature for 44 h. The brown solution was poured into dichloromethane (600 mL), extracted with water, with ice-cold 3 N sulfuric acid (500 mL), quickly, 5% sodium bicarbonate, and brine and then dried. Solvent was removed in vacuo to leave a viscous brown oil that was dissolved in a minimum amount of benzene and chromatographed over 250 g of silica gel with benzene as solvent. The color stayed at the top of the column, and 35.9 g (68%) of the required ester was eluted as a light orange solid. This material was crystallized from hexane to give 30 g of slightly yellow material that was taken directly into the next stage. The mother liquors were rechromatographed and then crystallized from hexane containing a trace of methanol to give nearly colorless prisms: mp 87.5–88.5 °C. Anal. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.02; H, 7.14; N, 4.26. IR (CH_2Cl_2) 1695 cm^{-1}; NMR ($CDCl_3$) δ 1.56 (s, 9 H), 2.25 (s, 3 H), 2.30 (s, 3 H), 5.37 (s, 2 H), 7.40 (s, 5 H), 9.0–9.4 (br s, 1 H); MS, *m/e* 329, 273, 91.

5-((*tert*-Butyloxy)carbonyl)-2-carboxy-3,4-dimethylpyrrole (19). A mixture of diester **18** (26.0 g, 0.0778 mol), 5% palladium on charcoal (5 g), triethylamine (5 drops), and tetrahydrofuran (260 mL) was stirred under an atmosphere of hydrogen at room temperature for 3 h. Catalyst was removed by filtration, and evaporation of the filtrate in vacuo left an off-white solid (18.5 g, 98%), used without further purification: mp

(43) Fischer, H.; Wecker, G. *Hoppe-Syler's Z. Physiol. Chem.* **1942**, *272*, 1.

(44) Grigg, R.; Johnson, A. W. *J. Chem. Soc.* **1964**, 3315.

209–210 °C (softening from 170 °C). Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.25; H, 7.16; N, 5.85. Found: C, 60.64; H, 7.21; N, 5.97. IR (KBr) 1698, 1667 cm^{-1}; MS, *m/e* 239, 183.

2-((*tert*-Butyloxy)carbonyl)-5-iodo-3,4-dimethylpyrrole (20). 2-((*tert*-Butyloxy)carbonyl)-5-carboxy-3,4-dimethylpyrrole (**19**) (16 g, 0.067 mol) was dissolved in a solution of sodium bicarbonate (16.5 g) in 130 mL of water and 130 mL of methanol. As the solution was stirred and heated at 60 °C, a mixture of potassium iodide (25 g) and iodine (17.3 g) in 30 mL of water–65 mL of methanol was added dropwise over 3 h while the reaction flask was protected from light. The reaction mixture was stirred 60 °C for 1 h and then poured into water (500 mL). The precipitate was collected in a dark room, washed with water, and dissolved in ether (300 mL). The etheral solution was dried ($MgSO_4$) and removal of solvent at reduced pressure left a yellow solid that was recrystallized from ether–petroleum ether: mp 138–139 °C; yield 20.5 g (96%). Anal. Calcd for $C_{11}H_{16}INO_2$: C, 41.14; H, 5.02; N, 4.36; I, 39.51. Found: C, 41.38; H, 5.07; N, 4.12; I, 39.80. IR (CH_2Cl_2) 1680 cm^{-1}; NMR ($CDCl_3$) δ 1.67 (s, 9 H), 1.97 (s, 3 H), 2.28 (s, 3 H), 8.66–9.20 (br s, 1 H); MS, *m/e* 321, 265. The compound is light sensitive.

