

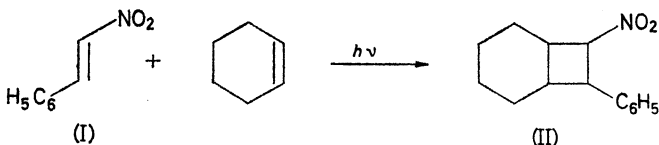
# PHOTOCHEMISTRY OF UNSATURATED NITROCOMPOUNDS

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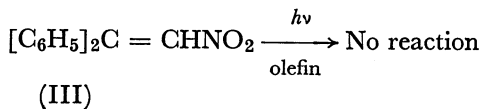
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The photochemistry of nitro compounds has received relatively little attention in recent years compared to that given to photochemical reactions of ketones. This is doubly surprising since the older literature describes a number of intriguing photochemical reactions of nitro compounds and the nitro group is known to undergo  $n \rightarrow \pi^*$  excitation analogous to that of ketones. We wish to report studies in two areas of nitro group photochemistry (i) photoaddition of unsaturated nitro compounds to olefins and (ii) the "photo-oxidation" of aromatic nitro compounds, which have led to realization of closely related rearrangements of the nitro group.

We selected  $\beta$ -nitrostyrene (I) for our initial studies in photoaddition because of its ready availability in quantity. Irradiation of  $\beta$ -nitrostyrene† in cyclohexene solution gives in good yield (70–80 per cent) the adduct (II) (two isomers). Similar irradiation of (I) in cyclopentene, styrene, 1,1-diphenylethylene and tetramethylethylene gives in each case a similar cyclobutane derivative. The structures of the adducts have been determined by use of spectroscopic methods [infrared, ultraviolet and n.m.r.], thermal



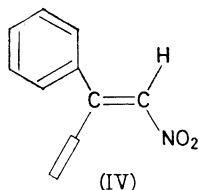
reversion to starting materials and the Nef reaction. A single major isomer is isolated in the photoaddition of  $\beta$ -nitrostyrene (I) to cyclopentene, 1,1-diphenylethylene and tetramethylethylene. This observation suggests that the isomers obtained in the photoaddition of  $\beta$ -nitrostyrene to cyclohexene are a result of *cis* and *trans* fused rings. In order to simplify the stereochemical problem we turned to  $\alpha$ -phenyl- $\beta$ -nitrostyrene (III). Irradiation of (III) under conditions



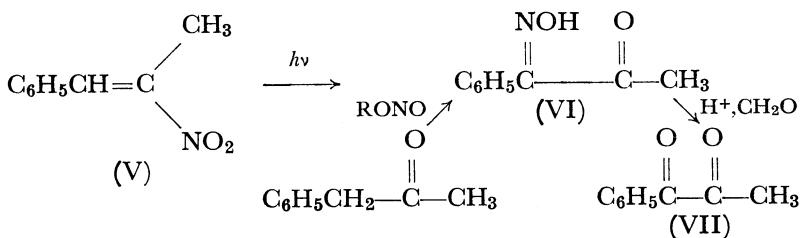
identical to those employed for  $\beta$ -nitrostyrene and using some of the same

† The *trans* isomer of  $\beta$ -nitrostyrene was used but  $\text{trans} \rightleftharpoons \text{cis}$  isomerization occurs rapidly on irradiation.

olefins as solvent gave no reaction. It seemed that the lack of reactivity of (III) in the photoaddition might be due to steric interference with the addition by a nonplanar aromatic ring (IV). Consequently, we attempted

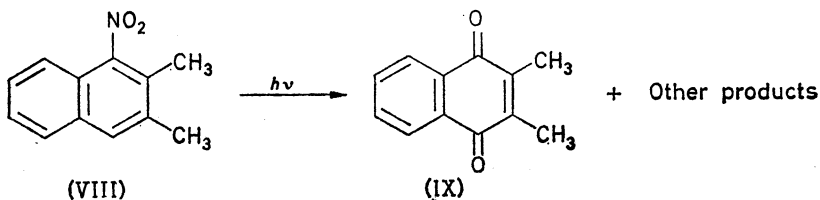


to evaluate the effect of methyl substituents on the reactivity of  $\beta$ -nitrostyrene. Irradiation of  $\beta$ -methyl- $\beta$ -nitrostyrene (V) in either styrene or tetramethylethylene gives the same product (VI) in 79 per cent yield. Both geometric isomers of (VI) are formed in the photoisomerization, but



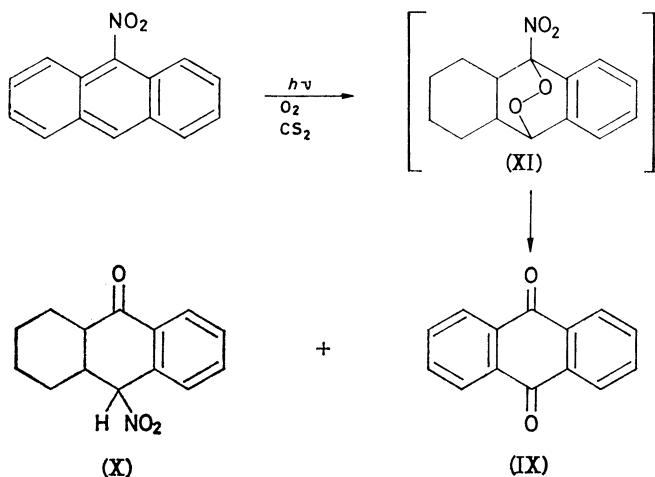
crystallization of the product gives only the more stable isomer, m.p. 161.5–162.5°. The structure of the photoisomer rests on spectral data, hydrolysis to the known diketone (VII) and comparison with authentic (VI) synthesized from 1-phenyl-2-propanone as previously described<sup>1</sup>. The rearrangement of  $\beta$ -methyl- $\beta$ -nitrostyrene to (VI) is, to the best of our knowledge, without precedent. The mechanistic path of this novel rearrangement will be discussed after consideration of some related photochemical transformations of aromatic nitro compounds.

