H, J = 5 Hz, CHOH), 3.68–3.10 (br m, 3 H, benzylic), 2.83–2.18 (br m, 1 H, NH); IR (Nujol) 3.07, 3.42, 6.72, 6.83, 7.27, 7.54, 7.67, 7.97, 8.17, 8.39, 8.47, 8.92, 9.57, 10.21, 10.55, 11.16, 11.67, 12.48, 12.83, 12.95, 13.27, 13.62, 14.08 μm.

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.55; H, 6.07; N, 6.36; mass spectrum m/e 223 (molecular ion).

Concentration of the chloroform filtrate yielded 10.13 g (45.4 mmol, 31%) of *syn*-10,11-dihydro-10,11-azacyclopropa-5*H*-dibenzo[*a*,*d*]cycloheptene-5-ol as an off-white solid: mp 163–165 °C; NMR ($CDCl_3$) δ 7.70–7.10 (m, 8 H, aromatic), 6.28 (br d, 1 H, J = 11 Hz, CHOH), 3.75–3.45 (br s, 2 H, benzylic), 2.82–1.97 (br m, 2 H, NH and OH); IR ($CHCl_3$) 2.98, 3.30, 6.70, 6.90, 7.10, 7.17, 7.60, 7.68, 8.00, 8.45, 8.82, 9.02, 9.51, 9.90, 10.56, 11.02, 11.27, 12.20, 12.51, 14.22 μm.

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.70; H, 6.08; N, 6.27. Mass spectrum calcd for $C_{15}H_{13}NO$: m/e 223.0997. Found: m/e 223.0989.

10,11-Dihydro-10,11-azacyclopropa-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (3). (a) From *anti*-10,11-Dihydro-10,11-azacyclopropa-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (10). To 15.20 g (96.2 mmol) of finely powdered potassium permanganate was added 200 mL of saturated aqueous magnesium sulfate. After the mixture was stirred for 10 min, a suspension of 20.00 g (89.6 mmol) of *anti*-10,11-dihydro-10,11-azacyclopropa-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (finely powdered) in 400 mL of methylene chloride was added. The mixture was stirred for 25 h, diluted with 500 mL of methylene chloride, washed with saturated aqueous sodium bisulfite and water, dried, treated with Darco, filtered, and concentrated in vacuo to give a light yellow solid which was recrystallized from ethanol to give 14.13 g (63.9 mmol, 71%) of the title compound as a white solid: mp 188–189 °C; NMR ($CDCl_3$) δ 7.71–7.10 (m, 8 H, aromatic), 3.66 (br m, 2 H, J = 9 Hz, benzylic), 3.31–2.63 (br m, 1 H, NH); IR ($CHCl_3$) 3.00, 3.30, 5.98 (s), 6.24, 6.70, 6.89, 7.19, 7.75, 8.08, 8.41, 8.68, 8.80, 9.14, 9.60, 10.50, 10.73, 11.00, 11.70, 12.20, 12.50, 14.04 μm.

Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.52; H, 5.09; N, 6.41; mass spectrum calcd for $C_{15}H_{11}NO$: m/e 221.0840. Found: m/e 221.0859.

(b) From *syn*-10,11-Dihydro-10,11-azacyclopropa-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (9). To 8.10 g (51.3 mmol) of potassium permanganate (finely powdered) was added 100 mL of saturated aqueous magnesium sulfate. After the mixture was stirred for 10 min, 10.00 g (44.8 mmol) of *syn*-10,11-dihydro-10,11-azacyclopropa-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (finely powdered) was added. The suspension was stirred for 5 min, and 200 mL of methylene chloride was added. The mixture was stirred for 16 h, diluted with 300 mL of methylene chloride, washed with saturated aqueous sodium bisulfite and water, dried, treated with Darco, filtered, and concentrated in vacuo to give a yellow solid which was recrystallized from ethanol to give 3.05 g of white solid. NMR and IR analyses showed the solid to be a 50:50 mixture of starting alcohol and 10,11-dihydro-10,11-azacyclopropa-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one. Complete conversion was not obtained.

