presence of $Ru_3(CO)_{12}$ and Et_3N[5] (Scheme III). The nucleophilic addition of diethylamine to such an intermediate **8** would take place at the carbonyl to give the 2-oxoalkyl carbamate **2a**. Addition of *n*-propylamine to the intermediate **8** would normally afford the *N*-alkylcarbamate **9**. Cyclization of **9** is then followed to give the 4-hydroxyoxazolidone **10** which on dehydration would give **7**.

α-Methylene cyclic carbonate **8** from propargyl alcohol **1a** is not stable compared with those derived from **1b** or **1c**, and reacts with another molecule of **1a** to give 2-oxoalkyl carbonate[5] in the presence of Et_3N. The high yield of **2a** may be caused by the enhanced nucleophilicity of diethylamine compared with that of the alcohol **1a**, the attack of which prevents **8** from decomposition or polymerization.

Experimental Section

Acetonitrile and amines were dried over P_2O_5 and CaH_2, respectively, and distilled. The other materials were used as purchased.

In a representative reaction, a mixture of acetonitrile (5 mL), $Ru_3(CO)_{12}$ (0.2 mmol), amine (50 mmol), and α-ethynyl alcohol (20 mmol) was placed in a 100-mL autoclave and stirred at 80 °C under 50 kg/cm^2 of initial pressure of CO_2 for 20 h. The amounts of products and unreacted alcohol were determined by GLC (10% FFAP, 2 m). The typical purification method of products was as follows. The reaction solvent was distilled off under reduced pressure, and the resulting residue, dissolved in 20 mL of ether, was washed with 30 mL of dilute HCl solution (3%) several times and with water. The organic layer was dried over $MgSO_4$ for one night. The crude products obtained by evaporating ether were passed through a preparative GLC (10% FFAP, 2 m, 200 °C, 1.5 kg/cm^2 He). The isolated products were identified by using infrared, NMR, and chemical ionization type mass spectra. Elemental analysis was also performed for carbamates and oxazolidones.

2-Oxopropyl *N,N*-diethylcarbamate (2a): IR (neat) 1720 (C=O), 1690 cm^{-1} (NCOO); ^{1}H NMR ($CDCl_3$) δ 1.16 (6 H, t, CH_3, J = 7 Hz), 2.17 (3 H, s, CH_3CO), 3.41 (4 H, q, NCH_2, J = 7 Hz), 4.73 (2 H, s, OCH_2); mass spectrum, m/e 174 ($M^+ + 1$).

Anal. Calcd for $C_8H_{15}NO_3$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.45; H, 8.89; N, 8.09.

1-Methyl-2-oxopropyl *N,N*-diethylcarbamate (2b): IR (neat) 1720 (C=O), 1690 cm^{-1} (NCOO); ^{1}H NMR ($CDCl_3$) δ 1.13 (6 H, t, CH_3, J = 7 Hz), 1.34 (3 H, d, CH_3CH, J = 7 Hz), 2.12 (3 H, s, CH_3CO), 3.29 (4 H, q, CH_2, J = 7 Hz), 4.93 (1 H, q, CH, J = 7 Hz); mass spectrum, m/e 188 ($M^+ + 1$).

Anal. Calcd for $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.48. Found: C, 57.50; H, 9.29; N, 7.42.

1,1-Dimethyl-2-oxopropyl *N,N*-diethylcarbamate (2c): IR (neat) 1720 (C=O), 1690 cm^{-1} (NCOO); ^{1}H NMR ($CDCl_3$) δ 1.16 (6 H, t, CH_3, J = 7 Hz), 1.46 (6 H, s, CH_3C), 2.14 (3 H, s, CH_3CO), 3.31 (4 H, q, CH_2, J = 7 Hz); mass spectrum, m/e 202 ($M^+ + 1$).

Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.68; H, 9.51; N, 6.96. Found: C, 59.38; H, 9.55; N, 7.00.

2-Oxopropyl *N,N*-pentamethylenecarbamate (3): IR (neat) 1725 (CO), 1695 cm^{-1} (NCOO); ^{1}H NMR ($CDCl_3$) δ 1.59 (6 H, m, CH_2), 2.14 (3 H, s, CH_3CO), 3.44 (4 H, m, NCH_2), 4.58 (2 H, s, OCH_2CO); mass spectrum, m/e 186 ($M^+ + 1$).

Anal. Calcd for $C_9H_{15}NO_3$: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.28; H, 8.36; N, 7.86.

2-Oxopropyl *N,N*-(oxydiethyl)carbamate (4): IR (neat) 1725 (CO), 1700 cm^{-1} (NCOO); ^{1}H NMR ($CDCl_3$) δ 2.16 (3 H, s, CH_3CO), 3.56 (4 H, m, NCH_2), 3.65 (4 H, m, OCH_2), 4.67 (2 H, s, OCH_2CO); mass spectrum, m/e 188 ($M^+ + 1$).

