of the integrated intensities of H-4,4′ of **2e** with twice that of H-1 of **4e**.[16]

***N*-Carbobenzoxy-2-oxa-3-oxo-6-aza-7-*endo*-methylbicyclo[3.2.2]nonane (2f) and *N*-Carbobenzoxy-2-oxo-3-oxa-6-aza-7-*endo*-methylbicyclo[3.2.2.]nonane (4f).** *N*-Carbobenzoxy-3-*endo*-methyl ketone **1f** (152 mg, 0.55 mmol) after 64 h afforded 140 mg of a mixture. Preparative TLC (1:1 hexane/ether) afforded at R_f 0.31 ketone **1f** (18 mg), at R_f 0.11 was 82 mg (51%) of lactone **2f** [NMR ($CDCl_3$) δ 7.45 (s, 5 H), 5.23 (s, 2 H), 4.7–4.4 (m, 2 H), 4.15 (br, H-7x), 2.95 (td, H-4,4′), 2.6–1.5 (br, 4 H), 1.40 (d, J = 7 Hz, 3 H);[17] IR (neat) 1690, 1730 cm^{-1}; high-resolution mass spectrum, m/e 289.1293, (calcd for $C_{16}H_{19}NO_4$ 289.1314)], and at R_f 0.13 was 19 mg (12%) of lactone **4f**: NMR ($CDCl_3$) δ 7.39 (s, 5 H), 5.21 (s, 2 H), 4.93–4.53 (m, H-5), 4.33 (m, H-4,4′), 4.03 (br, H-7x), 3.05 (m, H-1), 2.43–1.53 (br, 4 H), 1.34 (d, J = 6 Hz, 3 H); high-resolution mass spectrum, m/e 289.1307, calcd for $C_{16}H_{19}NO_4$ 289.1314. It was not possible to accurately determine the ratio **2f**/**4f** from the NMR spectrum of the crude reaction mixture because of overlap of H-1 of **4f** with H-4 of **2f**.

(16) Professor A. Holmes, University Chemical Laboratory, Cambridge, has found a 65:35 ratio of **2e**/**4e** with *m*-chloroperbenzoic acid/sodium bicarbonate (46% yield); personal communication.

(17) An NMR comparison of **2f** with a spectrum of the corresponding *N*-carbethoxy analogue provided by Professor M. Natsume, Research Foundation Itsuu Laboratory, Tokyo, Japan, was positive (see ref 3).

Lactones 2g and 4g. *N*-Carbobenzoxy-3-*endo*-carbomethoxy ketone **1g** (75 mg, 0.23 mmol) after 72 h afforded 90% unreacted ketone **1g**. After 3 weeks, 70 mg of a mixture was obtained which upon preparative TLC afforded 11 mg of ketone **1g**, 21 mg (32%; R_f 0.21) of lactone **2g** and 34 mg (53%; R_f = 0.32) of lactone **4g**. A ratio of **2g**/**4g** could not be accurately determined by proton NMR analysis of the crude reaction mixture.

Acknowledgment. We gratefully acknowledge technical assistance of Kevin Cannon.

Registry No. **1a**, 69386-57-8; **1b**, 83681-60-1; **1c**, 83681-61-2; **1d**, 65961-22-0; **1e**, 65961-25-3; **1f**, 83681-62-3; **1g**, 83709-53-9; **2a**, 69386-58-9; **2b**, 83681-63-4; **2c**, 83681-64-5; **2d**, 83681-65-6; **2e**, 83681-66-7; **2f**, 83681-67-8; **2g**, 83709-54-0; **4a**, 69386-59-0; **4b**, 83681-69-0; **4c**, 83681-70-3; **4d**, 65961-28-6; **4e**, 65961-29-7; **4f**, 83681-68-9; **4g**, 83709-55-1; PAA, 79-21-0; MCPBA, 937-14-4; trifluoroacetic anhydride, 407-25-0.

Supplementary Material Available: Spectral data, experimental details, and analytical data are available for **1b,c,f,g**, for the trifluoroperacetic acid and *p*-nitroperbenzoic acid oxidations of **1a**, for the preparation of the *N*-carbophenoxy- and *N*-(2,2,2-trichloroethoxy)carbonyl analogues of **1a** and the oxidation of these, and for the *N*-carbethoxy analogues of **1a** with peracetic and *m*-chloroperbenzoic acids (11 pages). Ordering information is given on any current masthead page.

