

# Dicyclopenta[*ef,kl*]heptalene (Azupyrene) Chemistry. Electrophilic Monosubstitution. Theory and Experiment<sup>1</sup>

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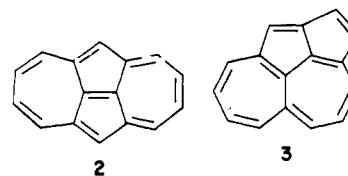
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**Abstract:** MNDO calculations were used to estimate the ground-state geometry, atom electron densities, heat of formation, ionization potential, gas-phase  $\Delta H$  values for protonation, and  $\Delta H$  and  $E_a$  values for electrophilic trifluoroacetylation and nitration with protonated trifluoroacetic anhydride and trifluoroacetyl nitrate, respectively, of azupyrene (**1**). The electron density at C-4 was greater than that at C-1, and C-3 was electron-deficient. Relative  $\Delta H$  values predicted C-1 to be more reactive than C-4 in each case. Relative  $E_a$  values predicted C-1 to be more reactive to protonated trifluoroacetic anhydride but C-4 to be more reactive to protonated trifluoroacetyl nitrate. Experimentally, protonation of solid **1** with  $\text{DClO}_4$  showed a C-1:C-4 D incorporation ratio of ca. 2:1, and trifluoroacetylation gave mostly 1-substitution with trifluoroacetic anhydride or trifluoroacetylpyridinium chloride. In contrast, nitration with trifluoroacetyl nitrate, 1-nitropyridinium fluoroborate, or nitronium fluoroborate gave very predominantly 4-substitution.

The  $4n$   $\pi$ -electron, nonbenzenoid hydrocarbon dicyclopenta[*ef,kl*]heptalene (azupyrene) (**1**) has been shown to have aromatic character with respect to its physical properties<sup>4</sup> and in a single electrophilic substitution reaction.<sup>5</sup> Gas-phase MNDO<sup>6</sup> calculations concerning the ground state of **1** and its reactivity with certain electrophiles, and the experimental behavior of **1** with these and other similar electrophiles are now reported.

The geometric parameters of **1** are not known. An attempted X-ray structure analysis revealed a disordered crystal.<sup>7</sup> The calculated (MNDO) atom electron densities are shown in Figure 1. The bond distances,  $\pi$  bond orders, and bond angles are given in Table I.

The concept of concentric  $\pi$ -electron systems was proposed a number of years ago to account for aromatic properties in cyclocondensed, conjugate-unsaturated,  $4n$  molecules.<sup>8a</sup> While the calculated parameters for **1** might be viewed as providing some indication of this, they appear to correspond somewhat better to the description of **1** according to component  $4n + 2$  and  $4n$  conjugated circuits as advanced by Randić.<sup>8b</sup> Similar parameters were recently found for the isomeric dicyclohepta[*ed,gh*]pentalene system (**2**)<sup>9</sup> but not for the isomeric pentaleno[6,1,2-*def*]heptalene structure (**3**).<sup>10</sup> The ground-state atom electron densities show a slightly greater value for C-4 than for C-1 and C-3 to be



electron-deficient. The heat of formation ( $\Delta H_f$ , Table II) and the ionization potential (7.389 eV) were also calculated.

**Protonation.** The calculated heats of reaction for gas-phase protonation were  $-181.2$  and  $-176.9$  kcal/mol for positions 1 and 4, respectively (Table II). An attempt to define a transition state by lengthening the hydrogen-azupyrene bond was not performed, as the relative ionization potentials (7.389 and 11.9) would cause bond cleavage in the direction of azupyrene cation plus hydrogen atom formation. As an approximation to solvation in aqueous acid, a hydrogen-bonded water molecule was included at each hydrogen of the reaction site. For position 1, the plane of the ring was retained as a symmetry plane. For position 4, the ring plane and the perpendicular mirror plane were retained. The adiabatic ionization potential of neutral  $\text{H}_2\text{O}$  was calculated to be 5.57 eV, so an attempt was made to achieve a transition-state structure by lengthening the C-H bond involving  $\text{H}_3\text{O}^{\delta+}$ . As positive charge developed in the latter, however, the  $\text{H}_3\text{O}^{\delta+}$  moiety tended to fold over and slide across the surface of the azupyrene rather than move away.