2-((*tert*-Butyloxy)carbonyl)-3,4-dimethylpyrrole (21). A mixture of 2-((*tert*-butyloxy)carbonyl)-5-iodo-3,4-dimethylpyrrole (**20**) (17.0 g, 0.053 mol), anhydrous sodium acetate (6.6 g, 1.5 equiv) and methanol (300 mL) was warmed until solution (yellow) was achieved. Adams catalyst (0.5 g) was added and the mixture was hydrogenated at room temperature and atmospheric pressure. Hydrogen uptake (ca. 1.5 L) was complete in about 2 h. The catalyst was removed by filtration (the filtrate was air sensitive), and the methanol was evaporated in vacuo. To the residue were added water and dichloromethane and the mixture was shaken. The organic layer was dried and evaporated in vacuo to yield a slightly yellow oil that soon began to crystallize as transparent, nearly colorless leaflets: yield 9.60 g (94%); mp 72–73 °C. The solid was sublimed at 50 °C (0.07 torr). Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.18. Found: C, 67.52; H, 8.81; N, 7.23. IR ($CHCl_3$) 1670 cm^{-1}; NMR ($CDCl_3$) δ 1.57 (s, 9 H), 2.02 (s, 3 H), 2.27 (s, 3 H), 6.67 (d, J = 3 Hz, 1 H), 9.3–9.6 (br, 1 H); MS, *m/e* 195, 139.

5-((Acetoxy)methyl)-2-((benzyloxy)carbonyl)-3,4-dimethylpyrrole (22). 2-((Benzyloxy)carbonyl)-3,4,5-trimethylpyrrole (**16**) (9.7 g, 0.04 mol) was dissolved in glacial acetic acid (250 mL). To the solution was added lead tetraacetate (17.7 g, 0.040 mol). The mixture was allowed to stir at room temperature for 16 h. The acetic acid was removed under reduced pressure, and the residue was dissolved in chloroform. The chloroform solution was extracted with aqueous sodium bicarbonate and then water, dried over anhydrous magnesium sulfate, and evaporated to give a pink solid. Recrystallization from ether–petroleum ether gave the product as long silky fibers: mp 115–116 °C; yield 11.5 g (96%). Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.35; N, 4.65. Found: C, 67.90; H, 6.41; N, 4.62. IR (CH_2Cl_2) 1740, 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.96 (s, 6 H), 2.25 (s, 3 H), 5.00 (s, 2 H), 5.26 (s, 2 H), 7.28 (br s, 5 H), 9.5 (br s, 1 H); MS, *m/e* 301.

5-((Benzyloxy)carbonyl)-5′-((*tert*-butyloxy)carbonyl)-3,3′,4,4′-tetramethyl-2,2′-dipyrromethane (23). 2-((*tert*-Butyloxy)carbonyl)-3,4-dimethylpyrrole (**21**) (1.95 g, 0.010 mol) was dissolved in a buffered solution consisting of anhydrous sodium acetate (2.5 g) and acetic acid (50 mL) at room temperature. To the solution was added the ((acetoxy)methyl)pyrrole (**22**) (3.0 g, 0.010 mol). The mixture was stirred and heated at 150 °C in an oil bath. In 1 min, all the solids dissolved to give a red solution. Then the reaction flask was raised such that its bottom just touched the oil bath. After half an hour, the reaction mixture was poured into water (500 mL) and allowed to stand at room temperature overnight. This was then extracted twice with chloroform (total 600 mL). The combined organic extracts were washed with 0.5 N $NaHCO_3$ (200 mL) and water, dried ($MgSO_4$), and evaporated to leave a dark red residue that was taken up in petroleum ether (60 mL). Two crops of crystals were collected: total yield 3.6 g (84%). Recrystallization from dichloromethane–petroleum ether gave material with mp 132.5–134 °C. Anal. Calcd for $C_{16}H_{32}N_2O_4$: C, 71.52; H, 7.39; N, 6.46. Found: C, 71.33; H, 7.47; N, 6.24. IR (CH_2Cl_2) 1675 cm^{-1}; NMR ($CDCl_3$) δ 1.47 (s, 9 H), 1.93 (s, 6 H), 2.23 (s, 3 H), 2.25 (s, 3 H), 3.76 (s, 2 H), 5.23 (s, 2 H), 7.27 (s, 5 H), 9.38 (br, 1 H), 9.95 (br, 1 H); MS, *m/e* 436, 380, 91.