Synthesis of (Polyfluoroalkyl)pyrroles and -porphyrins

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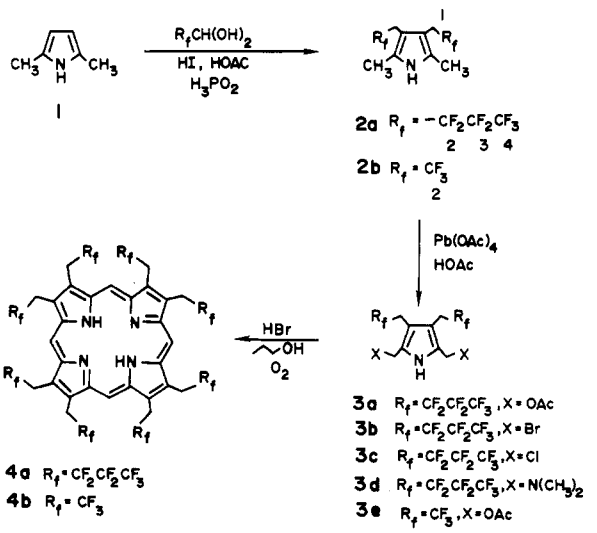
Octakis(1*H*,1*H*-heptafluorobut-1-yl)porphyrin **4a** has been prepared by acid-catalyzed self-condensations of 2,5-disubstituted acetoxymethyl, bromomethyl, and chloromethyl derivatives of 2,5-dimethyl-3,4-bis(1*H*,1*H*-heptafluorobut-1-yl)pyrrole (**2a**). The 2,5-bis[(dimethylamino)methyl] derivative **3e** failed to undergo a similar conversion to **4a**. Octakis(1*H*,1*H*-trifluoroeth-1-yl)porphyrin **4b** was prepared from the bis(acetoxymethyl)pyrrole **3e**, the lead tetraacetate oxidation product of **2b**. Pyrroles **2a,b** were obtained from the reductive alkylation of 2,5-dimethylpyrrole with the corresponding polyfluoro aldehyde hydrates. An alternate, more efficient conversion to porphyrin **4a** was achieved by the acid-catalyzed condensation of formaldehyde with 2,5-diiodopyrrole **6**. Pyrrole **6** was readily obtained from **2a** by oxidation with excess sulfuryl chloride and hydrolysis in aqueous THF followed by iodinative decarboxylation of the intermediate dicarboxypyrrole **5**.

In connection with a research program directed toward the preparation of perfluorinated porphyrins we report facile syntheses of octakis(1*H*,1*H*-heptafluorobut-1-yl)-porphyrin **4a** and octakis(1*H*,1*H*-trifluoroeth-1-yl)-porphyrin **4b**, two novel, polyfluorinated analogues of octabutyl and octaethylporphyrin. Each synthesis employs a functionalized derivative of the 2,5-dimethyl-3,4-bis-(polyfluoroalkyl)pyrroles **2a,b** as key intermediates in unprecedented pyrrole condensations leading to porphyrin.

Pyrroles **2a,b** were obtained from readily available 2,5-dimethylpyrrole by reductive alkylation with heptafluorobutyraldehyde hydrate and trifluoroacetaldehyde hydrate (Scheme I). This general alkylation procedure which is an extention of the pyrrole alkylations described by MacDonald[1,2] has proven to be of great utility in the preparation of tetrasubstituted pyrroles.

The oxidation of **2a,b** with lead tetraacetate in acetic acid at room temperature afforded the stable bis(acetoxymethyl) derivatives **3a,e** in nearly quantitative yields. Heating of **3a,e** under reflux with HBr in aqueous alcohol in the presence of oxygen provided porphyrins **4a,b**, which precipitated from the reaction mixture in 20% and 31% yields, respectively.

Scheme I

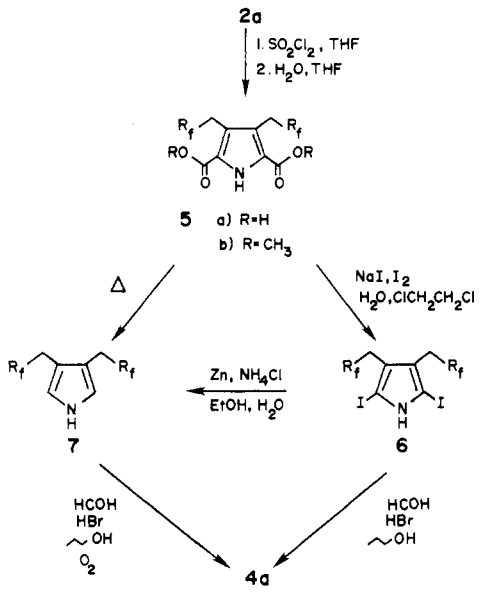


(1) Gregorovich, B. V.; Liang, K. S. Y.; Clugston, D. M.; MacDonald, S. F. *Can. J. Chem.* **1968**, *46*, 3291.