Experimentally, reaction of a chloroform solution of **1** with 68%  $\text{DClO}_4$  in  $\text{D}_2\text{O}$  gave rapid reaction with the formation of a solid presumed to be a polymer. A  $^1\text{H}$  NMR spectrum of the intermediate or product could not be obtained. However, the  $^1\text{H}$  NMR spectrum of the dissolved product from the treatment of crystalline **1** with the  $\text{DClO}_4$  reagent showed ca. 68% D incorporation at position 1 and 11% incorporation at position 4 (corrected for the respective numbers of equivalent positions) after 2 min. After 5- and 10-min periods, the percentages of D incorporation were 91% and 50% and approximately 100% and 55%, respectively. While it was not proven that these products were the thermodynamically more stable ones, this would seem probable. The total percentages exchanged were qualitatively checked by mass spectrographic analyses of the products from the quenched reactions.

**Trifluoroacetylation.** The electrophile trifluoroacetic anhydride (TFAA) and **1** are neutral, closed-shell molecules which would not tend to move close together in the gas phase. In solution, the solvent would assist in the reaction process. To partially represent solvent participation for the MNDO calculations, the carbonyl oxygen of the leaving trifluoroacetate portion was protonated. This caused a moderate change in the structure of the anhydride reagent and alleviated the difficulty of providing for the separation of

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(3) In part from: Kao, L. G., Ph. D. Thesis, University of Washington, 1981. And: Quenemoen, K. A. Ph.D. University of Washington, Thesis, 1984.

(4) Anderson, A. G., Jr.; Montana, A. F.; MacDonald, A. A.; Masada, G. M. *J. Org. Chem.* **1973**, *38*, 1445-1450. Anderson, A. G., Jr.; MacDonald, A. A.; Montana, A. F. *J. Am. Chem. Soc.* **1968**, *90*, 2993.

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(6) Dewar, M. J. S.; Theil, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907. Earlier simple HMO and CNDO/2 calculations had predicted substitution at the 1- or 4-positions, respectively (ref 4). The records of these have been lost.

(7) Performed by Prof. H. L. Ammon, Department of Chemistry, University of Maryland, University Park, MD.

(8) (a) Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484; **1954**, *22*, 1448. For the specific application to azupyrene and its cyclocondensed isomeric structures see: Zahradnik, R. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1039-1040. Zahradnik, R.; Michel, J.; Pancir, J. *Tetrahedron* **1966**, *22*, 1355-1356. Toyota, A.; Makajima, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2284-2287. (b) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444-450.

(9) Kabuto et al. (Kabuto, C.; Fujimori, K.; Yasunami, M.; Takasa, K.; Morita, N.; Asao, T. *Acta Crystallogr., Sect. C* **1983**, *C39*, 1245-1248) reported the structure by X-ray analysis of methyl 10-ethylidicyclohepta[*cd,gh*]pentalene-5-carboxylate while the present work was in progress.

(10) Linder et al. (Linder, H. J. *Chem. Ber.* **1969**, *102*, 2456) reported azulene and olefin structural components from X-ray analysis of this ring system of lesser symmetry.

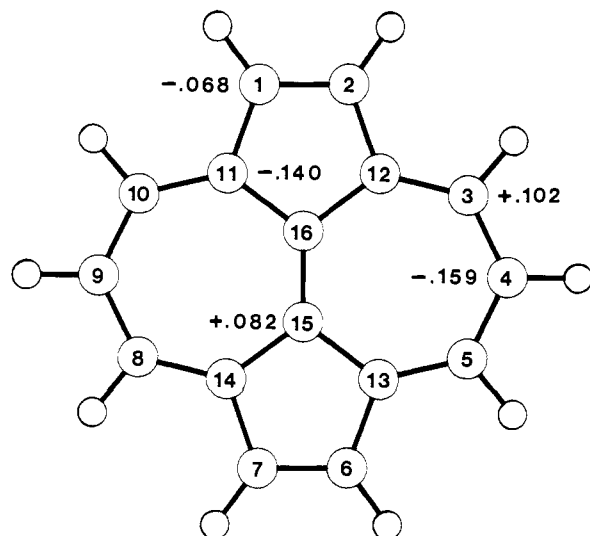


Figure 1. Calculated atom electron densities of azupyrene (1).

