

Synthesis of Tricarbonylcyclobuta[*l*]phenanthreneiron

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1,2-Dichloro-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene (II) was prepared both by photocycloaddition of phenanthrene to *trans*-dichloroethylene and by dichlorobisdecarboxylation of the 1,2-dicarboxylic acid (III) derived by hydrolysis of the photoadduct of phenanthrene with dimethyl maleate. Reaction of the dichloride (II) with *N*-bromosuccinimide, followed by chromatography on alumina, gave 1,2-dichloro-1,2-dihydrocyclobuta[*l*]phenanthrene (IV). Treatment of the product (IV) with enneacarbonyl-di-iron afforded tricarbonylcyclobuta[*l*]phenanthreneiron (V). Oxidative decomposition of compound (V) with cerium(IV) ion in the presence of cyclopentadiene gave the *endo*-adduct (VI).

SOME stable metal complexes of cyclobutadienes¹ as well as of benzocyclobutene² have been synthesised recently. While much attention is being devoted to the higher aromatic analogues of benzocyclobutene,³ little is known about the chemistry of cyclobuta[*l*]phenanthrenes, though the 1,2-diphenyl derivative is postulated as an unstable intermediate.⁴ We report here the synthesis of the tricarbonyliron complex (V) (see Scheme).

† Tentative stereochemical assignments for three stereoisomers (IIa), (IIb), and (IIc) are as follows; (IIa) *cis,trans,trans*-, (IIb) *cis,cis,cis*-, (IIc) *cis,trans,cis*-.

¹ P. M. Maitlis, *Adv. Organometallic Chem.*, 1966, **4**, 95; P. M. Maitlis and K. W. Eberius, 'Nonbenzenoid Aromatics,' ed. J. P. Snyder, vol. 2, p. 360.

The dichloro-compound (II) was prepared by two methods. The first involved the photocycloaddition of phenanthrene (I) to *trans*-dichloroethylene,⁵ and gave a mixture of three stereoisomers.† In the second, irradiation of phenanthrene with dimethyl maleate yielded the cycloadduct, which on hydrolysis gave the

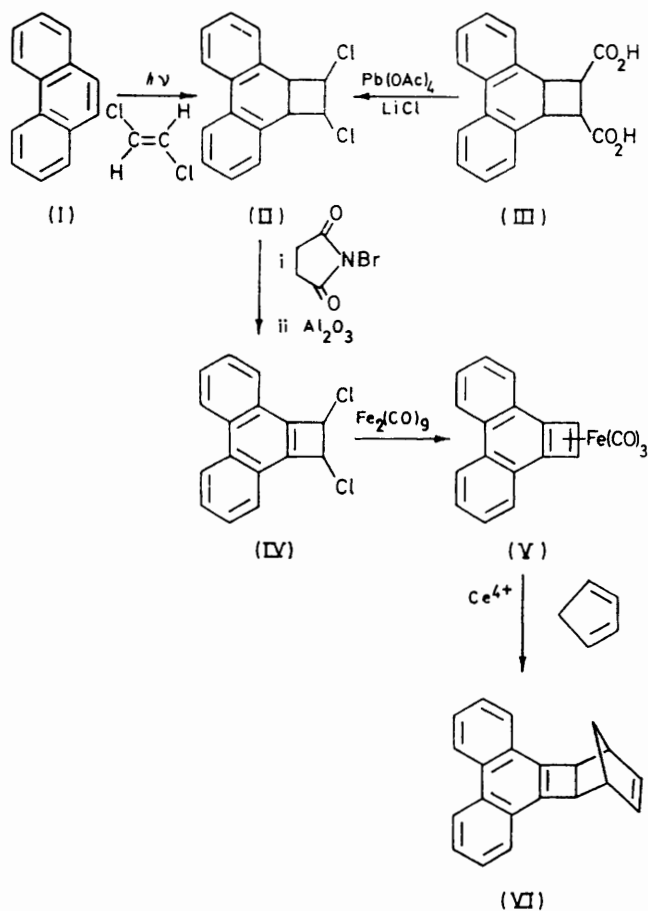
² G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 131.

³ M. P. Cava, B. Hwang, and J. P. Van Meter, *J. Amer. Chem. Soc.*, 1963, **85**, 4032; M. P. Cava and B. Hwang, *Tetrahedron Letters*, 1965, 2297; M. P. Cava, *Chem. Soc. Special Publ.*, No. 21, 1967, p. 175.

⁴ M. P. Cava and D. Mangold, *Tetrahedron Letters*, 1964, 1751.

⁵ T. Miyamoto, T. Mori, and Y. Odaira, *Chem. Comm.*, 1970, 1598.

dicarboxylic acid (III). Dichlorobisdecarboxylation with lead tetra-acetate and lithium chloride (modified



SCHEME

procedure for halogenodecarboxylation of monocarboxylic acids described by Kochi⁶) then gave compound (II).