(2) Roomi, M. N.; MacDonald, S. F. *Can. J. Chem.* **1970**, *48*, 139.

0022-3263/82/1947-5243$01.25/0

Scheme II



Dipyrromethanes and porphyrins have traditionally been prepared from mono(acetoxymethyl)pyrroles,[3,4] but to our knowledge this represents the first synthesis of a porphyrin directly from a bis(acetoxymethyl)pyrrole. The key mechanistic steps of the reaction are envisioned to be similar to the ones proposed for the formation of dipyrromethanes,[5] which involves the acid-catalyzed solvolysis of the acetoxymethyls followed by self-condensation with elimination of formaldehyde.

An investigation of other sources of pyrrylcarbinyl cations, suitable for the synthesis of **4a**, revealed **3a** to be the most practical precursor, due to its ease of preparation, stability, and yield of porphyrin. Bis(bromomethyl)pyrrole **3b** was prepared by refluxing a solution of **2a** and excess *N*-bromosuccinimide in carbon tetrachloride. The pyrrole was identified by ^1H NMR (CCl_4) of the crude reaction mixture and featured a broad triplet for C-1 at δ 3.20 (J = 20 Hz) and a singlet at δ 4.40 for the bromomethyl substituents. Rapid decomposition of the reaction mixture during workup, however, made isolation of **3b** difficult. The synthesis of the bis(chloromethyl) analogue **3c** proved to be equally unfavorable. Treatment of **2a** with 2 equiv of sulfuryl chloride CH_2Cl_2 at 0 °C gave **3c** as indicated by ^1H NMR (a broad triplet at δ 3.22 and a singlet at δ 4.53), but the reaction was consistently contaminated with either α-methyl- (at δ 2.30) or (dichloromethyl)- (at δ 6.63) pyrroles.[6] Heating of both **3b** and **3c** under reflux with HBr in 1-propanol did afford porphyrin **4a**; however, the yields were lower than for the corresponding reaction of bis(acetoxymethyl)pyrrole **3a**.

The stable bis[(dimethylamino)methyl]pyrrole **3d** was prepared by the reaction of α-unsubstituted pyrrole **7** with excess *N,N*-dimethylmethyleneammonium bromide[7] in refluxing dichloroethane. Its structure was confirmed by mass and ^1H and ^{13}C NMR spectral data. The reaction of **3d** with HBr under the conditions described above gave no evidence of porphyrin formation. However, addition of an equimolar amount of **7** to the same reaction mixture resulted in the formation of **4a**. This suggests that self-condensation of **3d** is inhibited by deactivation of the pyrrole ring, possibly due to protonation of the second (dimethylamino)methyl substituent.

An overall more efficient and equally convenient approach to the synthesis of porphyrin **4a** is summarized in Scheme II.[8] Oxidation of **2a** with excess sulfuryl chloride in refluxing THF[9] and hydrolysis of the intermediate bis(trichloromethyl)pyrrole with aqueous THF gave dicarboxypyrrole **5a** in 80% yield. Similarly, pyrrole **2a** was converted quantitatively to bis(carbomethoxy)pyrrole **5b** when solvolysis of the chlorination product was carried out with aqueous methanol. However, conversion of **5b** to **5a** was found to be inefficient under a variety of conditions. Thermal decarboxylation of **5a** at elevated temperatures (240–250 °C) was accompanied by considerable destruction of the pyrrole nucleus. A more practical procedure proved to be iodinative decarboxylation with sodium triiodide in 1,2-dichloroethane and water,[10] which provided a nearly quantitative conversion to diiodopyrrole **6**.

Our initial strategy required reduction of **6** to the α-free pyrrole **7** and subsequent condensation to porphyrin **4a**. The former was readily accomplished by catalytic hydrogenolysis with platinum oxide or by reduction with zinc dust and ammonium chloride in aqueous ethanol.[11] As we have reported earlier, the formation of porphyrins by means of acid-catalyzed condensations of α-free pyrroles with formaldehyde in alcoholic solvents is feasible with electron-donating[12] as well as with certain electron-withdrawing substituents[13] in the 3,4-positions of the pyrrole. 3,4-Bis(trifluoromethyl)pyrrole[14] is unreactive under such conditions; however, the deactivation of the pyrrole ring in **7** is moderated by the methylene carbon in the 1*H*,1*H*-heptafluorobutyl side chains. The reaction of **7** with formaldehyde in acidified 1-propanol and subsequent air oxidation for 21 days provided porphyrin **4a** in 30% yield.