[(4b,4c-Dihydro-8b*H*-azirino[2,1,3-*cd*]dibenzo[*a*,*f*]pyrrolizin-8b-yl)oxy]methane (4). To 13.9 mmol of dimsyl sodium in 60 mL of Me_2SO at room temperature was added dropwise a solution of 3.00 g (13.6 mmol) of **3** in 25 mL of dimethyl sulfoxide. The mixture was stirred for 10 min, and 0.855 mL (1.95 g, 13.7 mmol) of methyl iodide was added dropwise. The mixture was stirred for 1 h, poured into 330 mL of brine, and extracted with methylene chloride. The organic extracts were washed with brine, dried, filtered, and concentrated in vacuo to give a yellow solid. Recrystallization from 2-propanol gave 2.91 g (12.4 mmol, 91%) of the title compound as colorless crystals: mp 118–119 °C; NMR ($CDCl_3$) δ 7.45–6.97 (m, 8 H, aromatic), 4.12 (s, 2 H, benzylic), 3.59 (s, 3 H, OCH_3); IR ($CHCl_3$) 3.32, 3.51, 6.80, 6.98, 7.37, 7.90, 8.07 (s), 8.75, 8.88, 9.18, 9.51, 9.93, 10.38, 10.61, 10.81, 11.00, 11.40, 13.98 μm; UV (EtOH) λ_{max} 202 nm (ε 30 633), 220 sh (29 920), 240 (7426), 255 (1856).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 82.02; H, 5.47; N, 5.65; mass spectrum calcd for $C_{16}H_{13}NO$: m/e 235.0996. Found: m/e 235.0992.

10,11-Dihydro-5,10-imino-5-methoxy-11-chloro-5*H*-dibenzo[*a*,*d*]cycloheptene (11). A solution of 235 mg (1.00 mmol) of **4** in 50 mL of 3 N hydrogen chloride in ethanol was stirred for 3 h and concentrated in vacuo to give a white solid which was taken up in 25 mL of water. The solution was added to 50 mL of saturated aqueous sodium carbonate and extracted with methylene chloride. The organic extracts were dried, filtered, and concentrated in vacuo to give 390 mg of an oily solid which was chromatographed on a 20 cm × 20 cm × 2 mm plate of silica gel. After one chloroform development the plate was divided into four bands. The second band from the top contained 190 mg (0.70 mmol, 70%) of the title compound which crystallized and was washed with 2-propanol and hexane to give a white solid: mp 132–133 °C; NMR ($CDCl_3$) δ 7.67–7.05 (m, 8 H, aromatic), 5.44 (d, 1 H, J = 5.5 Hz, PhCH–NH), 4.79 (d, 1 H, J = 5.5 Hz, PhCHCl), 3.52 (s, 3 H, OCH_3), 2.70–2.40 (br s, 1 H, NH); IR ($CHCl_3$) 3.04, 3.38, 3.54, 6.94, 7.24, 7.52, 7.94, 8.14, 8.84, 9.29, 9.75, 9.90, 10.47, 10.67, 11.04, 11.52, 11.94, 12.27, 14.28, 14.58 μm.

Anal. Mass spectrum calcd for $C_{16}H_{14}NOCl$: m/e 271.0763. Found: m/e 271.0756.

Registry No. 3, 69208-47-5; **4**, 72301-59-8; **7**, 56157-32-5; **8**, 69208-45-3; **9**, 69208-46-4; **10**, 69256-74-2; **11**, 72301-60-1.