Reaction of the dichloride (II) with *N*-bromosuccinimide in the presence of dibenzoyl peroxide in carbon tetrachloride under reflux, followed by chromatography on alumina, gave 1,2-dichloro-1,2-dihydrocyclobuta[*l*]phenanthrene (IV), identified by its n.m.r. and u.v. spectra { τ 1.30—1.65 (2H), typical of the 4- and 5-protons of a phenanthrene ring (phenanthrene itself⁷ shows τ 1.35); u.v. spectrum similar to that reported⁸ for cyclobuta[*l*]phenanthrene}.

Treatment of compound (IV) with enneacarbonyl-di-iron in *n*-hexane at 50° for 3 h afforded the tricarbonyl-iron complex (V) (32%), which showed characteristic carbonyl absorptions at 2050 and 1960 cm^{-1} and n.m.r. signals at τ 1.50—1.70 (2H, m), 2.35—2.65 (6H, m), and 5.55 (2H, s).

Oxidative decomposition of the complex (V) with

⁶ J. K. Kochi, *J. Amer. Chem. Soc.*, 1965, **87**, 2500; *J. Org. Chem.*, 1965, **30**, 3265.

⁷ R. C. Fahey and G. C. Graham, *J. Phys. Chem.*, 1965, **69**, 4417; T. J. Batterham, L. Tsai, and H. Ziffer, *Austral. J. Chem.*, 1964, **7**, 163; P. M. G. Barin, K. D. Bartle, and J. A. S. Smith, *Tetrahedron*, 1965, **21**, 1087.

cerium(IV) ion in the presence of cyclopentadiene gave the *endo*-adduct (VI). The n.m.r. and u.v. spectra showed the presence of phenanthrene ring system, which indicates that addition took place at the 1- and 2-positions of cyclobuta[*l*]phenanthrene. The adduct (VI) was assigned the *endo*-configuration in the light of comparison of its n.m.r. spectrum with those⁹ of *endo*- and *exo*-tetracyclo[8,2,1,0^{2,9},0^{3,8}]trideca-3,5,7,11-tetraene.

EXPERIMENTAL

I.r. spectra were measured for potassium bromide discs with a JASCO IR-G spectrophotometer. N.m.r. spectra were recorded for 5% solutions in deuteriochloroform with tetramethylsilane as internal standard, unless otherwise stated, on a JEOL JNM-3H-60 spectrometer. U.v. spectra were taken for solutions in ethanol on a Hitachi-Perkin-Elmer UV-VIS spectrophotometer. Mass spectroscopic analyses were performed with a Hitachi RMU-6E spectrometer. Petroleum refers to the fraction of b.p. 30—60°.

Photocycloaddition of Phenanthrene to trans-Dichloroethylene.—A solution of phenanthrene (17.8 g) and *trans*-dichloroethylene (48.5 g) in ether (100 ml) was irradiated in a Pyrex vessel with a 500 W high-pressure mercury lamp under nitrogen at room temperature for 120 h. The ether and unchanged dichloroethylene were removed by distillation. The residue was chromatographed on alumina. Elution with petroleum gave 1,2-dichloro-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene consisting of three stereoisomers. Fractional recrystallisation from ethanol gave isomer (IIa) (4.6 g), isomer (IIb) (5.2 g), and isomer (IIc) (0.1 g). Isomer (IIa) had m.p. 145—160° (decomp.), τ 1.90—2.30 (2H, m, aromatic), 2.50—2.95 (6H, m, aromatic), and 5.00—6.55 (4H, m, methine) (Found: C, 69.55; H, 4.25%; M^+ , 274). $\text{C}_{16}\text{H}_{12}\text{Cl}_2$ requires C, 69.85; H, 4.4%; M^+ , 274). Isomer (IIb) had m.p. 161.5—163°, τ 2.00—2.30 (2H, m, aromatic), 2.50—2.90 (6H, m, aromatic), and 5.35—6.05 (4H, m, methine) (Found: C, 69.85; H, 4.5%; M^+ , 274). Isomer (IIc) had m.p. 190° (decomp.), τ [(CD_3)₂SO] 1.85—2.15 (2H, m, aromatic), 2.55—3.00 (6H, m, aromatic), 4.55—4.75 (2H, m, methine), and 5.60—5.80 (2H, m, methine) (Found: C, 69.95; H, 4.25%; M^+ , 274).

Photocycloaddition of Phenanthrene to Dimethyl Maleate.—A solution of phenanthrene (17.8 g) and dimethyl maleate (43.2 g) in ether (150 ml) was irradiated under similar conditions. Distillation under reduced pressure gave dimethyl 1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-1,2-dicarboxylate, b.p. 175—205° at 5.3×10^{-4} mmHg (27.3 g), which crystallised from benzene-petroleum as plates, m.p. 104—112°, ν_{max} 1725 cm^{-1} (CO_2Me), τ 2.10—2.55 (2H, m, aromatic), 2.80—3.20 (6H, m, aromatic), and 5.80—6.90 (10H, m, methine and methyl), λ_{max} 242, 273, 279, and 310 nm ($\log \epsilon$ 4.01, 4.18, 4.19, and 3.39) (Found: C, 74.3; H, 5.5%; M^+ , 322). $\text{C}_{20}\text{H}_{18}\text{O}_4$ requires C, 74.5; H, 5.65%; M^+ , 322).