5-((Benzyloxy)carbonyl)-3,3′,4,4′-tetramethyl-2,2′-dipyrromethane (24). The dipyrromethane diester **23** (4.4 g) was added to trifluoroacetic acid (35 mL), and the mixture was stirred until solution was complete. Nitrogen was bubbled through the solution for 1.5 h, during which time some precipitate formed. Solvent was removed, the residue was dissolved in dichloromethane, and the solution was washed with 1 M Na_2CO_3 and water and dried ($MgSO_4$). Removal of solvent left a residue that was dissolved in petroleum ether (15 mL) and refrigerated overnight. Two crops (2.1 g, mp 83–84 °C and 0.8 g, mp 79–83 °C) of small prisms were collected: total yield 85%; IR ($CHCl_3$ 1695, 1684 cm^{-1}; NMR ($CDCl_3$) δ 1.95 (s, 9 H), 2.25 (s, 3 H), 3.83 (s, 2 H), 5.23 (s, 2 H), 6.38 (br s, 1 H), 7.35 (s, 5 H), 7.9 (br s, 1 H), 9.3 (br s, 1 H); MS, *m/e* 336. Anal. Calcd for $C_{21}H_{24}N_2O_2$: C, 74.97; H, 7.19; N, 8.33. Found: C, 74.88; H, 7.27; N, 8.01.

5-((Benzyloxy)carbonyl)-3,3′,4,4′-tetramethyl-5′-(5-((benzyloxy)carbonyl)-3,4-dimethylpyrrol-2-yl)-2,2′-dipyrromethene Hydrochloride (26). The dipyrromethane **24** (2.00 g, 5.95 mmol) and the pyrrolecarboxaldehyde **25**[45] (1.05 g, 5.84 mmol) were dissolved in dichloromethane (500 mL). Gaseous hydrogen chloride was bubbled through the solution for 30 s, and the solution was allowed to stand at room temperature for 10 min with occasional swirling. The solvent was removed at reduced pressure, followed by addition and removal of a portion of dry benzene. Crystallization of the resulting red solid from dichloromethane–petroleum ether gave red, fluffy crystals: mp 155–160 °C dec; yield 3.1 g (86%). Recrystallization from the same solvent system gave mp 156–158 °C dec. Anal. Calcd for $C_{36}H_{38}ClN_3O_4$: C, 70.63; H, 6.26; N, 6.86; Cl, 5.70. Found: C, 70.69; H, 6.29; N, 6.81; Cl, 5.71. IR (CH_2Cl_2) 1705, 1695, 1615 cm^{-1}; NMR ($CDCl_3$) δ 2.03 (s, 6 H), 2.30 (s, 12 H), 4.35 (s, 2 H), 5.30 (s, 2 H), 5.50 (s, 2 H), 7.2–7.8 (m, 11 H), 11.1 (s, 1 H), 13.3 (s, 1 H), 15.7 (s, 1 H); MS, *m/e* 575 (free base), 91; UV–vis ($CHCl_3$) δ_{max} (ϵ) 499 (40 740), 280 (22 200), 256 nm (23 300).

7,8,12,13,17,18-Hexamethylsapphyrin (31). Tripyrrane diacid **15** was prepared by reduction of **26** (9 mg, 0.015 mmol) as described above. The product was dissolved in several milliliters of ethanol and added to a solution of 5,5′-diformyl-2,2″-bipyrrole (**32**, 3 mg, 0.016 mmol) in absolute ethanol (15 mL). *p*-Toluenesulfonic acid hydrate (46 mg) in absolute ethanol (ca. 2 mL) was added, and oxygen was bubbled through the solution immediately. Within 30 min the solution became green. The solution was stirred for 36 h at room temperature, evaporated in vacuo, and the residue was chromatographed with chloroform on grade I neutral alumina (9 g). Collection of the bright green fractions gave, after evaporation of solvent, 4.8 mg (71%): MS, *m/e* 459, 229.5; vis ($CHCl_3$, freed of ethanol) λ_{max} 677, 665, 617, 452, 430 sh.

Another synthesis[6] of **31** was effected, in low yield, by an unsymmetric variation of the 3 + 2 route.