Anal. Calcd for $C_8H_{13}NO_3$: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.82; H, 7.44; N, 7.55.

4-(2-Oxopropyl)morpholine (5): IR (neat) 1715 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 2.16 (3 H, s, CH_3CO), 2.45 (4 H, t, NCH_2, J = 4 Hz), 3.20 (2 H, s, NCH_2CO), 3.72 (4 H, t, OCH_2, J = 4 Hz); mass spectrum, m/e 144 ($M^+ + 1$).

4-Acetylmorpholine (6): IR (neat) 1635 cm^{-1} ($NCOCH_3$); ^{1}H NMR ($CDCl_3$) δ 2.09 (3 H, s, CH_3CO), 3.63 (8 H, m, OCH_2CH_2N); mass spectrum, m/e 130 ($M^+ + 1$).

3-Propyl-4-methyl-2-oxo-1,3-oxazoline (7a): IR (neat) 1740 (NCOO), 1655 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ 0.95 (3 H, t, CH_3, J = 7 Hz), 1.68 (2 H, m, CH_2, J = 7 Hz), 2.04 (3 H, d, CH_3, J = 1.5 Hz), 3.52 (2 H, t, NCH_2, J = 7 Hz), 6.61 (1 H, q, HC=, J = 1.5 Hz); mass spectrum, m/e 142 ($M^+ + 1$).

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.98; H, 8.05; N, 9.93.

3-Propyl-4,5-dimethyl-2-oxo-1,3-oxazoline (7b): IR (neat) 1740 (NCOO), 1695 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ 0.95 (3 H, t, CH_3, J = 7 Hz), 1.68 (2 H, m, CH_2, J = 7 Hz), 1.96 (3 H, s, CH_3), 2.02 (3 H, s, CH_3), 3.42 (2 H, t, NCH_2, J = 7 Hz); mass spectrum, m/e 156 ($M^+ + 1$).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.57; H, 8.57; N, 9.00.

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Registry No. **1a**, 107-19-7; **1b**, 2028-63-9; **1c**, 115-19-5; **2a**, 109687-47-0; **2b**, 109687-48-1; **2c**, 91017-18-4; **3**, 109687-49-2; **4**, 109687-50-5; **5**, 6704-35-4; **6**, 1696-20-4; **7a**, 109687-51-6; **7b**, 109687-52-7; CO_2, 124-38-9; Et_2NH, 109-89-7; $PrNH_2$, 107-10-8; $Ru_3(CO)_{12}$, 15243-33-1; piperidine, 110-89-4; morpholine, 110-91-8.

Dicyclopenta[*ef,kl*]heptalene (Azupyrene) Chemistry. Electrophilic Monosubstitution: Acetylation, Halogenation, and Thiocyanation. 1-(Ethoxymethyl)azupyrene and Dimethyl (1-Azupyrenylmethyl)malonate. Acetylazupyrene Geometry[1]

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In the previously reported studies on the electrophilic monosubstitution of the title compound **1** it was found that the ratios of 1- to 4-substitution were 6:1 for protonation, 13:1 for trifluoroacetylation, and ca. 1:35 for nitration.[3] An interpretation of these results based on MNDO calculations was presented. The present paper gives the experimental findings for the three additional reactions given in the title and the preparation of two other monosubstitution compounds.

Acetylation. The reaction of **1** with acetic anhydride and boron trifluoride etherate or acetyl chloride and aluminum chloride gave an 8:1 mixture of the 1-acetyl (**2**) and 4-acetyl (**3**) derivatives based on the NMR analysis of the unseparated reaction mixture. It was possible to separate these products by flash chromatography and characterize them by their ^{1}H NMR spectra. The majority of the maxima in the UV-vis spectrum of **2** corresponded to those observed earlier for the 1-trifluoroacetyl compound.[3b]

Halogenation. Treatment of a solution of **1** with bromine or with *N*-bromosuccinimide rapidly yielded a 11.5:1 mixture of 1-bromo- (**4**) and 4-bromoazupyrene (**5**) as determined by the NMR and mass spectra of the unseparated product mixture. Purification afforded a mixture

(1) Presented in part of the 39th Northwest Regional Meeting of the American Chemical Society, Moscow, Idaho, June 13-15, 1984.
(2) From: Daugs, E. D. Ph.D. Thesis, University of Washington, 1985.
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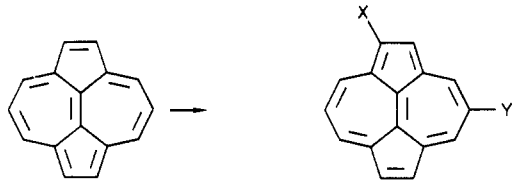
of 4 and 5 containing a small amount of dibromo compound.