Hydrolysis of the Diester.—The diester (5 g) was heated under reflux with aqueous 20% sodium hydroxide (60 ml) for 8 h. The resulting solid was filtered off and treated with hydrochloric acid to give the dicarboxylic acid (III) (3.4 g), m.p. 245—250° (decomp.) (from acetone), ν_{max} .

⁸ J. P. Anhalt, E. W. Friend, and E. H. White, *J. Org. Chem.*, 1972, **37**, 1015.

⁹ H. E. Simmons, *J. Amer. Chem. Soc.*, 1961, **83**, 1651.

1690 cm^{-1} (CO_2H) (Found: C, 73.65; H, 5.1%; M^+ , 294. $\text{C}_{18}\text{H}_{14}\text{O}_4$ requires C, 73.45; H, 4.8%; M^+ , 294).

Dichlorobisdecarboxylation of the Dicarboxylic Acid (III).—A suspension of the acid (III) (1.1 g), lead tetra-acetate (4.2 g), and lithium chloride (0.4 g) in acetonitrile (40 ml) was refluxed for 1 h, then filtered and evaporated. The residue was chromatographed on silica gel. Elution with benzene gave the dichloro-compound (II) (120 mg).

Reaction of Compound (II) with N-Bromosuccinimide.—Compound (IIa) (1.65 g) was dissolved in carbon tetrachloride (50 ml) and *N*-bromosuccinimide (4.3 g) and a few crystals of dibenzoyl peroxide were added. The mixture was refluxed for 1.5 h and filtered; the filtrate was washed with aqueous sodium thiosulphate and then dried (Na_2SO_4). The solvent was distilled off and the residue was chromatographed on alumina. Elution with petroleum gave 1,2-dichloro-1,2-dihydrocyclobuta[1]phenanthrene (IV) (1.06 g), needles, m.p. 126.5–127° (from ethanol), τ 1.30–1.65 (2H, m, aromatic), 2.00–2.65 (6H, m, aromatic), and 4.43 (2H, s, methine), λ_{max} 247, 255, 265sh, 279, 288, and 301 nm ($\log \epsilon$ 4.67, 4.79, 4.36, 4.03, 3.99, and 4.03) (Found: C, 70.35; H, 3.45%; M^+ , 272. $\text{C}_{16}\text{H}_{10}\text{Cl}_2$ requires C, 70.35; H, 3.7%; M^+ , 272).

Reaction of Compound (IV) with Enneacarbonyldi-iron.—A mixture of compound (IV) (3.55 g) and enneacarbonyldi-iron (14.7 g) in *n*-hexane (150 ml) was heated with stirring at ca. 50° for 3 h. The reddish-brown solid was filtered off and washed with benzene. Filtrate and washings were combined and chromatographed on alumina. Elution with

benzene gave tricarbonylcyclobuta[1]phenanthreneiron (V), (1.44 g), yellow needles, m.p. 200° (decomp.), ν_{max} 2050 and 1960 cm^{-1} (CO), τ 1.50–1.70 (2H, m, aromatic), 2.35–2.65 (6H, m, aromatic), and 5.55 (2H, s, ring protons) [Found: C, 66.6; H, 3.0. $\text{C}_{16}\text{H}_{10}\text{Fe}(\text{CO})_3$ requires C, 66.7; H, 2.95%]. The complex (V) is sensitive to light in solution; therefore the entire procedure was carried out in semi-darkness.

Oxidative Decomposition of the Complex (V) with Cerium(IV) Ion in the Presence of Cyclopentadiene.—Cerium(IV) ammonium nitrate (5 g) was added in portions to an ice-cooled solution of the complex (V) (706 mg) and cyclopentadiene (0.18 ml) in acetone (25 ml). Stirring was continued for an additional 30 min after which the mixture was poured into brine. The solution was extracted with benzene and the combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was chromatographed on alumina. Elution with petroleum gave 8c,9,12,12a-tetrahydro-endo-9,12-methanobenzo[3,4]cyclobuta-[1,2-1]phenanthrene (VI) (176 mg), plates, m.p. 132–133.5° (from *n*-hexane), τ (CCl_4) 1.35–1.70 (2H, m, aromatic), 2.35–2.80 (6H, m, aromatic), 4.55–4.70 (2H, t, vinylic), 6.16–6.30 (2H, m, benzylic), 6.80–7.15 (2H, m, bridgehead), 7.85–8.10 (1H, m, methine), and 8.15–8.40 (1H, m, methine), λ_{max} 250sh, 256, 273, 282, 295, and 306 nm ($\log \epsilon$ 4.65, 4.72, 4.23, 3.83, 3.85, and 3.94) (Found: C, 94.0; H, 5.95%; M^+ , 268. $\text{C}_{21}\text{H}_{16}$ requires C, 94.0; H, 6.0%; M^+ , 268).

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