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### A SYNTHESIS OF ACEANTHRYLENE

R. Sangaiah<sup>a</sup>; A. Gold<sup>a</sup>

<sup>a</sup> Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina at Chapel Hill, Chapel Hill, NC

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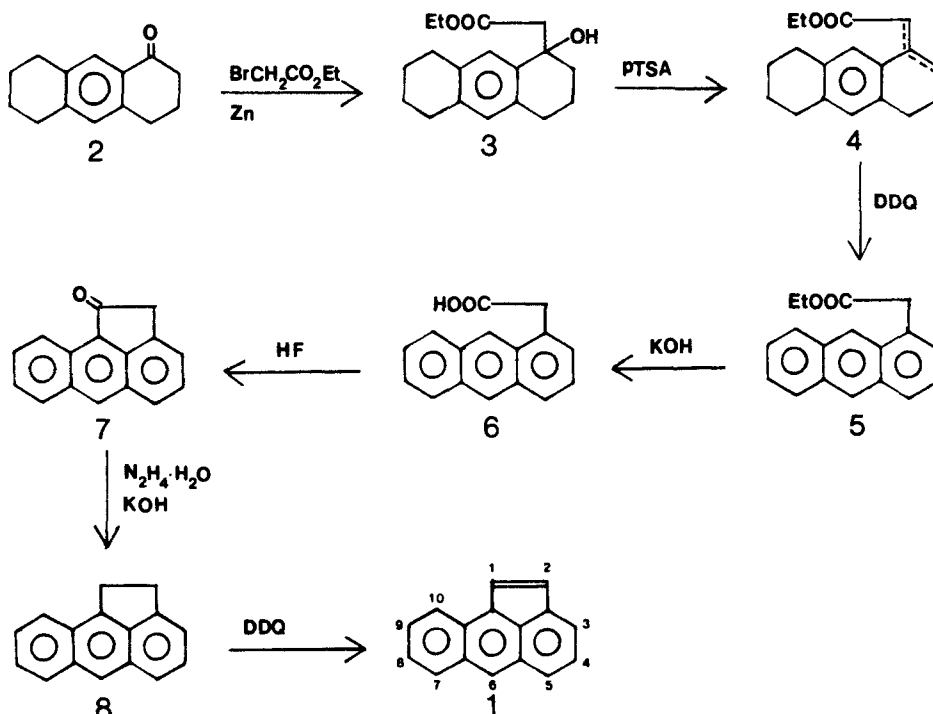
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## A SYNTHESIS OF ACEANTHRYLENE

Submitted by R. Sangaiah\* and A. Gold  
(03/15/84)

Department of Environmental Sciences and Engineering  
School of Public Health  
University of North Carolina at Chapel Hill  
Chapel Hill, NC 27514

Cyclopenta-fused aromatic ring systems such as aceanthrylene (1) are of interest both biochemically<sup>1</sup> and from a physico-chemical standpoint.<sup>2</sup> Until recently, a convenient synthesis for aceanthrylene had not appeared in the literature.<sup>3</sup> We report an alternate synthesis of aceanthrylene in high purity and in a 20% overall yield (from the tetralin precursor<sup>4,5</sup>) by the route shown.<sup>6</sup>



## EXPERIMENTAL SECTION

Compounds 3-8 have been reported via routes different from that utilized in this study. The sequence of reactions leading from 3 through 8 will therefore be described briefly; detailed procedures may be found in ref. 4.

Ethyl 1-Anthrylacetate (5).— To a suspension of activated zinc dust (5 g, 77 mmol) and iodine (0.2 g, 1.6 mmol) in refluxing benzene, was added a solution of ethyl bromoacetate (2 g, 12 mmol) and ketone 2 (1.77 g, 8.9 mmol) in benzene-ether (1:1, 40 ml). After the addition, the reaction mixture was heated under reflux for 2 hrs then treated with cold, dilute (1:10) HCl and ester 3 (2.16 g, 85%) was obtained as a liquid from the organic extract. Ester 3 was dehydrated by refluxing for 2 hrs in dry benzene (300 ml) with *p*-toluenesulfonic acid (100 mg). The mixture of exo- and endocyclic olefins 4 (1.82 g, 85%) was aromatized by refluxing in benzene (300 ml) for 6 hrs with DDQ (5 g, 22 mmol) and the filtrate chromatographed on neutral alumina (benzene eluent) to yield 5 as a viscous oil (1.50 g, 84%).

