A PHOTOCHEMICAL SYNTHESIS OF CALYCANINE

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Abstract—Calycanine, a degradation product of the alkaloid calycanthine, has been synthesised by a photochemical reaction.

IN 1960, Woodward et al. proposed¹ the structure I for the alkaloid calycanthine,



originally isolated from the seeds of *Calycanthus glaucus*, Willd., and subsequently studied^{2.3} by a variety of workers. Structure I has been confirmed⁴ by X-ray analysis.

The chemical evidence hinges on the structure of the weak base, calycanine, $C_{16}H_{10}N_2$, arising from dehydrogenation³ of the alkaloid. Calycanine was formulated¹ as quinolino(4',3',3,4)quinoline (II), and this structure was confirmed¹ by synthesis. Two further syntheses by conventional methods have appeared.^{5.6} We wish to report a new, one-step synthesis of calycanine by a photochemical reaction.

The oxidative photocyclization of stilbenes to phenanthrenes has been studied' in some detail and, recently, Cava and Schlessinger showed⁸ it to be applicable to aromatic Schiff bases, thereby producing phenanthridines. Badger *et al.* have recorded⁹ the oxidative photocyclization of benzylidene aniline to phenanthridine itself: by analogy, the anil of 4-formylquinoline should yield calycanine. This has proved to be the case.

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п

EXPERIMENTAL

M.ps were taken on a Kofler hot stage apparatus. IR spectra (either a Perkin-Elmer 137 or 621 spectrophotometer as indicated); UV spectra (Cary 14 spectrophotometer); NMR spectra (Perkin-Elmer R10 spectrometer). Microanalyses were performed by A. Bernhardt Ltd., Mülheim.

Materials. Lepidine and selenium were laboratory reagent grade. Aniline was general purpose reagent grade. Conc. H_3SO_4 was AnalaR grade.

Apparatus. The Irradiation apparatus was of the immersion type, the quartz probe being made of "Vitreosil" (transparent, thin wall) as supplied by Thermal Syndicate Ltd. (Northumberland, England).

The light source was a Hanovia U.V.S. 250W straight arc tube (507/7), catalogue number 05051 as supplied by Englehard-Hanovia Ltd. (Slough, England).

Solns being irradiated were stirred magnetically.

Selenium dioxide was prepared according to the method of Rabjohn,¹⁰ and resublimed in a stream of O₂ to give colourless needles.

4-Formylquinoline was prepared according to Kaplan.¹¹ It formed colourless needles, m.p. $51-52^{\circ}$ from ligroin. IR: 1695 cm⁻¹ (Perkin-Elmer 137) $\tau - 0.55$ (1H)].

4-Formylquinoline anil was prepared according to Hamer.¹³ It was obtained as yellow platelets, m.p. 85° (76%) from ether ligroin. [τ 0.9–2.9 (complex multiplet), UV: 204 (4.73), 243 (4.35), 334 (4.11)].

6,12-Diazachrysene (Calycanine) (II). 4-Formylquinoline anil (100 mg) in conc. H_sSO_4 (300 ml) was irradiated for 24 hr under dry O_s . The soln was poured on to crushed ice, made alkaline by the addition of conc. NaOH and extracted with ether. The ethereal soln was washed with water, dried (Na_sSO₄) and evaporated to give a yellow solid (59 mg). Recrystallization from pyridine-EtOH^{1,3} gave pale yellow needles (53 mg), m.p. 310°.

The IR spectra (nujol mull, Perkin-Elmer 621 spectrophotometer) of this material and of an authentic specimen of calycanine were superposable. The mass spectrum showed a molecular ion at 230. UV (EtOH): 267 (4.75), 334 (3.83), 353 (3.67), 370 (3.63) and 332 (3.82), inflexion. (Found: C, 83.12; H, 4.34; N, 12.11. Calc. for $C_{18}H_{10}N_{18}$: C, 83.45; H. 4.38; N, 12.17%. Mol. wt. 230.)

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