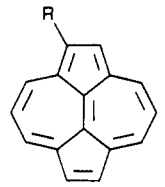
1

2, X = $COCH_3$, Y = H
3, X = H, Y = $COCH_3$
4, X = Br, Y = H
5, X = H, Y = Br
6, X = Cl, Y = H
7, X = H, Y = Cl
8, X = SCN, Y = H
9, X = H, Y = SCN
10, X = $COCF_3$, Y = H
11, X = H, Y = $COCF_3$

Analogously, reaction of 1 with chlorine gave a rapid reaction which was terminated when the presence of dichloro substitution product was observed. Again, it was not possible to separate the monosubstitution products 6 and 7 from each other or completely from small amounts of 1 and dichloro product, but high-field ^1H NMR enabled the identification of the peaks characteristic for 6 and 7 in a ratio of 11.5:1. Unexpectedly, however, the reaction of 1 with *N*-chlorosuccinimide was relatively slow (3 days under reflux) and gave a quite different ratio (3:2) of 6 to 7. This lower selectivity compared to *N*-bromosuccinimide suggested that a different mechanism was operating. The addition of a radical inhibitor (dihydrobenzoquinone) further retarded the rate but the product ratio was changed only to ca. 2:1. Hypochlorite, which has been shown to chlorinate azulene[4] and other aromatic compounds,[5] was also found to give a 3:2 ratio of 6 and 7.

Thiocyanation. The behavior of thiocyanogen toward 1 was examined and found to form 8 and 9 in a ratio of 10.1:1, very close to that for the halogens.

1-(Ethoxymethyl)azupyrene and Dimethyl (1-Azupyrenylmethyl)malonate. (Dimethylamino)methylation of 1 had been found earlier to occur at the 1-position.[6] The quaternary salt from this product was treated with sodium ethoxide to form 1-(ethoxymethyl)azupyrene (12) and with sodium dimethyl malonate to form dimethyl (1-azupyrenylmethyl)malonate (13), both in good yield.



12, R = $CH_2OCH_2CH_3$
13, R = $CH_2CH(CO_2CH_3)_2$

Acetylazupyrene Geometry. The ^1H NMR signal for H-2 of 1-(trifluoroacetyl)azupyrene (10)[7] had been observed to be a quartet (J = 2.2 Hz) arising from through-bond coupling with the ^{19}F atoms of the trifluoro group. The signal for H-3 and H-5 of 4-(trifluoroacetyl)azupyrene (11), however, was a simple singlet. ^1H–^{19}F coupling (J = 2.3 Hz) was observed in the analogous 1-(trifluoroacetyl)-azulene[8] and phenyl hexafluorobutyl ketone[9] compounds. These data indicated a nonplanar geometry of the trifluoroacetyl group and the attached ring in 11.

Drawings for 10 and 11 were constructed with the aromatic ring and carbonyl group in the same plane. The bond lengths and angles were those calculated by MNDO[3a,9] or the experimental values for azulene from X-ray data[10] were used for the azupyrene ring and the literature values[11] were used for the trifluoroacetyl group. Both models gave a shorter calculated ring hydrogen–fluorine distance for 11 (1.35 and 1.28 Å) than for 10 (1.76 and 1.80 Å).

This hydrogen–fluorine distance was experimentally examined by means of the nuclear Overhauser effect (NOE)[12] with the corresponding 1- and 4-acetyl derivatives 2 and 3 as the models.[13] A sample containing a mixture of 2 and 3 was used to provide a direct comparison. An H-2 to H-3 distance of 2.58 Å in 2 was obtained from the earlier MNDO geometry.[3a] This and the % NOE of H-3 from H-2 irradiation were used to correlate % NOE values to internuclear distances for 2 and 3, as the chemical shifts of H-2 and H-3 in 2 were too close to permit use of the % NOE of H-2 from irradiation of H-3. The % NOE of H-3 (H-5) of 3 was found to be 3.88 ± 0.08% by irradiation of the acetyl methyl group. This corresponded to an average internuclear distance of 2.50 ± 0.04 Å. Irradiation of the methyl group in 2 gave 2.5 ± 0.1% NOE for H-2 corresponding to an average internuclear distance of 2.69 ± 0.04 Å. The lack of an observable NOE for H-10 of 2 indicated a preferred acetyl conformation having the methyl toward H-2, analogous to that found for 1-acetylazulene.[14] Since these NOE results are for the average ring hydrogen–methyl hydrogen distance through all rotations, and for both H-3 and H-5 in 3, the shortest distance will be significantly nearer to the calculated values for 10 and 11 in each case. The sum of this evidence is consistent with out-of-plane geometry for the 4-acetyl and 4-trifluoroacetyl group and, for the latter, this is the reason for the absence of ring hydrogen–fluorine coupling.[15]