Table I. MNDO Calculated Geometry of Azupyrene

bond	length, Å	$\pi$ order	angle	deg
C-1-C-2	1.379	0.814	C-1-C-2-H-2	124.3
C-1-C-11	1.451	0.464	C-1-C-2-C-12	109.4
C-10-C-11	1.400	0.629	C-1-C-11-C-16	107.4
C-3-C-4	1.398	0.646	C-12-C-3-H-3	115.9
C-11-C-16	1.472	0.428	C-11-C-16-C-12	105.8
C-15-C-16	1.401	0.654	C-16-C-12-C-3	129.3
C-1-H-1	1.082		C-12-C-3-C-4	129.5
C-3-H-3	1.100		C-3-C-4-C-5	128.5
C-4-H-4	1.097		C-11-C-16-C-15	127.0

Table II. MNDO Calculated  $\Delta H$  Values for Protonation

species	$\Delta H_f^a$	$\Delta H_{rxn}^a$
H <sup>+</sup>	326.67	
C <sub>6</sub> H <sub>6</sub>	21.20	
C <sub>6</sub> H <sub>7</sub> <sup>+</sup>	208.38	-139.5
<b>1</b>	113.54	
[H-1(C-1)] <sup>+</sup> <sup>b</sup>	259.01	-181.2
[H-1(C-4)] <sup>+</sup> <sup>b</sup>	263.30	-176.9
[H <sub>2</sub> O-H-1-H <sub>2</sub> O] <sup>+</sup> (C-1) <sup>c</sup>		-55.1
[H <sub>2</sub> O-H-1-H <sub>2</sub> O] <sup>+</sup> (C-4) <sup>c</sup>		-51.0

<sup>a</sup> Kilocalories/mole. <sup>b</sup> C-1 or C-4 protonated **1**. <sup>c</sup> C-1 or C-4 protonated from **1**·H<sub>2</sub>O + H<sub>3</sub>O<sup>+</sup>.

Table III. MNDO Calculated Transition-State Bond Lengths for the Protonated Trifluoroacetic Anhydride-Benzene Model

bond	length, Å	bond	length, Å
C-1-benzene	2.070	C-2-O	1.280
C-1-CF <sub>3</sub>	1.345	C-2-CF <sub>3</sub>	1.630
C-1=O	1.221	C-2-OH	1.299
C-1-O	1.498	O-H	0.958

oppositely charged species in the gas phase.

A second difficulty was that full geometry optimizations of an asymmetrical transition state with the large azupyrene molecule were prohibitively time-consuming. Therefore, a transition-state structure was found with benzene as the aromatic compound, and the electrophile in this transition-state geometry (Figure 2, Table III) was attached, correspondingly, to **1** for the energy calculation. The azupyrene geometries used were those calculated for protonation at the respective positions. The assumptions implicit in the use of the model structure appreciably increased the uncertainties in the absolute values obtained for the energies but had a smaller effect on the relative values for these. Both  $\Delta H$  and  $E_a$  predictions for this reaction favored position 1 over position 4 (Table IV).

The <sup>1</sup>H NMR spectrum of the product isolated from the initial experiments on this reaction showed formation of the 1-tri-

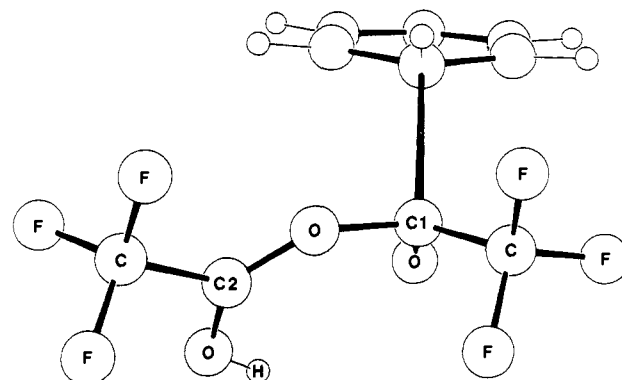


Figure 2. Calculated model transition-state structure for protonated trifluoroacetic anhydride and benzene.

Table IV. MNDO Calculated  $\Delta H$  and  $E_a$  Values for Trifluoroacetylation

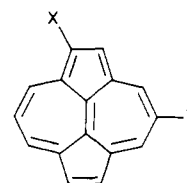
species	$\Delta H_f^a$	$\Delta H_{rxn}^a$	$E_a^a$
TFAA <sup>b</sup>	-402.49		
TFAH <sup>c</sup>	-235.81		
TFA-1(C-1) <sup>d</sup>	-62.14	-9.0	
TFA-1(C-4) <sup>d</sup>	-59.11	-5.97	
HTFAA <sup>+</sup>	-192.95		
[HTFAA-1(C-1)] <sup>+</sup> <sup>e</sup>	-60.83		18.6
[HTFAA]-1(C-4)] <sup>+</sup> <sup>e</sup>	-59.88		19.5
[HTFAA-C <sub>6</sub> H <sub>6</sub> ] <sup>+</sup> <sup>f</sup>	-138.49		33.3

<sup>a</sup> Kilocalories/mole. <sup>b</sup> Trifluoroacetic anhydride. <sup>c</sup> Trifluoroacetic acid. <sup>d</sup> Trifluoroacetyl-1. <sup>e</sup> C-1 or C-4 transition state with protonated TFAA and **1**. <sup>f</sup> Transition state with protonated TFAA and benzene.