Treibs reported the formation of dipyrromethenes from monoiodopyrroles and various aldehydes.[11] An extension of this method to the synthesis of porphyrins from diiodopyrroles was investigated. It was found that reaction of **6** with formaldehyde and HBr in refluxing 1-propanol provided **4a** in 31% yield. The porphyrin precipitated during the course of the reaction and was collected by filtration in an essentially pure form. Allowing the filtrate to stand exposed to air for 14 days provided another 4% of **4a**. This procedure obviates the usual prolonged air oxidation and completes an efficient four-step synthesis of **4a**.

The ^1H NMR spectra of all compounds containing polyfluorobutyl substituents include a distinctive broad

(3) Siedel, W.; Winkler, F. *Justus Liebigs Ann. Chem.* **1943**, *554*, 162.
(4) Johnson, A. W.; Kay, I. T.; Markham, E.; Price, R.; Shaw, K. B. *J. Chem. Soc.* **1959**, 3416. Clezy, P. S.; Liepa, A. J. *Aust. J. Chem.* **1970**, *23*, 2443.
(5) Paine, J. B., III. "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, **1978**; Vol. 1, p 168.
(6) 2,5-Diformyl-3,4-bis(1*H*,1*H*-heptafluorobut-1-yl)pyrrole, a potential precursor in the synthesis of expanded porphyrin macrocycles, platyrins (Berger, R. A.; LeGoff, E. *Tetrahedron Lett.* **1978**, 4225), was obtained from the hydrolysis of the corresponding 2,5-bis(dichloromethyl)pyrrole, a stable solid isolated from the reaction of **2a** with excess SO_2Cl_2 in CH_2Cl_2 at 0 °C.
(7) Böhme, H.; Hilp, M.; Koch, L.; Ritter, E *Chem. Ber.* **1971**, *104*, 2018.
(8) Porphyrin **4b** was also prepared by this method, however in lower overall yield than from **3e**.
(9) See ref 5, pp 160–162.
(10) Battersby, A. R.; Hunt, E.; McDonald, E.; Paine, J. B., III; Saunders, J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1008.
(11) Treibs, A.; Kolm, H. G. *Justus Liebigs Ann. Chem.* **1958**, *614*, 176.
(12) (a) Cheng, D. O.; LeGoff, E. *Tetrahedron Lett.* **1977**, 1469. (b) Chamberlin, K. S.; LeGoff, E. *Heterocycles* **1979**, *12*, 1567.
(13) These include monoacyl and monoester alkylpyrroles (see ref 12a and: Chamberlin, K. S.; LeGoff, E. *Synth. Commun.* **1978**, 579) and bis(*N,N*-dialkylcarboxamide)pyrroles (Kaesler, R. W.; LeGoff, E., submitted for publication in *J. Org. Chem.*).
(14) The syntheses of 3,4-bis(trifluoromethyl)pyrroles have been described: Leroy, J.; Cantacuzene, D.; Wakselman, C. *Synthesis* **1982**, 313. Kaesler, R. W.; LeGoff, E. *J. Org. Chem.* **1982**, *47*, 4779.

triplet for the C-1 methylene, a result of long-range coupling with adjacent fluorines. Similarly, a broad quartet is observed for pyrroles **2b** and **3e** and porphyrin **4b**. The ^{13}C proton-decoupled NMR spectra for the pyrrolic intermediates[15] show two singlet resonances at 106–128 ppm (72.29 ppm for α-C in **6**) characteristic of α and β pyrrole carbons. The 1*H*,1*H*-heptafluorobutyl substituents give a distinctive ^{13}C–^{19}F coupling pattern which at 62.9 MHz is recognized as a triplet assigned to C-1, a triplet of triplets assigned to C-2, a triplet of quartets of multiplets assigned to C-3, and a quartet of triplets assigned to C-4. A considerably less complicated ^{13}C–^{19}F coupling pattern is observed for the trifluoroethyl substituents in **2b** and **3e**. Both C-1 and C-2 give quartets with characteristic coupling constants of 31 and 276 Hz, respectively.