Experimental Section

General. Chemicals were reagent grade and not further purified unless otherwise indicated. Dry, O_2-free N_2 or Ar was used. $CHCl_3$, CH_2Cl_2, *n*-hexane, and mixed hexanes were purified and dried. Precoated TLC plates were obtained from MCB Manufacturing Chemists, Inc., Cincinnati, OH. Analytical plates (0.25 mm) were prepared with silica gel 60F-254. Chromatography columns were prepared with Merck silica gel grade 60, 230–400 mesh. Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Vancouver, British Columbia. Spectral data were recorded on the following instruments: UV–vis, Hewlett-Packard 8450A spectrophotometer (1.0-cm quartz cells); NMR, Bruker CXP-200 or Bruker WM 500 cryospectrometers with Me_4Si as internal standard; mass spectra. Hewlett-Packard 5985 GC/MS System with 30-m (DB-5) fused silica capillary or, for exact mass, V.G. Micromass 7070 H GC/M5 and associated VG 2035 F/B Data System[16] with perfluorokerosine

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as the standard. Because of the small quantities of products and the difficult separations involved, compounds were not obtained analytically pure.

1- and 4-Acetylazupyrene (2 and 3). Method A. The addition of a mixture of 50 μL (0.41 mmol) of acetic anhydride and 50 μL (0.41 mmol) of $BF_3{\cdot}OEt_2$ with stirring to a green solution of 63 mg (0.31 mmol) of azupyrene (1) in 20 mL of CH_2Cl_2 under Ar caused the color to turn to red. The reaction was monitored by TLC (CH_2Cl_2) (R_f: azupyrene, 0.91; 1-acetylazupyrene, 0.58 (green); 4-acetylazupyrene, 0.53 (yellow); diacetylazupyrene, 0.2–0.3). After 4 h under reflux, 10 mL of H_2O was added to the cooled mixture, and the separated organic layer was extracted with 10% $NaHCO_3$ and dried (Na_2SO_4). The solvent was removed and the residue chromatographed on a 4 in. × 1 in. flash silica gel column with CH_2Cl_2. After a green band of azupyrene, a green band of acetylazupyrene (34 mg, 46%) was obtained. The ^1H NMR spectrum of the acetylazupyrene product, mp 129–130 °C after sublimation at 150 °C and 0.2 Torr, indicated an 8:1 of **2** to **3**: mass spectrum, m/e (relative intensity) 244 (M^+, 100), 229 ($M^+ - 15$, 82), 201 ($M^+ - 43$, 66), 200 ($M^+ - 44$, 46); exact mass, m/e 244.0879 ($C_{18}H_{12}O$ requires 244.0888).

Flash chromatography with a 24 in. × 0.75 in. silica gel column (CH_2Cl_2) separated **2** as dark green platelets, mp 129–130 °C after recrystallization from CH_2Cl_2: UV–vis (hexanes) λ_{max} (log ε) 239 (4.52), 250 (4.58), 262 (4.56), 271 (4.59), 290 (4.46), 305 (3.25), 474 (3.30), 486 (3.56), 498 nm (4.14); ^1H NMR ($CDCl_3$), δ 2.96 (s, 3, CH_3), 7.17 (t, 1, H-4, J = 9.5 Hz), 7.45 (t, 1, H-9), J = 9.7 Hz), 8.23 (d, 1, H-7, J = 4.5 Hz), 8.26 (d, 1, H-6, J = 4.5 Hz), 8.51 (d, 1, H-5, J = 9.5 Hz), 8.53 (d, 1, H-3, J = 9.5 Hz), 8.60 (d, 1, H-8, J = 9.7 Hz), 8.71 (s, 1, H-2), 9.96 (d, 1, H-10, J = 9.7 Hz). Isomer **3** was obtained as a yellow solid, mp 119–121 °C: UV–vis (hexanes) λ_{max} (log ε) 241 (4.41), 261 (4.66), 270 (4.73), 295 (4.32), 328 (4.39), 352 (3.90), 369 (3.99), 380 (4.34), 4.04 (3.04), 468 (3.11), 480 nm (3.52); ^1H NMR ($CDCl_3$) δ 2.92 (s, 3, CH_3) 7.48 (t, 1, H-9, J = 9.7 Hz), 8.32 (d, 2, H-1, 7, J = 4.5 Hz), 8.43 (d, 2, H-2, 6, J = 4.5 Hz), 8.65 (d, 2, H-8,10, J = 9.7 Hz), 9.30 (s, 2, H-3,5).

