The Photochemical Rearangement of 3-(2-Nitroprop-1-enyl)indole

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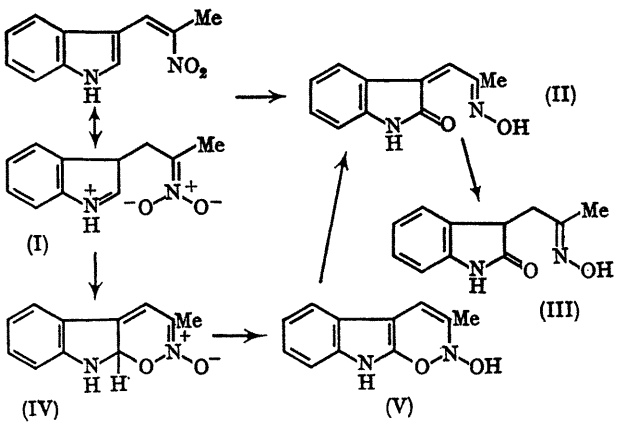
INTEREST has recently been shown in the photochemistry of $\alpha\beta$-unsaturated nitro-compounds.[1-4] In particular, β-methyl-β-nitrostyrene is converted into 1-phenyl-1-hydroxyiminopropan-2-one on irradiation in acetone,[2] and an analogous reaction is reported for 6-nitrochloesta-3,5-diene.[1,2] We report a different reaction path-way, for the photolysis of 3-(2-nitroprop-1-enyl)indole[5] (I).

Irradiation of this compound in methanol solution (5 mg./ml.), with a medium-pressure mercury arc surrounded by a water-cooled Pyrex filter, gave, on distillation of the solvent and chromatography on neutral alumina, a crystalline product (44%). T.l.c. (silica gel) indicated this to be a mixture of three components; the major component was isolated as orange crystals, m.p. 214—216°, by repeated crystallisation from acetone, and had ν_{max} 3180, 1682, 1643, and 1613 cm.$^{-1}$, and λ_{max} 255 (ϵ 16,000) and 322 nm. (ϵ 11,000). Mass spectra showed the parent ion (*m/e* 202) and fragment ions at 185, 174, and 144. This product was identical in all respects with the known oxindole derivative (II).[6,†] Hydrogenation with palladium as catalyst of the crystalline mixture afforded the authentic dihydro-derivative (III)[6] in high yield. The two minor products of this reaction are therefore considered to be *cis–trans* isomers of the principal product, and at least one of them is formed on further irradiation of the principal photoproduct.



This rearrangement can most easily be rationalised in terms of the cyclic intermediates (IV) and (V), followed by ring cleavage to form the oxindole (II); an analogous cyclisation of an $\alpha\beta\gamma\delta$-unsaturated ketone to a pyran has been reported.[7]

(*Received, December 5th*, 1968; *Com.* 1665.)

† The stereochemistry of this compound is not known with certainty.

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