The visible spectra of porphyrins **4a,b** display an unexpected phyllo-type absorption which is in sharp contrast to the etio-type absorption observed for octabutyl-[12b] and octaethylporphyrin.[16] An etio absorption is the pattern normally associated with porphyrins of high substitution and symmetry.[16]

Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (Nujol mull) were obtained on a Perkin-Elmer 237 grating spectrophotometer. Electronic absorption spectra were measured on a Cary 219 spectrophotometer. Mass spectra were obtained on a Finnigan 4000 instrument at 70 eV. NMR (in $CDCl_3$ or as noted with Me_4Si as an internal standard) were recorded on a Bruker WM-250 instrument (^1H NMR at 250 MHz and ^{13}C NMR at 62.9 MHz). Elemental analyses were performed by Galbraith Laboratories, Inc. 2,5–Dimethylpyrrole was purchased (Aldrich) or prepared as previously described.[17] $Pb(OAc)_4$ was freshly prepared,[18] and heptafluorobutyraldehyde hydrate and trifluoroacetaldehyde hydrate were commercially available (Columbia) and used without further purification.

2,5-Dimethyl-3,4-bis(1*H*,1*H*-heptafluorobut-1-yl)pyrrole (2a). According to the general procedure of MacDonald,[2] a solution of **1** (8.20 g, 86.3 mmol) and heptafluorobutyraldehyde hydrate (46.6 g, 2.5 equiv) in acetic acid (100 mL), 47% HI (100 mL), and 58% H_3PO_2 (20 mL) was magnetically stirred under a nitrogen atmosphere at 100 °C for 3.5 h. The dark red solution was diluted with water (100 mL) and CH_2Cl_2 (100 mL) and cooled in an ice bath. NH_4OH (400 mL) was added slowly with stirring, and the mixture was extracted with CH_2Cl_2. The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated. Distillation (0.08 mm, 68 °C) of the resulting dark red oil gave 25.4 g (64%) of **2a** as a colorless oil which solidified upon standing. An analytical sample was obtained by recrystallization from hexane: mp 32.5–33.0 °C; ^1H NMR δ 2.18 (6 H, s), 3.15 (4 H, t, J = 19.9 Hz), 7.69 (1 H, br s); ^{13}C NMR δ 11.28, 26.15 (t, J = 23.3 Hz), 106.72, 109.41 (tqm, J = 261.5, 39.0, ~2 Hz), 117.22 (tt, J = 251.6, 31.5 Hz), 118.21 (qt, J = 286.2, 33.3 Hz), 125.98; mass spectrum, m/e (relative intensity) 459 (15, M^+), 290 (100), 120 (34), 69 (17); IR 3525 (NH), 1230 (CF) cm^{-1}. Anal. Calcd for $C_{14}H_{11}NF_{14}$: C, 36.60; H, 2.40. Found: C, 36.40; H, 2.50.

2,5-Dimethyl-3,4-bis(1*H*,1*H*-trifluoroeth-1-yl)pyrrole (2b). The above procedure was followed using **1** (7.00 g, 7.37 mmol) and trifluoroacetaldehyde hydrate (21.4 g, 2.5 equiv) in acetic acid (90 mL), 47% HI (90 mL), and 58% H_3PO_2 (18 mL). Distillation (0.10 mm, 57 °C) gave 7.6 g (40%) of **2b** as a colorless oil which solidified upon standing. An analytical sample was obtained by recrystallization from hexane: mp 53.0–53.5 °C; ^1H NMR δ 2.13 (6 H, s), 3.18 (4 H, q, J = 11.0 Hz), 7.58 (1 H, br s); ^{13}C NMR δ 11.03, 29.57 (q, J = 30.5 Hz), 107.85, 125.42, 126.91 (q, J = 276.5 Hz); mass spectrum, m/e (relative intensity) 259 (35, M^+), 258 (12), 190 (100); IR 3460 (NH), 1270, 1135, (CF) cm^{-1}. Anal. Calcd for $C_{10}H_{11}NF_6$: C, 46.33; H, 4.25. Found: C, 46.46; H, 4.24.

2,5-Bis(acetoxymethyl)-3,4-bis(1*H*,1*H*-heptafluorobut-1-yl)pyrrole (3a). A solution of **2a** (2.00 g, 4.36 mmol) and $Pb(OAc)_4$ (4.26 g, 2.2 equiv) in acetic acid (50 mL) and acetic anhydride (2.0 mL) was stirred under a nitrogen atmosphere at 25 °C for 20 h. CH_2Cl_2 (150 mL) was added, and the solution was washed with water followed by saturated aqueous $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. Recrystallization from CH_2Cl_2–hexane gave 2.40 g (96%) of **3a** as colorless crystals: mp 60–61 °C; ^1H NMR δ 2.07 (6 H, s), 3.31 (4 H, t, J = 19.5 Hz), 5.02 (4 H, s), 9.37 (1 H, br s); ^{13}C NMR δ 20.85, 25.85 (t, J = 24.1 Hz), 56.99, 110.89, 109.40 (tqm, J = 265.2, 37.9, ~2 Hz), 116.61 (tt, J = 252.5, 31.5 Hz), 118.19 (qt, J = 287.6, 34.2 Hz), 127.83, 172.11; mass spectrum, m/e (relative intensity) 575 (4, M^+), 516 (16), 473 (20), 43 (100); IR 3350 and 3250 (NH), 1750 and 1720 (CO), 1220 (CF) cm^{-1}. Anal. Calcd for $C_{18}H_{15}NO_4F_{14}$: C, 37.56; H, 2.61. Found: C, 37.45; H, 2.63.