Method B. A 0.3-mL (0.1 mmol of acetyl chloride) portion of a mixture of 0.1 g (0.75 mmol) of $AlCl_3$, 0.07 mL (0.81 mmol) of acetyl chloride, and 2 mL of CH_2Cl_2 was added to 11 mg (0.05 mmol) of azupyrene in 5 mL of CH_2Cl_2 under Ar, and the red solution was stirred for 5 min. Water (2 mL) was added, and the mixture was worked up as described in method A. ^1H NMR analysis of the product showed an 8:1 mixture of **2** to **3**.

1- and 4-Bromoazupyrene (4 and 5). Method A. To a stirred, cooled (ice bath) solution of 28.5 mg (0.141 mmol) of azupyrene in 30 mL of CCl_4 in a 100-mL flask bearing a condenser was added 7.2 μL (0.141 mmol) of Br_2 by evaporation through a side inlet tube. TLC analysis (CCl_4) showed azupyrene (R_f 0.72), bromoazupyrene (R_f 0.76), dibromoazupyrene (R_f 0.80), and a red, immobile product. The mixture was filtered through a 3 in. × 0.5 in silica gel column (CCl_4), and GC/MS analysis of the residue (32 mg) from the filtrate showed ca. 55% (17.6 mg) of azupyrene (m/e 202), 40% (12.8 mg) of bromoazupyrene (m/e 282), and 5% (1.6 mg) of dibromoazupyrene (m/e 358).

Three fractions were collected from flash chromatography (CCl_4) over a 20 in. × 1 in. silica gel column. GC/MS analysis showed the first to contain ca. 35% bromoazopyrene and 65% dibromoazupyrene, the second to contain ca. 82% bromoazopyrene and 13% dibromoazupyrene plus 5% azupyrene, and the third to contain ca. 38% bromoazupyrene and 4% dibromoazupyrene plus 58% azupyrene. Sublimation of the second fraction [150 °C (0.1 Torr)] gave 11.8 mg of red-brown needles, mp 164–165 °C, containing (high-field ^1H NMR) 9.7 mg (25% yield) of bromoazupyrene with a 11.5:1 ratio of **4** to **5** and 1.5 mg (3% yield) of dibromoazupyrene: ^1H NMR ($CDCl_3$) [for **4**] δ 7.33 (t, 1, H-4, J = 9.5 Hz), 7.41 (t, 1, H-9, J = 9.5 Hz), 8.35 (d, 1, H-6, J = 4.5 Hz), 8.39 (d, 1, H-7, J = 4.5 Hz), 8.42 (s, 1, H-2), 8.55 (d, 1, H-5, J = 9.5 Hz), 8.64 (d, 1, H-3, J = 9.5 Hz), 8.67 (d, 1, H-8, J = 9.5 Hz), 8.72 (d, 1, H-10, J = 9.5 Hz), [for **5**] δ 8.30 (d, 2, H-2,6 J = 4.5 Hz), 8.33 (d, 2, H-1,7, J = 4.5 Hz), 8.90 (s, 2, H-3,5) [hidden, H-8,9,10]; mass spectrum, m/e (relative intensity) 282 (M^+ ^{81}Br, 97), 280 (M^+ ^{79}Br, 100), 201 ($M^+ - 79$ or 81, 38), 200 ($M^+ - 80$ or 82, 83); exact mass, m/e 279.9848 ($C_{16}H_9{}^{79}Br$ requires 279.9887), 281.9825 ($C_{16}H_9{}^{81}Br$ requires 281.9867), 357.9013 ($C_{16}H_8{}^{79}Br_2$ requires 357.8992), 361.8952 ($C_{16}H_8{}^{81}Br_2$ requires 361.8952).

Method B. A 0.51-mL (0.0576 mmol of NBS) portion of a solution of 0.803 g (4.51 mmol) of *N*-bromosuccinimide in 40.0 mL of $CHCl_3$ was added to a cooled (ice bath), stirred solution of 11.0 mg (0.0545 mmol) of azupyrene in 20 mL of $CHCl_3$. The ice bath was removed after 5 min and the stirring continued for an additional 10 min. GC/MS analysis showed a mixture of bromo-, dibromo-, and unchanged azupyrene (85:12:3:). Filtration through a 3 in. × 1 in. silica gel column (CCl_4) and removal of the solvent gave 13.5 mg of product calculated (high-field ^1H NMR) to contain 11.5 mg (75% yield) bromoazupyrene and 1.6 mg (8% yield) of dibromoazupyrene with a ca. 11.5:1 ratio of 4 to **5**.