Electrophilic Trifluoroacetylation of Dicyclopenta[*ef*,*kl*]heptalene (Azupyrene)[1,2]

Arthur G. Anderson, Jr.,* Gary M. Masada,[3] and Glenn L. Kao

Department of Chemistry, University of Washington, Seattle, Washington 98195

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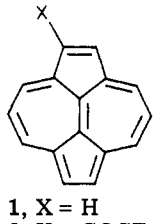
The spectral properties (IR, ^1H NMR, and ESR), diamagnetic susceptibility, and stability to heat and air of the nonbenzenoid, 4n π electron hydrocarbon azupyrene (**1**)



1, X = H
2, X = $COCF_3$

were indicative of aromatic character,[4] but it remained to show that electrophilic substitution rather than addition was the preferred mode of reaction and, if this were the case, to determine the most reactive position.

The symmetry of the structure simplifies the application of molecular orbital calculations to predict the primary site for bonding to an electrophile. Boekelheide et al.[5] calculated that the (equivalent) open positions on the five-membered ring would have the highest ground-state electron density. This often corresponds to the most reactive position in aromatic molecules, but the atom-localization energy is probably a more reliable indicator.[6] Accordingly, simple Hückel (HMO) and CNDO/2 calcu-

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(2) Taken in part from the Ph.D. Thesis of G.M.M., University of Washington, 1972.
(3) NIH Predoctoral Fellow, 1968–1970.
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lations of this type were performed.[7] The former selected the 1 position and the latter the 3 position.

Attempts to show the position of protonation by observing the change in the ^1H NMR spectrum on formation of the conjugate acid were not successful. Concentrated (72%) perchloric acid effected reversible protonation but obscured the absorption of the conjugate acid.[8] Hexafluorophosphoric acid (65%) and tetrafluoroboric acid (48%) were not sufficiently strong.[8] Sulfuric acid (96%) led to rapid darkening and apparent decomposition,[8] and trifluoromethanesulfonic acid caused polymerization. The amount of 1 available did not permit the extension of these experiments.

Treatment of 1 with trifluoroacetic anhydride at room temperature afforded a 73% (ca. 100% net) yield of a crystalline monotrifluoroacetyl derivative with no indication of disubstitution products. The ^1H NMR spectrum of this compound was reasonably interpretable only with the structure 2 resulting from substitution in the 1 position. The assignments (with the corresponding chemical shift values for 1 given in parentheses) were δ 8.03 (s, 1, H-2) (8.4), 8.28 (d, 2, H-3 and H-5) (8.68), 6.975 (t, 1, H-4) (7.34), 8.64 (d, 2, H-6 and H-7) (8.4), 9.675 (d, 1, H-8) (8.68), 7.28 (t, 1, H-9) (7.34), and 8.36 (d, 1, H-10) (8.68). These assignments are consistent with shielding of H-2 by the adjacent trifluoroacetyl group, retention of the signals for H-3, H-5, H-8, and H-10 as doublets and, concomitantly, of the signals for H-4 and H-9 as triplets, absorption at lower field for H-9 than H-4 as the result of both inductive and resonance effects (the latter places a partial positive charge at C-9 but not at C-4), and H-10 shielded more than H-8.

Confirmation was provided by decoupling experiments. Irradiation at δ 7.28 (H-9) affected only the doublets at δ 9.675 (H-8) and 8.36 (H-10). Similarly, irradiation at δ 6.975 (H-4) affected only the doublet at δ 8.28 (H-3 and H-5). Thus the remaining doublet (δ 8.64) must be from H-6 and H-7, and the remaining singlet (δ 8.03) from H-2.

These results establish that 1 undergoes electrophilic aromatic substitution readily and in the 1 position.

Experimental Section

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. NMR spectra were recorded on a Varian HA-100 spectrometer in chloroform with tetramethylsilane as the internal reference. Ultraviolet and visible spectra were obtained with a Cary Model 14 spectrophotometer using 1-cm quartz cells. Trifluoroacetic anhydride was freshly distilled from P_2O_5. Triethylamine was distilled from KOH and stored over Na_2SO_4. Dichloromethane was distilled from P_2O_5 and stored over Na_2SO_4. *n*-Hexane was washed successively with sulfuric acid, water, aqueous $NaHCO_3$, and water and then dried (Na_2SO_4) and distilled tilled from Na. Chloroform was reagent grade. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