5,5′-Diformyl-2,2′-bipyrrole (32). A cold, stirred solution of 2,2′-bipyrrole[15] (61 mg, 0.46 mmol) in dry *N,N*-dimethylformamide (2.5 mL), under nitrogen, was treated with phosphorus oxychloride (0.15 mL, 250 mg, 1.63 mmol). The solution was stirred for 1 h in a warm-water bath and poured into water (50 mL) containing sodium acetate (6 g). This mixture was heated on the steam bath for 0.5 h and then refrigerated overnight. The precipitated yellow solid was collected and sublimed at 200 °C (0.1 torr) to give the dialdehyde (66 mg, 76%): mp 258–260 °C dec.

Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.82; H, 4.28; N, 14.89. Found: C, 63.83; H, 4.40; N, 14.87. IR (KBr) 3330, 1690 cm^{-1}; NMR (CD_3SOCD_3) δ 7.0–7.3 (m, 4 H), 9.65 (s, 2 H), 12.49 (br s, 2 H); MS *m/e* 188; UV (CH_3OH) λ_{max} (ϵ) 3777 (25 250), 362 (25 300), 250 (5730).

Method A. 2-(2-Cyano-2-(methoxycarbonyl)vinyl)-5-formyl-3,4-dimethylpyrrole[24] (47). The following procedure proved to be easier and less dangerous than that reported in the literature.[24] Phosphorus oxychloride (1.67 mL) was injected over about 1 min into a flask closed by a serum cap and containing ice-cold *N,N*-dimethylformamide (10 mL, distilled from calcium hydride) under dry nitrogen. The mixture was added over 15 min with mechanical stirring to a solution of 2-(2-cyano-2-(methoxycarbonyl)vinyl)-3,4-dimethylpyrrole[24] (**50**) (1.021 g) in dry *N,N*-dimethylformamide (20 mL) cooled in ice and under nitrogen. After the addition the ice bath was removed, and stirring was continued for 4 h. The mixture was then poured into an aqueous solution (250 mL) of anhydrous sodium acetate (12 g), stirred briefly, and kept at ca. 3 °C overnight. The crystalline product (1.1 g) was pure enough for use in preparation of 2,5-diformyl-3,4-dimethylpyrrole (**13**) as described previously:[24] mp 158–160 °C; NMR ($CDCl_3$) δ 10.0 (br s, 1 H), 9.88 (s, 1 H), 8.07 (s, 1 H), 3.94 (s, 3 H), 2.31 (s, 3 H), 2.21 (s, 3 H); IR ($CHCl_3$) 3460, 2227, 17724, 1667, 1592 cm^{-1}.

Method B. 2-(2-Cyano-2-(methoxycarbonyl)vinyl)-3,4,5-trimethylpyrrole[27] (**46**) (6.60 g, 0.030 mol) was dissolved in dichloromethane (100 mL), and a solution of sulfuryl chloride (8.64 g, 5.2 mL, 0.064 mol) in dichloromethane (100 mL) was added over 1 h at room temperature. The resulting solution was refluxed briefly (steam bath) and then evaporated to dryness in vacuo.

The resulting solid 5-(dichloromethyl)pyrrole was warmed in tetrahydrofuran (100 mL) and treated with water (25 mL). After heating for ~10 min, the organic phase was isolated. The aqueous phase was extracted once with ethyl acetate (100 mL) and discarded. The combined organic phases were evaporated and the solids recrystallized from

(45) Badger, G. M.; Ward, A. D. *Aust. J. Chem.* **1964**, *17*, 649.

ethanol-water: yield 3.42 g (first crop) (48.7%).

5,5'-Bis(2-cyano-2-(ethoxycarbonyl)vinyl)-3,3',4,4'-tetramethyl-2,2'-bipyrrole (56). 2-(2-Carbethoxy-2-cyanovinyl)-5-iodo-3,4-dimethylpyrrole[27] (**55**) (3.44 g, 0.010 mol) was dissolved in *N,N*-dimethylformamide (20 mL) in a loosely stoppered Erlenmeyer flask. Copper bronze (5 g, BDH) was added at room temperature, and the stirred suspension was heated slowly. The original green color became orange-brown after the addition of the copper. As the solution was warmed, yellow solids (presumably the copper chelate of the iodopyrrole) crystallized out, making the copper bronze appear to clot. Iodine crystals (ca. 0.2 g) were added to activate the copper bronze. The mixture was then heated to, and just maintained at, the boiling point, with continued stirring, for 1 h.