2,5-Bis(acetoxymethyl)-3,4-bis(1*H*,1*H*-trifluorometh-1-yl)pyrrole (3e). The above procedure was followed by using **2b** (1.00 g, 3.86 mmol) and $Pb(OAc)_4$ (3.8 g, 2.2 equiv) in acetic acid (70 mL) and acetic anhydride (2.0 mL). Recrystallization from CH_2Cl_2-hexane gave 1.40 g (97%) of **3e** as colorless crystals: mp 117.5–118.5 °C; ^1H NMR δ 2.05 (6 H, s), 3.34 (4 H, q, J = 10.8 Hz), 5.03 (4 H, s), 9.23 (1 H, br s); ^{13}C NMR δ 20.79, 29.14 (q, J = 31.5 Hz), 56.84, 111.96, 126.08 (q, J = 276.51 Hz), 127.11, 171.96; mass spectrum, m/e (relative intensity) 375 (7, M^+), 316 (27), 274 (47), 273 (61), 43 (100); IR 3330 (NH), 1750 and 1725 (CO), 1245 (CF), 1145 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO_4F_6$: C, 44.80; H, 4.00. Found: C, 45.01; H, 4.06.

Octakis(1*H*,1*H*-heptafluorobut-1-yl)porphyrin (4a) Prepared from 3a. A solution of **3a** (0.48 g, 0.835 mmol) and 48% HBr (3.0 mL) in 1-propanol (20 mL) was heated at 100 °C for 60 h with a slow stream of O_2 bubbled through the reaction mixture. The solution was allowed to stand in a large open beaker for 14 days. Filtration and recrystallization from acetone gave 0.073 g (20%) of **4a**: mp 282–283 °C: ^1H NMR (acetone-d_6, 80 °C) δ –3.21 (2 H, br s), 5.34 (16 H, t, J = 18.4 Hz), 10.62 (4 H, s); UV–vis (acetone) λ_{max} 627 nm (ϵ_m 1400), 599 (1200), 574 (5900), 529 (4900), 499 (17 800), 402 (294 000); IR 3275 (NH), 2850 (CH), 1220 (CF) cm^{-1}. Anal. Calcd for $C_{52}H_{22}F_{56}N_4$: C, 35.33, H, 1.25. Found: C, 35.38, H, 1.16.

Octakis(1*H*,1*H*-trifluoroeth-1-yl)porphyrin (4b). The above procedure was followed by using **3e** (0.68 g, 1.81 mmol) and 48% HBr (9.0 mL) in 1-propanol (50 mL). Recrystallization from acetone–1-propanol gave 0.135 g (31%) of **4b**: mp >310 °C; ^1H NMR (acetone-d_6) δ –3.33 (2 H, br s), 5.44 (16 H, q, J = 10.5 Hz), 10.85 (4 H, s); mass spectrum, m/e (relative intensity) 966 (31 M^+), 965 (10), 483 (27), 105 (25), 44 (100), 40 (13); UV–vis (acetone) λ_{max} 627 nm (ϵ_m 1500), 599 (1300), 572 (6000), 527 (5100), 498 (17,600), 401 (276,000); IR 3325 (NH), 2850, (CH), 1230 (CF), 1170 cm^{-1}. Anal. Calcd for $C_{36}H_{22}F_{24}N_4$: C, 44.72; H, 2.28. Found: C, 44.77; H, 2.55.