Table V. MNDO Calculated Transition-State Bond Lengths for the Protonated Trifluoroacetyl Nitrate-Benzene Model

bond	length, Å	bond	length, Å
N-benzene	2.190	C-OH	1.339
N=O	1.165	O-H	0.950
N-O	3.169	C-CF <sub>3</sub>	1.608
O-C	1.225		

fluoroacetyl derivative **4** (73%).<sup>5</sup> Subsequent repetition of the reaction as originally described (TFAA plus trimethylamine), with



- 4**, X=COCF<sub>3</sub>; Y=H  
**5**, X=H; Y=COCF<sub>3</sub>  
**6**, X=H; Y=NO<sub>2</sub>  
**7**, X=NO<sub>2</sub>; Y=H

a BF<sub>3</sub>-etherate catalyst, or with trifluoroacetylpyridinium chloride as the reagent, and high-resolution spectral analysis of the product revealed ca. 7% of a second product: the 4-substituted compound **5**. It was of interest to observe spin-spin coupling of the fluorines with H-2 in the 1-derivative but no corresponding coupling in the 4-derivative. The transition states for the BF<sub>3</sub>-etherate catalyzed, and the trifluoroacetylpyridinium reactions would more closely resemble the calculation model in having a neutral leaving group.

**Nitration.** The calculations for this reaction paralleled those for trifluoroacetylation with the substitution of trifluoroacetyl nitrate (TFAN) for TFAA. As before, the carbonyl oxygen of the trifluoroacetate moiety was protonated. This changed the structure of the electrophile markedly, placing most of the positive charge on the NO<sub>2</sub> portion and lengthening the O-N bond to 2.37. This approximated a neutral trifluoroacetic acid loosely bonded to NO<sub>2</sub><sup>+</sup> (Figure 3, Table V). Again, the relative  $\Delta H$  values favored position 1 by about 3 kcal/mol. The  $E_a$  for position 4, however, was the lower by ca. 11 kcal/mol (Table VI).

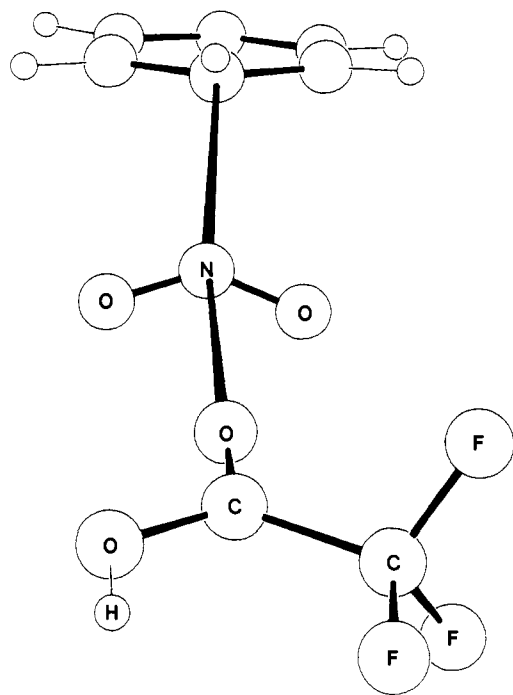


Figure 3. Calculated model transition-state structure for protonated trifluoroacetyl nitrate and benzene.

Table VI. MNDO Calculated  $\Delta H$  and  $E_a$  Values for Nitration

species	$\Delta H^f$	$\Delta H_{rxn}^a$	$E_a^a$
TFAN <sup>b</sup>	-183.77		
TFAN <sup>c</sup>	-235.81		
NO <sub>2</sub> -1(C-1) <sup>d</sup>	132.10	-33.48	
NO <sub>2</sub> -1(C-4) <sup>d</sup>	134.93	-30.65	
HTFAN <sup>+</sup>	-5.59		
[HTFAN-1(C-1)] <sup>+e</sup>	110.09		2.1
[HTFAN-1(C-4)] <sup>+e</sup>	99.31		-8.7 <sup>g</sup>
[HTFAN-C <sub>6</sub> H <sub>6</sub> ] <sup>+f</sup>	27.96		12.34

<sup>a</sup> Kilocalories/mole. <sup>b</sup> Trifluoroacetyl nitrate. <sup>c</sup> Trifluoroacetic acid. <sup>d</sup> 1- or 4-Nitroazopyrene (6 or 7). <sup>e</sup> C-1 or C-4 transition state with protonated TFAN and 1. <sup>f</sup> Transition state for benzene and protonated TFAN. <sup>g</sup> Interpreted to indicate a lower value than for C-1.