1- and 4-Chloroazupyrene (6 and 7). Method A. Chlorine gas diluted by Ar was slowly added to a stirred, cooled solution of 27.0 mg (0.0134 mmol) of azupyrene in 50 mL of CCl_4. The reaction was stopped when TLC (CCl_4) analysis showed the presence of dichloroazupyrene (R_f 0.83) in addition to azupyrene (R_f 0.74) and chloroazupyrene (R_f 0.80). The solvent was removed, and the residue was chromatographed on a 3 in. × 1 in. silica gel column (CCl_4). GC/MS analysis of the product (30 mg) indicated the presence of ca. 14 mg (47%) of azupyrene (m/e 202), 13.5 mg (45%) of chloroazupyrene (m/e 236, 238), 1.5 mg (5%) of dichloroazupyrene (m/e 270, 272), and 0.9 mg (3%) trichloroazupyrene (m/e 304.306).

The eluent from flash chromatography on a 20 in. × 1 in. silica gel column (CCl_4) was collected as three fractions: GC/MS analysis of the 11.0 mg of red-brown needles, mp 188–191 °C, from the green middle fraction showed 82% monochloroazupyrene, 6% dichloroazupyrene, and 12% azupyrene. The high-field ^1H NMR spectrum indicated a ca. 11.5:1 ratio of **6** to **7**: mass spectrum m/e (relative intensity) 238 (M^+ ^{37}Cl, 33) 236 (m^+ ^{35}Cl, 100); ^1H NMR ($CDCl_3$) [for **6**] δ 7.34 (t, 1, H-4, J = 9.5 Hz), 7.39 (t, 1, H-9, J = 9.5 Hz), 8.30 (s, 1, H-2), 8.35 (d, 1, H-6, J = 4.5 Hz), 8.39 (d, 1, H-7, J = 4.5 Hz), 8.54 (d, 1, H-5, J = 9.5 Hz), 8.63 (d, 1, H-3, J = 9.5 Hz), 8.67 (d, 1, H-8, J = 9.5 Hz), 8.72 (d, 1, H-10, J = 9.5 Hz), [for **7**] δ 7.36 (t, 1, H-9, J = 9.5 Hz), 8.30 (d, 2, H-2,6, J = 4.5 Hz), 8.40 (d, 2, H-1,7, J = 4.5 Hz), 8.67 (d, 2, H-8,10, J = 9.5 Hz), 8.75 (s, 2, H-3,5).

Method B.[17] A mixture of 33.7 mg (0.167 mmol) of azupyrene, 21.0 mg (0.157 mmol) of *N*-chlorosuccinimide, and 6 mL of $CHCl_3$ was refluxed for 3 days. The cooled mixture was filtered through a 1 in. × 1 in. silica gel column (CCl_4). The eluate condensate was flash chromatographed on a 24 in. × 1 in. silica gel column (CCl_4) and afforded two fractions. High-field ^1H NMR showed one (25.9 mg) to contain ca. 90% (23.3 mg, ca. 63% yield) of chloroazupyrene, 9% dichloroazupyrene, and 1% unchanged azupyrene and the second (8.7 mg) to contain 15% chloroazupyrene (ca. 66.5% total, 84.5% net yield) and 85% azupyrene. The ratio of **6** to **7** in both the crude and partially separated products was 3:2. The same ratio was obtained from a 4-day room temperature reaction. Exact mass, m/e 236.0409 ($C_{16}H_9{}^{35}Cl$ requires 236.0393), 238.0377 ($C_{16}H_9{}^{37}Cl$ requires 238.0363), 269.9944 ($C_{16}H_8{}^{35}Cl_2$ requires 270.0003).

Method C. A solution of 6.0 mg (0.042 mmol) of $Ca(OCl)_2$ in 1 mL of H_2O was added with stirring to 8.5 mg (0.042 mmol) of azupyrene dissolved in 10 mL of CH_2Cl_2. Small pieces of solid CO_2 were added. The reaction progress was monitored as in method A, and the reaction was stopped after 30 min by washing with 10% $NaHCO_3$. The solvent was removed from the dried (Na_2SO_4) organic layer to give 11 mg of product mixture. GC/MS analysis showed ca. 24% (2.6 mg) unchanged azupyrene, 60% (6.6 mg) of chloroazupyrene, and 16% (1.8 mg) of dichloroazupyrene. Flash chromatography (20 in. × 1 in. silica gel column, CCl_4) gave 4.0 mg of a fraction which contained (high-field ^1H NMR) 87% chloroazupyrene, 12% dichloroazupyrene, and 1% azupyrene with a 3:2 ratio of **6** to **7**.