1-Anthrylacetic Acid (6).— Ester 5 (1.5 g, 5.5 mmol) was heated with aqueous KOH (45%, 10 ml) and methanol (40 ml) for 2 hrs on a steam bath. Distillation of methanol and acidification with conc. HCl yielded 6 (1.16 g, 90%), mp. 170°, lit.<sup>4</sup> 170-171°.

1-Oxo-1,2-dihydroaceanthrylene (7).— Intramolecular cyclization of 6 (1.0 g, 4.2 mmol) was accomplished in anhydrous HF (100 ml) over 15 hrs. Chromatography on silica (benzene eluent) yielded 7 (0.8 g, 87%), mp. 157-158°, lit.<sup>8</sup> 151-152°.

Aceanthrene (8).— A mixture of ketone 7 (600 mg, 2.7 mmol), diethyleneglycol (50 ml), hydrazine monohydrate (1.0 g) and KOH (1.0 g) was refluxed for 6 hrs, cooled to room temperature, and poured into excess water. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2x50 ml) and the organic extract was washed with water (100 ml), and dried (Na<sub>2</sub>SO<sub>4</sub>). The crude product obtained

after removal of solvent was purified by chromatography on silica gel with hexane as eluent to give 8 (450 mg, 80%), mp. 114-115°, lit.<sup>9</sup> 113-114°.

Aceanthrylene (1).— A mixture of 8 (204 mg, 1 mmol) and DDQ (250 mg, 1.1 mmol) in dry benzene (20 ml) was refluxed for 6 hrs. The cooled solution was filtered and the filtrate chromatographed on silica gel. Elution by hexane and collection of the red non-fluorescent band afforded 141 mg. (70%) of aceanthrylene (1), mp. 94-95°.

UV-vis (heptane),  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ ): 236(5.4), 255(5.66), sh 290(1.0), 345(0.46): 362(0.91), 380(0.46), 400(0.51), 423(0.30) nm; <sup>1</sup>H NMR (250 MHz, acetone-d<sub>6</sub>):  $\delta$  7.17(d, 1H, H<sub>2</sub>, J<sub>1,2</sub> = 5.3 Hz), 7.49(dd, 1H, H<sub>4</sub>, J<sub>3,4</sub> = 6.5 Hz, J<sub>4,5</sub> = 8.5 Hz), 7.64(dd, 2H, H<sub>8</sub>, J<sub>7,8</sub> = J<sub>8,9</sub> = 8.5 Hz; H<sub>9</sub>, J<sub>9,10</sub> = 8.5 Hz), 7.71(d, 1H, H<sub>1</sub>, J<sub>1,2</sub> = 5.3 Hz), 7.88 (d, 1H, H<sub>3</sub>, J<sub>3,4</sub> = 6.5 Hz), 8.06(d, 1H, H<sub>5</sub>, J<sub>5,4</sub> = 8.5 Hz), 8.17(d, 1H, H<sub>7</sub>, J<sub>7,8</sub> = 8.5 Hz), 8.37(d, 1H, H<sub>10</sub>, J<sub>10,9</sub> = 8.5 Hz), 8.59 (s, 1H, H<sub>6</sub>); mass spectrum with major fragments at m/z 202(M<sup>+</sup>), 101(M<sup>2+</sup>), 88; accurate mass determination of empirical formula: expected for C<sub>16</sub>H<sub>10</sub>, 202.0783; found, 202.0786 ( $\Delta$  = 0.3 ppm).

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### SELECTIVE HALOGENATION OF FLAVONOLS

#### BY HYDROHALOGENIC ACIDS IN OXIDATION SYSTEM

Submitted by Masataka Ichikawa<sup>+</sup>, Satoshi Hibino<sup>+</sup>, Mizuo Onishi<sup>++</sup>, James F. (10/07/84) Hatcher<sup>++</sup>, A. Mahir Pamukcu<sup>++</sup> and George T. Bryan<sup>++</sup>

<sup>+</sup>Faculty of Pharmacy & Pharmaceutical Sciences  
Fukuyama University, Fukuyama, Hiroshima 729-02, JAPAN

<sup>++</sup>Division of Clinical Oncology, Department of Human Oncology  
Wisconsin Clinical Cancer Center  
600 Highland Avenue, Madison, WI 53792

Kaemferol (Ia) and quercetin (Ib), common flavonols occurring as glycones, are widely distributed in varying concentrations in vegetables and fruits consumed by humans.<sup>1-3</sup> Quercetin and kaempferol are mutagenic