2,5-Dicarboxy-3,4-bis(1*H*,1*H*-heptafluorobut-1-yl)pyrrole (5). To a magnetically stirred 1000-mL flask equipped with an efficient condenser and containing **2a** (7.00 g, 15.3 mmol) in dry THF (30 mL) under a nitrogen atmosphere was added SO_2Cl_2 (12 mL) via pipet as rapidly as possible (vigorous reaction!). This was stirred for 3 min, and additional sulfuryl chloride (6 mL) was added. After 3 min, hot (60 °C) 80% aqueous THF (200 mL) was added (vigorous reaction!) and the solution was refluxed for 3 h. The mixture was poured into water (500 mL) and thoroughly extracted with Et_2O. The Et_2O fractions were combined and extracted with saturated aqueous $NaHCO_3$. The combined $NaHCO_3$ fractions were washed with Et_2O, heated on a steam bath, and slowly acidified with concentrated HCl. After cooling suction filtration and thorough washing with water gave 6.33 g (80%) of **5** as a white powder. An analytical sample was obtained by recrystallization from hexane–Et_2O (20:1): mp 270–272 °C dec; ^1H NMR (acetone-d_6) δ 3.92 (4 H, t, J = 20.0 Hz); ^{13}C NMR δ 26.38 (t, J = 22.6 Hz), 110.09 (tqm, J = 262.6, 37.1, ~2 Hz), 117.67 (tt, J = 253.5, 31.5 Hz), 118.98 (qt, J = 286.8, 33.3 Hz), 119.20, 126.05, 161.52; mass spectrum (CI, CH_4), m/e 520 (M + 1 ion);

(15) Solubility considerations prohibited ^{13}C NMR measurements for porphyrins **4a,b**.

(16) Smith, K. M., Ed. "Prophyrins and Metalloporphyrins"; Elsevier: New York, **1975**; pp 19–23.

(17) Young, D. M.; Allen, C. F. H. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. 2, p 219.

(18) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 537.

IR 3420 (NH), 3150-2460 (OH), 1680 (CO), 1220 (CF) cm^{-1}. Anal. Calcd for $C_{14}H_7NO_4F_{14}$: C, 32.37; H, 1.35. Found: C, 32.46; H, 1.37.

2,5-Diiodo-3,4-bis(1*H*,1*H*-heptafluorobut-1-yl)pyrrole (6). Precautions against direct illumination should be taken during all the following operations. A solution of I_2 (3.0 g) and NaI (3.2 g) in water (14 mL) was added to a flask wrapped in aluminum foil and charged with **5** (1.0 g, 1.93 mmol) and $NaHCO_3$ (1.5 g) in water (40 mL) and $ClCH_2CH_2Cl$ (40 mL). The two-phase mixture was stirred under a nitrogen atmosphere at 25 °C for 48 h. $NaHSO_3$ was added slowly until the red color dissipated, and the solution was extracted with CH_2Cl_2. The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated on a rotatary evaporator, yielding 1.27 g (97%) of **6** as a slightly red solid. This product appeared quite pure by NMR and TCL and was used directly in the preparation of **7** and **4a**. An analytical sample was obtained by recrystallization from petroleum ether (30-60 °C) at -10 °C: mp 78-82 °C dec; ^1H NMR δ 3.28 (4 H, t, J = 19.0 Hz), 8.25 (1 H, br s); ^{13}C NMR δ 29.13 (t, J = 23.1 Hz), 72.29, 109.14 (tqm, J = 264.2, 38.9, ~2 Hz), 116.90 (tt, J = 253.4, 30.5 Hz), 118.07 (qt, J = 290.8, 34.2 Hz), 119.02; mass spectrum, m/e (relative intensity) 683 (58, M^+), 514 (78), 345 (23), 268 (51), 114 (34), 69 (100); IR 3470 (NH), 1230 (CF) cm^{-1}. Anal. Calcd for $C_{12}H_5NF_{14}I_2$: C, 21.08; H, 0.73. Found: C, 21.45; H, 0.80.

3,4-Bis(1*H*,1*H*-heptafluorobut-1-yl)pyrrole (7). A suspension of **6** (1.60 g, 2.34 mmol), zinc dust (1.00 g), NH_4Cl (1.60 g), and 95% EtOH (40 mL) was stirred under a nitrogen atmosphere at 75 °C for 15 h. The excess zinc was filtered and washed with CH_2Cl_2 (20 mL). The filtrate was diluted with water (100 mL) and extracted with CH_2Cl_2. The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated, yielding 0.98 g (98%) of **7** as a pale yellow oil. This product appeared quite pure by NMR and TLC and was used directly in the prepartion of **4a**: ^1H NMR δ 3.24 (4 H, t, J = 19.5 Hz), 6.77 (2 H, d, J = 2.75 Hz), 8.22 (1 H, br s); ^{13}C NMR δ 27.22 (t, J = 23.8 Hz), 109.62 (tqm, J = 263.6, 37.9, ~2 Hz), 110.76, 116.78 (tt, J = 252.5, 30.5 Hz), 118.37 (qt, J = 287.6, 34.2 Hz), 119.53; mass spectrum, m/e (relative intensity) 431 (14, M^+), 412 (8), 262 (100), 142 (15), 93 (31), 69 (39); IR (neat) 3500 (NH), 1220 (CF) cm^{-1}.