1- and 4-Thiocyanoazupyrene (8 and 9). A solution of Br_2 in CCl_4 was added dropwise to a suspension of 40.4 mg (0.125 mmol) of $Pb(SCN)_2$ in 5 mL of CCl_4 with stirring until the bromine color remained. Then a small amount of $Pb(SCN)_2$ was added

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(17) This procedure was a modification of that reported by: Masada, G. M., Ph.D. Thesis, University of Washington, 1972, p 77.

to remove the color. The solution was decanted from the $PbBr_2$ precipitate and added to a cold (ice bath) solution of 23.0 mg (0.11 mmol) of azupyrene in 20 mL of CCl_4. The reaction mixture was stirred for 10 min and then allowed to warm to room temperature.. The solvent was removed (N_2 stream), and the residue was flash chromatographed on a 12 in. × 1 in. silica gel column (5% hexanes in CH_2Cl_2). Three green fractions were collected and analyzed by MS. The first (R_f 0.95) contained azupyrene (m/e 202) plus a trace of bromoazupyrene (m/e 280.282). The second (R_f 0.78) contained thiocyanoazupyrene (m/e 259). The third (R_f 0.62) contained a trace of dithiocyanoazupyrene (m/e 316). The second fraction amounted to 26 mg (91%) of **8** plus **9** in a ratio of 10:1 (high-field ^1H NMR) as a brown solid, mp 165–167 °C: UV–vis (hexanes) λ_{max} (log ϵ) 256 (4.59), 268 (4.71), 291 (4.43), 310 (4.21), 338 (3.99), 351 (3.85), 363 (3.73), 410 (3.33), 456 (3.42), 476 (3.59), 488 nm (4.02); ^1H NMR ($CDCl_3$) [for **8**] δ 7.27 (t, 1, H-9, J = 9.5 Hz), 7.41 (t, 1, H-4), J = 9.5 Hz), 8.30 (s, 2, H-6,7), 8.49 (d, 1, H-10, J = 9.5 Hz), 8.51 (s, 1, H-2), 8.57 (d, 1, H-8, J = 9.5 Hz), 8.62 (d, 2, H-3,5, J = 9.5 Hz), [for **9**] δ 7.47 (t, 1, H-9, J = 9.5 Hz), 8.31 (d, 2, H-1, 7, J = 4.5 Hz), 8.38 (d, 2, H-2,6, J = 4.5 Hz), 8.67 (d, 2, H-8,10, J = 9.5 Hz), 8.80 (s, 2, H-3,5); mass spectrum, m/e (relative intensity) 260 (M^+ + 1, 19), 259 (M^+, 100) 227 (M^+ – 32, 54), 214 (M^+ – 45, 31), 200 (M^+ – 59, 20); exact mass, m/e 259.0456 ($C_{17}H_9SN$ requires 259.0441).

1-(Ethoxymethyl)azupyrene (12).[18] To a solution of 15 mg (0.0374 mmol) of (1-azupyrenylmethyl)trimethylammonium iodide[6] in 4 mL of absolute ethanol was added with stirring 0.4 mL of 0.95 M sodium ethoxide (0.38 mmol) in ethanol. The mixture was refluxed for 1 h and then cooled. The reaction was quenched with 20 mL of H_2O, and the whole was extracted with CH_2Cl_2 (3 × 15 mL). The solvent was removed from the separated, combined, washed (H_2O), and dried (Na_2SO_4) organic layers. Chromatography on a 12 in. × $^1/_2$ in. silica gel column (10% hexanes in CH_2Cl_2) gave a small green band of azupyrene and a second green band which afforded 6.0 mg (62%) of **12** as green needles, mg 61–63 °C after sublimation at 140 °C and 0.3 Torr: UV–vis (hexanes) λ_{max} (log ϵ) 254 (4.67), 267 (4.91), 286 (4.51), 301 (4.26), 311 (4.23), 335 (3.94), 346 (4.07), 358 (3.53), 372 (2.70), 408 (2.85), 442 (3.08), 452 (3.18), 460 (3.08), 472 (3.45), 484 nm (4.03); ^1H NMR ($CDCl_3$), δ 1.33 (t, 3, CH_3, J = 7.1 Hz), 3.71 (q, 2, CH_2, J = 7.1 Hz), 5.39 (s, 2, CH_2), 7.33 (t, 1, H-4, J = 9.5 Hz), 7.38 (t, 1, H-9, J = 9.5 Hz), 8.38 (d, 1, H-6, J = 4.5 Hz), 8.40 (d, 1, H-7, J = 4.5 Hz), 8.41 (s, 1, H-2), 8.62 (d, 1, H-3, J = 9.5 Hz), 8.66 (d, 1, H-5, J = 9.5 Hz), 8.69 (d, 1, H-8, J = 9.5 Hz), 8.73 (d, 1, H-10, J = 9.5 Hz); mass spectrum, m/e (relative intensity) 261 (M^+ + 1, 12), 260 (M^+, 55), 216 (M^+ – 44, 34), 215 (M^+ – 45, 100), 213 (M^+ – 47, 15), 202 (M^+ – 58, 17); exact mass, m/e 260.1200 ($C_{19}H_{16}O$ requires 260.1201).