Reaction of 1 with TFAN plus triethylamine, NO<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>, or 1-nitropyridinium fluoroborate formed 6. The mass spectrum of a product from the TFAN reaction indicated the presence of a trace amount of unidentified dinitro compound. The <sup>1</sup>H NMR spectra of the reaction products showed additional very small peaks, and further purification of a combined product sample permitted the tentative identification by high-resolution NMR of a few percent of the 1-isomer 7.

**Discussion.** Although the reaction conditions used in the calculations only roughly approximate those in the experiments, the results are in good agreement. For protonation, the relative  $\Delta H$  values and for trifluoroacetylation the relative  $\Delta H$  and  $E_a$  values were supported by the experimental findings. For nitration, the difference in the  $E_a$  values apparently dominated the smaller, opposite difference in the  $\Delta H$  values. A comparison of the calculated charge distributions in the transition states for the similar trifluoroacetylation and nitration reactions was revealing (Table VII). Each reaction favored the site for which the aromatic ring had the smaller positive charge. This difference was greater for the nitration reaction, and experimentally this formed essentially only one product. The calculated differences in charge distribution (+0.4 on the trifluoroacetyl group and +1.0 on the nitro group) suggested that the transition state involving the more positive nitro group and the more negative ring site would occur earlier on the reaction path and that electrostatic interactions could play a significant role. Steric factors were separately considered, and molecular models of the  $\sigma$ -bonded intermediates showed more hindrance at C-4 by H-3 or H-5 than at C-1 by H-2 or H-10 for

Table VII. MNDO Calculated Transition-State Charge Distributions

species	ring	electrophile <sup>a</sup>	leaving group <sup>b</sup>
[HTFAA-1(C-1)] <sup>+c</sup>	0.70	-0.11	0.41
[HTFAA-1(C-4)] <sup>+c</sup>	0.72	-0.13	0.41
[HTFAN-1(C-1)] <sup>+d</sup>	1.18	-0.18	0.0
[HTFAN-1(C-4)] <sup>+d</sup>	0.95	0.05	0.0

<sup>a</sup> Trifluoroacetyl or nitro moiety. <sup>b</sup> Trifluoroacetic acid. <sup>c</sup> C-1 or C-4 transition state with protonated TFAA and 1. <sup>d</sup> C-1 or C-4 transition state with protonated TFAN and 1.

reaction at the carbonyl of a trifluoroacetyl group but not for reaction at the nitro group of TFAN or 1-nitropyridinium fluoroborate, in agreement with the experimental findings. The finding of a difference in steric crowding at the two positions suggested that the degree of solvation of the electrophile could be a factor if, for example, the transition states with the trifluoroacetylation reagents required more solvation stabilization than those with the nitration reagents. Olah et al. showed that nitropyridinium ions react as the intact ion and that 1-nitro-2,6-dimethylpyridinium ion exhibited an insignificant steric effect on aromatic nitration.<sup>11</sup> We found, in agreement, that reaction of this reagent with 1 also formed 6.

### Experimental Section

Chemicals were reagent grade and not further purified unless otherwise indicated. Tank N<sub>2</sub> or Ar was passed through concentrated H<sub>2</sub>SO<sub>4</sub>, over Na<sub>2</sub>SO<sub>4</sub> or CaCl<sub>2</sub> and then over NaOH pellets and finally, over reduced BTS (BASF Cu·Al<sub>2</sub>O<sub>3</sub>) catalyst. Trifluoroacetic acid anhydride (TFAA) was distilled from P<sub>2</sub>O<sub>5</sub>. CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> were dried over CaCl<sub>2</sub> and distilled from P<sub>2</sub>O<sub>5</sub>. Pyridine and triethylamine were dried over KOH pellets and distilled from BaO. Quinoline was stored over KOH pellets and then distilled prior to use. *n*-Hexane was shaken with a mixture of concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, washed successively with H<sub>2</sub>O, aqueous NaHCO<sub>3</sub>, and H<sub>2</sub>O, dried (Na<sub>2</sub>SO<sub>4</sub>), and distilled from Na. DClO<sub>4</sub> was purchased from Aldrich Chemical Co., Milwaukee, WI. Precoated TLC plates were obtained from MCB Manufacturing Chemists, Inc., Cincinnati, OH. Analytical plates (0.25 mm) and preparative plates (2 mm) were prepared with Silica Gel 60F-254. Plates were visualized with UV light or I<sub>2</sub> vapor. Chromatography columns were prepared with Merck Silica Gel Grade 60, 230–400 mesh. Melting points were taken on a Thomas-Hoover or a Fischer-Johns apparatus and are uncorrected. Elemental analyses were performed by Canadian Micro-analytical Service, Ltd., Vancouver, British Columbia. Spectral data were recorded on the following instruments: UV and visible, Varian Superscan 3 or Hewlett-Packard 8450A spectrophotometer (1.0-cm quartz cells); IR, Beckman Acculab TM 4 spectrophotometer (NaCl prisms); NMR, Varian CFT-20, Bruker CXP-200, and Bruker WM 500 Cryospec spectrometers with Me<sub>4</sub>Si as internal standard; mass spectra, Hewlett-Packard 5985 GC/MS System with 30-m (DB-5) fused silica capillary or V. G. Micromass 7070 H GC/MS and associated VG 2035 F/B Data System<sup>12</sup> with perfluorokerosene as the standard.