1-Trifluoroacetyldicyclopenta[*ef*,*kl*]heptalene (2). To a solution of 80.8 mg (0.4 mmol) of the hydrocarbon 1 in 7 mL of dichloromethane was added 0.28 mL (2 mmol) of triethylamine, and the whole was chilled (ice bath) while an atmosphere of N_2 was introduced through a condenser. Then 0.3 mL (2 mmol) of trifluoroacetic anhydride was added with stirring (magnetic bar). The bath was removed and the stirring continued at room temperature for 3-4 days.[9] The reaction mixture was then filtered through a short silica gel G column (chloroform eluant). The eluted material was concentrated and chromatographed over a silica gel CC-7 column. Elution with *n*-hexane removed unchanged 1 (20.31 mg, 25.1%) and a 1:1 chloroform-*n*-hexane mixture removed 2 (87.32 mg, 73.2%), mp 144-146 °C. Sublimation at 96 °C (0.5 torr) afforded fine, reddish brown needles: mp 144-145 °C; UV max (cyclohexane) 240 (ϵ 1.47 × 10^4), 264 (2.1 × 10^4), 300 (9.1 × 10^3), 315 (7.35 × 10^3), 334 (4.1 × 10^3), 354 sh (8.65 × 10^2), 384 (2.38 × 10^3), 410 (1.21 × 10^3), 438 (8.22 × 10^2), 475 (9.5 × 10^2), 499 sh (1.64 × 10^3), 511 nm (5.1 × 10^3); NMR ($HCCl_3$) δ 6.975 (t, 1), 7.28 (t, 1), 8.03 (s, 1), 8.28 (d, 2), 8.36 (d, 1), 8.64 (d, 2), and 9.675 (d, 1). Anal. Calcd for $C_{18}H_9OF_3$: C, 72.49; H, 3.04. Found: C, 72.56; H, 2.93.

Registry No. 1, 193-85-1; 2, 72541-89-0.

(7) We thank Professor Martin Gouterman for assistance with these.
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(9) The reaction progress could be monitored by TLC on silica gel G with *n*-hexane as the eluant.

Electrophilic Addition of Benzeneselenenyl Chloride to Hydroxyalkynes[1]

Crist N. Filer,* David Ahern, Robert Fazio, and Emma J. Shelton

Ligands Group, New England Nuclear, Boston, Massachusetts 02118

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Cyclofunctionalization of compounds 1 (Scheme I) possessing proximate nucleophile X using benzeneselenenyl chloride (PhSeCl) is a powerful and elegant synthetic method leading to the formation of various heterocyclic compounds 3. Among the nucleophiles X successfully used in this synthon have been hydroxyl,[2] carboxyl,[3] urethane,[4] and carbon,[5,6] and the products derived from this cyclization have been those as predicted by Baldwin's rules for ring closure.[7] To date, however, only olefins have been reported as the unsaturated component in this cyclization scheme. We now report on the first attempt to utilize alkynes as the unsaturated moiety in a cyclofunctionalization reaction with PhSeCl.

Several lines of evidence suggested that alkynes might be substituted for olefins in a cyclofunctionalization reaction. It has been demonstrated that alkynes like olefins, in the absence of internal or external nucleophiles, electrophilically add PhSeCl in 1,2 fashion to yield well-characterized adducts.[8a] Since the cyclofunctionalization of olefins apparently proceeds through an intramolecular nucleophilic interception of a putative seleniranium cation 2,[2b] we reasoned that a similar utilization of alkynes 4 might allow for an intramolecular attack on an intermediate selenirenium cation 5,[8] yielding vinyl selenides 6 as shown in Scheme I. Also, Baldwin's rules for ring closure indicate that many favored modes of cyclization for alkynes exist.[7] It is not surprising then that there are numerous

(1) Presented in part at the 9th Northeast Regional Meeting of the American Chemical Society, Syracuse, NY, Oct 1979; see abstract No. ORGN-7.
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