The yellow solids redissolved, and a permanent deep burgundy-red color set in as the reaction progressed. The mixture was allowed to cool somewhat, before being diluted with tetrahydrofuran (100 mL) and filtered to remove the excess copper. The solids were rinsed with tetrahydrofuran (300-400 mL) until the washings were nearly colorless and then with a solution of concentrated hydrochloric acid (20 mL) in THF (80 mL) and finally with water (400 mL), all of the washings and filtrates being collected together. The solids deposited from the aqueous solution were collected and rinsed with water. The bipyrrole is a striking purple color; in an especially finely divided form, the color is a pure Harvard crimson. If any bipyrrole appeared to remain in solution (a red color), it was recovered by further aqueous dilution. Addition of yet more water allowed the recovery of a modest quantity of the deiodinated monomer, 2-(2-cyano-2-(ethoxycarbonyl)vinyl)-3,4-dimethylpyrrole.[24]

The combined solids were boiled with dichloromethane (300-400 mL) in several portions and filtered hot, to remove gray cuprous iodide, which was rinsed until the filtrates were only pale orange. The solvent was displaced with ethanol at the boiling point and concentrated to approximately 50 mL, before being allowed to cool. The solids, most of which had crystallized during the concentration, were collected and rinsed with ethanol and then hexane. The yield of dark purple fluffy needles was 0.76 g (35%).

An analytical sample was recrystallized from dichloromethane-95% ethanol: mp infusible below 300 °C. Anal. Calcd for $C_{24}H_{26}N_4O_4$: C, 66.34; H, 6.03; N, 12.90. Found: C, 65.90; H, 5.95; N, 12.75. IR (KBr) 3400, 2200, 1710, 1570 cm^{-1}; MS, *m/e* 434; NMR (CF_3CO_2H) δ 1.47 (t, J = 7 Hz, 6 H), 2.33 (s, 12 H), 4.50 (q, J = 7 Hz, 4 H), 8.26 (s, 2 H), 9.72 (s, 2 H).

Preparation of a Zn(II) Derivative of Decamethylsapphyrin (57). Decamethylsapphyrin (**12**) (55 mg, 0.10 mmol) in chloroform (80 mL) was heated to reflux for 1 h and then allowed to cool to room temperature. A solution containing zinc acetate dihydrate (100 mg), anhydrous sodium acetate (120 mg), and methanol (3 mL) was added. The resulting solution was stirred at room temperature for 4 h and then allowed to stand at room temperature for 1 day. Chloroform (80 mL) was added and the solution was washed twice with water (20 mL) and dried over a small amount of anhydrous magnesium sulfate. The solution was evaporated to give a sparkling solid that was in turn dissolved in chloroform and put in a desiccator containing petroleum ether. Several days later, the crystals were collected: yield 37 mg; IR (KBr) 1590 cm^{-1}; vis ($CHCl_3$) λ_{max} 696, 681, 630, 584, 462 nm; MS (see above).

Preparation of Cobalt(II) Decamethylsapphyrin (58). To methanol (10 mL) were added $CoCl_2 \cdot 6H_2O$ (100 mg, 0.42 mmol) and anhydrous sodium acetate (360 mg, 4.4 mmol). The mixture was stirred thoroughly, and NaCl was removed by filtration. Decamethylsapphyrin (**12**) (50 mg, 0.097 mmol) was added to chloroform (80 mL), heated at reflux for 1 h, and allowed to cool to room temperature. The two solutions were combined, stirred for 1 h, and then allowed to stand at room temperature for 2 days. Chloroform (40 mL) was added and the resulting solution was extracted with water (15 mL). The organic layer was dried over $MgSO_4$ and concentrated to 10 mL. This solution was placed in a desiccator containing petroleum ether. After 5 days (when the volume of solution had increased to 18 mL), 33 mg of sparkling, dark blue crystals were collected: vis ($CHCl_3$) λ_{max} 692, 638, 595, 468 nm.