**Azopyrene (1).** This was synthesized by the route described by Jutz<sup>7</sup> except that *N*-cyclopentylidenedimethylammonium fluoroborate, mp 169–170°C, prepared in 94% yield by the method of Leonard<sup>13</sup> was used in place of the perchlorate salt. The hydrocarbon was obtained as greenish gold leaflets, mp 259–260°C (lit.<sup>7,11</sup> 257–259, 250–258°C), after sublimation at 150°C and 0.5 torr.

**H-D Exchange.** A solution of 0.5 mL (4.7 mmol) of 68% DClO<sub>4</sub> in D<sub>2</sub>O was added slowly with stirring to 10 mg (0.05 mmol) of azopyrene (1) which had been precipitated (solvent evaporation) as a thin layer on the walls of a dry flask under N<sub>2</sub>. Separate reactions were quenched after 2, 5, and 10 min by the addition of 2 mL of H<sub>2</sub>O. The azopyrene was extracted into 2 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the solvent was removed from the washed (H<sub>2</sub>O), dried (Na<sub>2</sub>SO<sub>4</sub>) solution. The residue was dissolved in CDCl<sub>3</sub> or Me<sub>2</sub>SO-*d*<sub>6</sub> for spectral analysis. Two minute product: <sup>1</sup>H NMR  $\delta$  7.40 (t, 1.78, H-4, 9), 8.40 (s, 1.29, H-1, 2, 6, 7), 8.68 (d, 4, H-3, 5, 8, 10) with intensities corresponding to 11%, 68%, and 0% D exchange, respectively; MS, *av m/e* 204.1 corresponding to 2.6 D incorporated (calcd 2.9). Five minute product: <sup>1</sup>H NMR  $\delta$  7.40 (t, 1, H-4, 9), 8.40 (s, 0.35, H-1, 2, 6, 7) 8.68 (d, 4, H-3, 5, 8, 10), with intensities corre-

(11) Olah, G. A.; Subhash, C. N.; Olah, J. A.; Pearson, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 3507–3510.

(12) Funding by NIH Biomedical Research Development Grant 1508 RR 09082 is gratefully acknowledged.

(13) Leonard, N. J.; Paukstelis, J. V. *J. Org. Chem.* **1963**, *28*, 3021.

sponding to 50%, 91%, and 0% D exchange, respectively; MS, av  $m/e$  205.9 corresponding to 4.3 D incorporated (calcd 4.65). Ten minute product:  $^1\text{H NMR}$   $\delta$  7.40 (t, 0.9, H-4, 9), 8.40 (s, 0, H-1, 2, 6, 7), 8.68 (d, 4, H-3, 5, 8, 10) corresponding to 55%, 100%, and 0% exchange, respectively; MS, av  $m/e$  205.7 corresponding to 4.1 D incorporated (calcd 5.1).<sup>14</sup>