Dimethyl (1-Azupyrenylmethyl)malonate (13). To the cooled, stirred solution formed by warming 34.4 mg (0.72 mmol) of NaH and 5.0 mL of dimethyl sulfoxide under Ar to 60 °C in a 25-mL flask equipped with a condenser and addition funnel was added 0.17 mL (1.5 mmol) of dimethyl malonate. After 5 min a mixture of 31 mg (0.077 mmol) of (1-azupyrenylmethyl)trimethylammonium iodide[6] and 4.0 mL of dimethyl sulfoxide was added. After heating at 50 °C for 30 min water (5 mL) was added to the cooled mixture and the whole then poured into 50 mL of H_2O and extracted with CH_2Cl_2 (3 × 30 mL). The concentrated (to 50 mL) organic solution was washed (H_2O, 5 × 50 mL) and dried (Na_2SO_4), and the solvent was then removed. Flash chromatography (12 in. × $^1/_2$ silica gel column with 1:1 CH_2Cl_2/benzene) gave, after a small yellow foreband, 22 mg (82%) of **13** as a crystalline yellow solid, mp 93–95 °C after sublimation at 160 °C and 0.2 Torr: UV–vis (CH_3CN) λ_{max} (log ϵ) 253 (4.75), 266 (4.96), 287 (4.57), 302 (4.33), 312 (4.29), 336 (4.03), 346 (4.07), 359 (3.62), 410 (3.00), 442 (3.20), 452 (3.30), 472 (3.49), 484 nm (4.05); ^1H NMR ($CDCl_3$) δ 3.71 (s, 6, CH_3), 4.13 (m, 3, CH, CH_2), 7.34 (t, 1, H-9, J = 9.5 Hz), 7.38 (t, 1, H-4, J = 9.5 Hz), 8.26 (s, 1, H-2), 8.38 (d, 1, H-7, J = 4.5 Hz), 8.40 (d, 1, H-6, J = 9.5 Hz), 8.59 (d, 1, H-10, J = 9.5 Hz), 8.62 (d, 1, H-3, J = 9.5 Hz), 8.65 (d, 1, H-8, J = 9.5 Hz), 8.69 (d, 1, H-5, J = 9.5 Hz); exact mass, m/e 346.1215 ($C_{22}H_{18}O_4$ requires 346.1205).

(18) The procedure was adapted from that used for the preparation of 1-(methoxymethyl)azulene: Anderson, A. G., Jr.; Anderson, R. G., Fujita, T. S. *J. Org. Chem.* **1962**, *27*, 4535.

Nuclear Overhauser Experiments. A $CDCl_3$ solution of a sample containing 69% of **3** and 31% of **2** was subjected to the following sequence at 500 MHz: Irradiate at frequency A (on resonance: 6895.46 Hz for CH_3 of **3**; 6911.31 Hz for CH_3 of **2**) with 40-ms pulse width; delay 0.7 s; observe with 90° pulse at 10 μs; aquire 8K spectrum. Repeat 10 times with two dummy scans. Irradiate at 4217.84 Hz (off resonance) and repeat sequence as described above. Subtract off resonance from on resonance. Repeat for 16 cycles with 1.8-s delay.

A control spectrum of 128 shots and a receiver delay of 2.504 s with two dummy scans was used. The integration parameters were kept constant. % NOE values (3.88 ± 0.08 for H-3 (H-5) of 3, 2.5 ± 0.1% for H-2 of 2) were obtained by dividing the area of the enhanced peak by the area of the peak in the control spectrum and were the average of values determined by plotted integrals and NMR computer digital integration.

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Synthesis and Crystal Structure of a Novel Tripyrrane-Containing Porphyrinogen-like Macrocycle

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Although a tremendous amount of effort has been devoted to the synthesis and study of tetrapyrrole macrocycles,[1] only a few examples of structurally characterized macrocycles containing a larger or smaller number of pyrroles have been reported.[2-4] Novel pyrrole-containing macrocycles are, nonetheless, currently attracting interest as synthetic targets, either as models for various naturally occurring systems[2,5-7] or because they may display unusual physical,[8-12] chemical,[13,14] or coordination properties.[3,4,15]

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