Acknowledgment. We thank the National Institutes of Health (GM04229 (R.B.W.) and GM29198 (D.D.)) and the Canadian Natural Sciences and Engineering Research Council for financial support. M.M.K. thanks the N.I.H. for a predoctoral fellowship (1966-1970). The work reported here is taken in part from the Harvard Ph.D. Theses of M.M.K., 1970, and J.B.P. III, 1973.

Registry No. 2, 86568-79-8; **4**, 86568-80-1; **6**, 86584-08-9; **12**, 86568-81-2; **13**, 51952-99-9; **14**, 86568-82-3; **15**, 86568-83-4; **16**, 4424-76-4; **17**, 86568-84-5; **18**, 86568-85-6; **19**, 86568-86-7; **20**, 86568-87-8; **21**, 50634-34-9; **22**, 65038-94-0; **23**, 86568-88-9; **24**, 86568-89-0; **25**, 59435-08-4; **26**, 86568-90-3; **30**, 86584-09-0; **31**, 86568-91-4; **32**, 86568-92-5; **39**, 2199-46-4; **46**, 59435-00-6; **47**, 59700-08-2; **50**, 59434-99-0; **55**, 59435-16-4; **56**, 86568-93-6; **57**, 86568-98-1; **58**, 86568-99-2; sapphyrin dihydrochloride, 86568-94-7; decamethylsapphyrin dihydrochloride, 86568-95-8; 2-((benzyloxy)carbonyl)-3,4-dimethyl-2-chloroformylpyrrole, 86568-96-9; 2,2'-dipyrrole, 10087-64-6; 2-(2-cyano-2-(methoxycarbonyl)vinyl]-5-dichloromethyl-3,4-dimethylpyrrole, 86568-97-0; 2-(2-cyano-2-(methoxycarbonyl)vinyl)-3,4-dimethylpyrrole, 59434-99-0.

Electron Spin Resonance and Chemical Studies on the 6-(Trimethylsilyl)cyclohexadienyl and Related Radicals[1]

Mitsuo Kira, Hisashi Sugiyama, and Hideki Sakurai*

Contribution from the Department of Chemistry, Tohoku University, Sendai 980, Japan. *Received March 28, 1983*

Abstract: Various 3,6-disubstituted cyclohexadienyl radicals were generated and investigated by ESR at low temperature. Analysis of the ESR parameters indicated that the significant out-of-plane deformation of the carbon framework of 6-Me_3Si- and 6-Me_3Ge-substituted cyclohexadienyl radicals (**1**, **6**, and **7**) occurred to gain stabilization due to the effective hyperconjugation between the substituted methylene pseudo-π orbital and the π SOMO, while the 6-unsubstituted (**2**, **3**, and **4**) and 6-*t*-Bu (**5**) cyclohexadienyl radicals were essentially planar. Investigation of the fate of the 3,6-bis(trimethylsilyl)cyclohexadienyl radical (**6**) showed strong evidence for the temperature-dependent reversibility of the silyl radical addition to aromatics. The spontaneous elimination of the trimethylsilyl radical from **6** was proved by spin-trapping experiments.

Cyclohexadienyl and a wide variety of substituted cyclohexadienyl radicals have been studied by ESR spectroscopy.[2-12] One of the interesting features of cyclohexadienyl radicals is the large hyperfine splitting constants (hfsc's) of the methylene protons

(1) Part 178: Chemistry of Organosilicon Compounds.

(2) (a) Fischer, H. *Kolloid Z. Z. Polym.* **1962**, *180*, 64. (b) *Z. Naturforsch. A*, **1962**, *17*, 693. (c) *J. Chem. Phys.* **1962**, *37*, 1094.

(3) (a) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *38*, 773. (b) *Ibid.* **1963**, *39*, 2147. (c) Ohnishi, S.-I.; Tanei, T.; Nitta, I. *Ibid.* **1962**, *37*, 2402.

0002-7863/83/1505-6436$01.50/0 © 1983 American Chemical Society