**Trifluoroacetylation. Method A.** Trifluoroacetic anhydride (0.2 mL, 1.4 mmol) and  $\text{BF}_3$ -etherate (0.1 mL, 0.8 mmol) were added with stirring to 10 mg (0.05 mmol) of a solution of azupyrene in 10 mL of  $\text{CH}_2\text{Cl}_2$  under anhydrous conditions under Ar. The reaction was stirred overnight at room temperature and monitored by TLC (1:1 hexanes- $\text{CH}_2\text{Cl}_2$ ). After the addition of 10 mL of  $\text{H}_2\text{O}$ , the solvent was removed from the separated, washed (10%  $\text{NaHCO}_3$ ), and dried ( $\text{Na}_2\text{SO}_4$ ) organic layer. Chromatography on a silica gel column (3  $\times$  1 in.) with hexanes removed unchanged azupyrene and  $\text{CH}_2\text{Cl}_2$  eluted the red trifluoroacetyl product. GCMS showed one component at  $m/e$  298 (calcd for  $\text{C}_{18}\text{H}_9\text{OF}_3$ , 298). High-resolution  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) (for 1-trifluoroacetylazupyrene) (**4**)  $\delta$  7.20 (t, 1, H-4), 7.55 (t, 1, H-9), 8.25 (dd, 2, H-6, 7), 8.52 (d, 1, H-5), 8.54 (d, 1, H-3), 8.63 (d, 1, H-8), 8.88 (q, 1, H-2), 9.91 (d, 1, H-10)<sup>15</sup> and (for 4-trifluoroacetylazupyrene) (**5**)  $\delta$  7.64 (t, 1, H-9), 8.38 (d, 2, H-1, 7), 8.50 (d, 2, H-2, 6), 8.72 (d, 2, H-8, 10), 9.32 (s, 2, H-3, 5) in a ratio of 9:1 in agreement with the spectrum of the product obtained from the repetition of the earlier procedure.<sup>5</sup>

**Method B.** To a solution of 7.43 mL (0.1 mol) of trifluoroacetic acid in 1 mL of DMF was added 10.9 mL (0.15 mol) of thionyl chloride under anhydrous conditions. The mixture was gently refluxed for 1 h. Fractional distillation gave 4.812 g of product, bp 22  $^\circ\text{C}$ , presumed to be trifluoroacetyl chloride.

To a well-stirred solution of 30.2 mg (0.228 mmol) of the acid chloride in 2 mL of  $\text{CHCl}_3$  under dry  $\text{N}_2$  at 0  $^\circ\text{C}$  was added slowly 27.1 mg (0.342 mmol) of pyridine in 2 mL of  $\text{CHCl}_3$  and the mixture stirred for 30 min at 0  $^\circ\text{C}$ . A 2.2-mL (ca. 0.125 mmol) portion of the presumed trifluoroacetylpyridinium chloride solution at room temperature was added slowly to a well-stirred solution of 23 mg (0.114 mmol) of azupyrene in 25 mL of  $\text{CHCl}_3$  under dry  $\text{N}_2$ . After 2 days, the reaction was quenched with 1 N hydrochloric acid-ice-water (1:1). The separated organic layer was washed (1 N hydrochloric acid, then  $\text{H}_2\text{O}$ ), dried ( $\text{Na}_2\text{SO}_4$ ), concentrated, and chromatographed over silica gel CC-7 with *n*-hexane-chloroform (2:1). Azupyrene (13.7 mg, 59.6%) and 1-trifluoroacetylazupyrene (**4**) (10.2 mg, 30%), mp 144-146  $^\circ\text{C}$ <sup>5</sup> were obtained. The  $^1\text{H NMR}$  spectrum of the latter was identical with that of method A.

**Nitration. Method A.** A solution of 5 mmol of 1-nitropyridinium fluoroborate in 5 mL of acetonitrile was prepared by the method of Olah et al.<sup>16</sup> A 0.31-mL (ca. 0.287 mmol) portion was added slowly (syringe)

to be a stirred solution of 57.3 mg (0.284 mmol) of a solution of azupyrene (**1**) in a few mL of  $\text{CHCl}_3$  under  $\text{N}_2$  at 25  $^\circ\text{C}$ . After 24 h, the reaction was quenched with cold, 1 N hydrochloric acid. The separated organic layer was washed (1 N hydrochloric acid then  $\text{H}_2\text{O}$ ), dried ( $\text{Na}_2\text{SO}_4$ ), and chromatographed on a silica gel CC-7 column. Elution with *n*-hexane removed unchanged azupyrene (29 mg, 50.6%). Then a reddish fraction was eluted with 1:1  $\text{CHCl}_3$ -*n*-hexane. Removal of the solvent gave 28 mg (40%) of 4-nitroazupyrene (**6**) as brownish-red crystals, mp 165-166  $^\circ\text{C}$ : UV/vis (*n*-hexane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 239 (4.37), 265 (4.50), 292 (4.00), 305 (4.02), 325 (3.98) 338 (4.34), 403 (3.94), 409 (3.92), 438 (3.58), 473 (3.25), 480 (3.16), 487 (3.08), 510 nm (2.88);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.68 (t, 1, H-9), 8.49 (d, 2, H-1, 7), 8.58 (d, 2, H-2, 6), 8.80 (d, 2, H-8), 10), 9.80 (s, 2, H-3, 4); MS,  $m/e$  (rel intensity) 247 ( $\text{M}^+$ , 8.71), 248 ( $\text{M} + 1^+$ , 15.6), 215, 214, 213, 201 (100), 200 (93), 189, 174, 106, 100, 99, 94; high-resolution Ms,  $m/e$  247.0607 ( $\text{C}_{16}\text{H}_9\text{NO}_2$  requires 247.0633).