Octakis(1*H*,1*H*-heptafluorobut-1-yl)porphyrin (4a) Prepared from 6. A solution of **6** (1.19 g, 1.74 mmol), 37% formaldehyde (8.0 mL), and 48% HBr (2.5 mL) in 1-propanol (70 mL) was heated at 100 °C for 35 h. The mixture was cooled and suction filtered. Recrystallization from acetone gave 0.238 g (31%) of **4a**. The filtrate was allowed to stand in a large open beaker for 14 days. Filtration and recrystallization from acetone gave another 0.030 g (4%) of **4a**.

Octakis(1*H*,1*H*-heptafluorobut-1-yl)porphyrin (4a) Prepared from 7. A solution of **7** (0.78 g, 1.80 mmol), 37% formaldehyde (7.0 mL), and 48% HBr (1.6 mL) in 1-propanol (60 mL) was heated 100 °C for 48 h. The mixture was allowed to stand in a large open beaker for 21 days. Filtration of the reaction mixlture and recrystallization from acetone gave 0.240 g (30%) of **4a**.

Registry No. **1**, 625-84-3; **2a**, 83650-62-8; **2b**, 83664-26-0; **3a**, 83650-63-9; **3b**, 83650-70-8; **3c**, 83650-71-9; **3d**, 83650-72-0; **3e**, 83650-64-0; **4a**, 83650-65-1; **4b**, 83650-66-2; **5a**, 83650-67-3; **6**, 83650-68-4; **7**, 83650-69-5; heptafluorobutyraldehyde, 375-02-0; trifluoroacetaldehyde, 75-90-1; formaldehyde, 50-00-0.

Cycloaddition Reactions of 3-(Phenylthio)-3-buten-2-one: Synthesis of Functionalized Dihydropyran Derivatives and Their Ring-Opening Reactions

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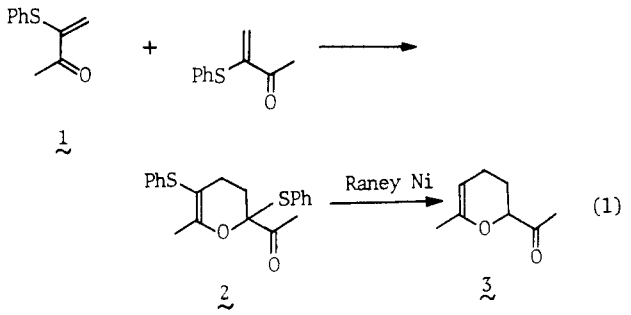
3-(Phenylthio)-3-buten-2-one (**1**) reacted with nucleophilic olefins such as vinyl ethers, vinyl sulfide, and enamine to give 1,4-cycloaddition products and/or Michael adducts **7-17** in fairly good yields. Treatment of 2-acetyl-2,5-bis(phenylthio)-3,4-dihydro-6-methyl-2*H*-pyran (**2**) with various acids or mercury(II) chloride gave the cyclopentanone **19**. In addition, the dimer **2** was converted into 3-(phenylthio)-7-octene-2,6-dione (**23**) by the three steps.

1,4-Cycloaddition reactions of hetero dienes have attracted considerable attention from both synthetic and mechanistic standpoints. Particularly, α,β-unsaturated carbonyl compounds have been utilized in the synthesis of dihydropyrans.[1] However, little is known about reactivities of the enones substituted with functional groups in spite of the likely versatility of the expected adducts. In the course of our studies on annelation reactions,[2] we found that 3-(phenylthio)-3-buten-2-one (**1**) could be quantitatively dimerized and desulfurized to give 2-acetyl-3,4-dihydro-6-methyl-2*H*-pyran (**3**, eq 1). These results prompted us to examine the reactivities of the butenone **1** as a hetero diene with the intent to prepare



(1)

dihydropyrans **5** and/or γ,δ-unsaturated ketones **6** (eq 2). We report here the reaction of 3-(phenylthio)-3-buten-2-one (**1**) with olefinic compounds **4** and the ring opening reactions of the adducts, especially the dimer **2**.

The butenone **1** was treated with ethyl vinyl ether in an autoclave to give 3,4-dihydro-2-ethoxy-6-methyl-5-(phe-

(1) For a review, see: Desimoni, G.; Tacconi, G. *Chem. Rev.* **1975**, *75*, 651.

(2) Takaki, K.; Okada, M.; Yamada, M.; Negoro, K. *J. Org. Chem.* **1982**, *47*, 1200.

0022-3263/82/1947-5246$01.25/0