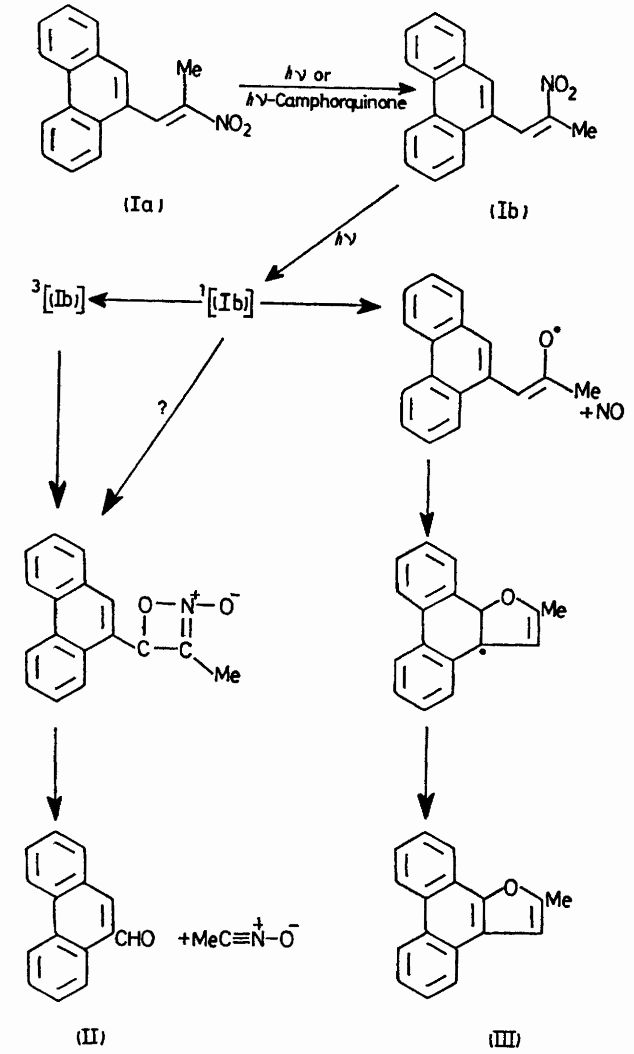
Photochemical Reactions of an αβ-Unsaturated Nitro Compound

By Paul M. Crosby, Kinglsey Salisbury,* and Glenn P. Wood
(*Department of Chemistry, The University, Southampton* SO9 5NH)

Summary *E*-1-(9-Phenanthryl)-2-nitroprop-1-ene on irradiation in dioxan or sensitization with camphorquinone gives the *Z* isomer which is photochemically reactive and produces phenanthrene-9-carboxaldehyde and a novel furan product; the mechanism of product formation has been explored.



Scheme

During the last few years a number of novel and interesting photochemical reactions of αβ-unsaturated nitro compounds have been uncovered. We report on the photochemistry of an αβ-unsaturated nitro compound which provides a further example of photochemical cleavage to a carbonyl compound and also provides the first example of a reaction pathway leading to a furan.

Irradiation of a dioxan solution of the nitroalkene (Ia), prepared by a Knoevenagel reaction, using light from a Pyrex-filtered medium-pressure mercury lamp gave phenanthrene-9-carboxaldehyde (II) and the furan derivative (III). The structure of (III) was indicated by its u.v., i.r., and n.m.r. spectra and later proved by an independent synthesis.[2] As will be shown presently, the chemical yields of (II) and (III) can be controlled by the use of different solvents and electronic quenchers but in the above experiment the yields were 25 and 5% for (II) and (III) respectively.

The dependence of product formation upon irradiation time indicated an induction period and by careful analytical and preparative t.l.c. this was shown to be due to the initial formation of the *Z* isomer (Ib). Compounds (II) and (III) were formed only after >90% conversion of (Ia) into (Ib). Furthermore, direct irradiation of (Ib) did not give (Ia). [Thus it is unlikely that there is any twisted electronic state common to the photochemical reaction pathway of (Ia) and (Ib)]. These results indicate that on excitation, (Ia) gives (Ib) which, on excitation gives (II) and (III).

Ferrioxalate actinometry allowed the quantum yields of formation of (Ib) [from (Ia)] and (II) and (III) [from (Ib)] to be measured: ϕ (Ib) = 0·50; ϕ (II) = $8·5 \times 10^{-3}$; ϕ (III) = $2·5 \times 10^{-3}$. Compound (Ib) was also obtained by the triplet sensitization of (Ia) using camphorquinone (E_T = 209 kJ mol^{-1}), a reaction which resulted in a near quantitative (>90%) conversion of (Ia) into (Ib).

In contrast with irradiation in dioxan, irradiation of (Ia) in the heavy-atom solvent 1-bromohexane gave (II) [ϕ (II) = $1·1 \times 10^{-2}$] but not (III) [ϕ (III) $< 10^{-4}$] indicating a triplet-state precursor to (II) and an excited singlet-state precursor to (III). Further evidence for the multiplicities of the reactive states came from a triplet quenching experiment using anthracene (E_T 178 kJ mol^{-1}). Although ideal conditions could not be achieved because of extended spectral overlap of anthracene and (Ib), under conditions such that anthracene absorbed less than 15% of the exciting radiation (366 nm) the ratio ϕ(II)/ϕ(III) was 2·5 compared to 3·5 in the absence of anthracene.

Based on the above results and by analogy with known reaction pathways of related systems, the reaction pathways in the Scheme are put forward.

We thank the S.R.C. for studentships to P.M.C. and G.P.W.

(*Received*, 20*th January* 1975; *Com.* 060.)

---

[1] O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, *J. Amer. Chem. Soc.*, 1966, **88**, 5550; G. E. A. Coombes, J. M. Grady, and S. T. Reid, *Tetrahedron*, 1967, **23**, 1341; R. Hunt and S. T. Reid, *J.C.S. Perkin I*, 1972, 2527; J. T. Pinhey and E. Rizzardo, *Tetrahedron Letters*, 1973, 4057.

[2] F. R. Japp and N. H. J. Miller, *J. Chem. Soc.*, 1885, 11.