**Method B.** A solution of 48.96 mg (0.288 mmol) of  $\text{AgNO}_3$  in 4 mL of acetonitrile was added, slowly with stirring, to a solution of 41.98 mg (0.317 mmol) of trifluoroacetyl chloride in 4 mL of acetonitrile under  $\text{N}_2$  at 0  $^\circ\text{C}$ . The precipitate which formed was allowed to settle. A 4.36-mL (ca. 0.157 mmol of trifluoroacetyl nitrate) portion of the supernatant liquid was removed with a syringe and added slowly to a stirred solution of 24 mg (0.143 mmol) of azupyrene and 0.1 mL (0.71 mmol) of trimethylamine in  $\text{CHCl}_3$  under  $\text{N}_2$ . After 2 h, the mixture was filtered through a short silica gel CC-7 column with  $\text{CHCl}_3$  as the eluent. The eluted solution was washed (1 N hydrochloric acid), dried ( $\text{Na}_2\text{SO}_4$ ), concentrated to ca. 1 mL, and chromatographed on a silica gel CC-7 column. No azupyrene was recovered. Elution with  $\text{CHCl}_3$ -*n*-hexane (1:1) removed a brownish-yellow band. Sublimation of the residue from this fraction at 95  $^\circ\text{C}$  and 0.5 torr gave 36.4 mg of crystalline product. The  $^1\text{H NMR}$  of this showed the major component to be **6**. The mass spectrum indicated the presence of a small quantity of unidentified dinitro product: ms,  $m/e$  292 ( $\text{M}^+$ ), 246 ( $\text{M}^+ - \text{NO}_2$ ).

**Method C.** Nitronium tetrafluoroborate (0.133 g, 1 mmol) was dried over  $\text{P}_2\text{O}_5$  at 0.1 torr and then placed under Ar and dissolved in 5 mL of dry acetonitrile. An aliquot (0.25 mL, 0.05 mmol) of the solution was added slowly to 10 mg (0.05 mmol) of azupyrene in 5 mL of dry acetonitrile under Ar. The red mixture was stirred for 1 min.  $\text{H}_2\text{O}$  (5 mL) was added, and the organic material was extracted into ca. 30 mL of  $\text{CH}_2\text{Cl}_2$ . The separated organic layer was washed ( $\text{H}_2\text{O}$ , then 10%  $\text{NaHCO}_3$ ) and dried ( $\text{Na}_2\text{SO}_4$ ) before removal of the solvent. The residue was transferred with the minimum amount (ca. 1 mL) of  $\text{CH}_2\text{Cl}_2$  to a silica gel column. Elution with  $\text{CH}_2\text{Cl}_2$ -hexanes (1:9) removed 4 mg (40%) of unchanged azupyrene, and  $\text{CH}_2\text{Cl}_2$  then eluted 4 mg (33%) of red crystalline product. The  $^1\text{H NMR}$  of this was identical with that from method A.

**Evidence for 1-Nitroazupyrene (7).** Rechromatography of a combined product sample from methods A and C afforded a sample of more pure mononitro product. In addition to the absorption due to **6**, small peaks indicative of **7** were observed high-resolution  $^1\text{H NMR}$   $\delta$  7.20 (t,  $J = 9.5$  Hz, H-4), 7.45 (t,  $J = 9.5$  Hz, H-9), 8.22 (d,  $J = 4.5$  Hz, H-7), 8.50 (d,  $J = 9.5$  Hz, H-3, 5 or 8), 8.54 (d,  $J = 9.5$  Hz, H-3, 5, or 8), 8.80 (s, H-2), 9.61 (d,  $J = 9.5$  Hz, H-10). Anal. ( $\text{C}_{16}\text{H}_9\text{NO}_2$ ) C, H, N.

(14) Material recovered for MS analysis contained some unexchanged solid azupyrene. A qualitative correction for this was made based on the excess height of the  $m/e$  202 peak.

(15) Recorded at 310 K. The earlier spectrum (ref 4) was recorded at <300 K.

(16) Olah, G. A.; Olah, J. A.; Overchuck, N. A. *J. Org. Chem.* **1965**, *30*, 3373-3376.