Photochemical Transformations of Cannabinol

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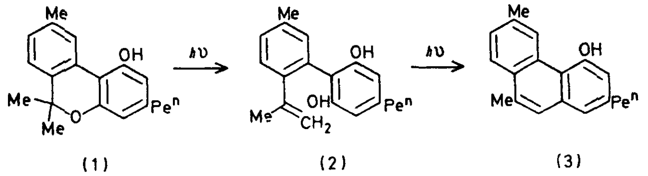
Summary Ultra-violet irradiation of cannabinol in ethanol results in ring opening to give the isomeric diol, which subsequently undergoes photoinduced dehydration and ring closure to a substituted phenanthrene.

IN a previous paper[1] we noted that solutions of cannabis constituents in ethanol undergo photochemical transformations yielding a stable, highly fluorescent product. We now report preliminary observations on the photochemical reactivity of cannabinol (**1**).



(1) (2) (3)

Peⁿ = *n*- pentyl

G.l.c. and t.l.c. analyses of the reaction mixture during the irradiation of cannabinol in ethanol (10^{-2} M) at 25 °C (λ 285 nm, bandpass 20 nm, 2 kW xenon source) has shown that two major products are produced. The first to appear was identified on the basis of mass spectral and g.l.c. evidence as the isomeric diol (**2**), *m/e* 310 (M^+), 295, 281, 267, 238, and 223, which results from a photoinduced ring opening and hydrogen transfer. An analogous reaction of 2,2-disubstituted chromenes has previously been reported,[2] in which irradiation of 2,2-dimethylchromene in acetone or benzene results in the formation of 2-(3-methylbuta-1,3-dienyl)phenol as sole product. Compound (**2**) has in fact been identified as a minor constituent of cannabis resin,[3] and has been assigned the trivial name cannabinodiol.

After several hours irradiation the second product begins to appear in significant quantity. Spectroscopic evidence indicates that a hydroxyphenanthrene chromophore is present [λ_{max} (EtOH) absorption 256, 277, 307, 343, and 360 nm; fluorescence 365, 382, and 402 nm]. High resolution mass spectral studies confirm the proposed substituted phenanthrene structure (**3**), *m/e* 292·1830 (M^+), 277, 263, 249, 246, 235, and 191.

Isolation of (**2**) by t.l.c. followed by irradiation of the extract has shown that the reaction takes place in two sequential stages, the first involving ring opening of cannabinol to form (**2**), which in turn undergoes photoinduced dehydration and ring closure to give the highly fluorescent hydroxyphenanthrene (**3**).

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[2] A. Padwa and G. A. Lee, *J.C.S. Chem. Comm.*, 1972, 795.

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