Our initial studies on aromatic nitro compounds stemmed from the observation that a sample 2,3-dimethyl-1-nitronaphthalene (prepared for other purposes) decomposed in the presence of ordinary laboratory light. Irradiation of 2,3-dimethyl-1-nitronaphthalene (VIII) in solution (acetone or 95 per cent ethanol) gave 2,3-dimethyl-1,4-naphthoquinone (IX) among a variety of other products. Examination of the literature for analogous transformations brought forward reports of the photo-oxidation of 9-nitroanthracene to anthraquinone<sup>2, 3</sup> (IX) and 9-nitroanthrone (X)<sup>2</sup>. It has

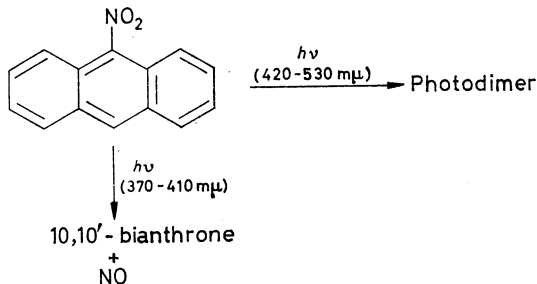


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been suggested<sup>2</sup> that the peroxide (XI) is an intermediate in the production of (IX) and (X). More recently it has been reported that 9-nitroanthracene

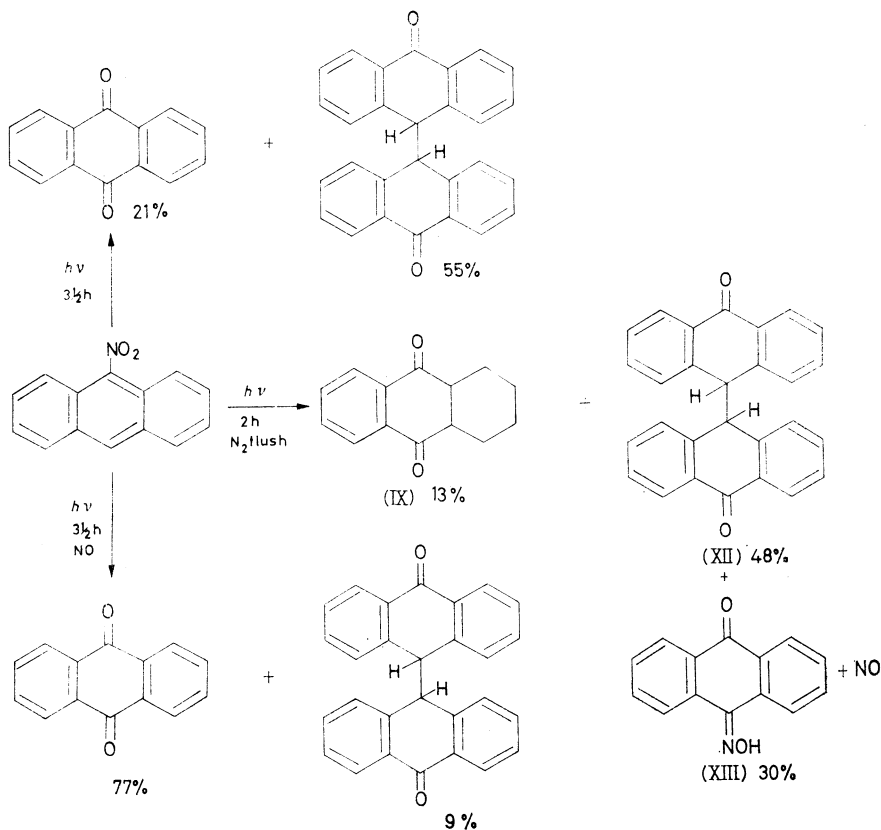


on irradiation with light of wavelength 420–530  $\mu$  gives the photodimer while light of wavelength 370–410  $\mu$  gives 10,10'-bianthrone and nitrogen (II) oxide<sup>4</sup>.



Our work on the aromatic nitrocompounds began in earnest with the observation that the "photo-oxidation" of 2,3-dimethyl-1-nitro-naphthalene and 9-nitroanthracene to 2,3-dimethyl-1,4-naphthoquinone and anthraquinone does not require oxygen but proceeds smoothly in degassed solutions. The peroxide (XI) is thus excluded as an intermediate, and less obvious mechanistic paths must be considered. Irradiation of solutions of 9-nitroanthracene with a mercury arc source encased in a Pyrex immersion well gave anthraquinone (IX, 21 per cent) and 10,10'-bianthrone (XII, 55 per cent). Irradiation of 9-nitroanthracene for shorter periods with continuous nitrogen flush (to sweep out gaseous products) gave nitrogen(II) oxide, anthraquinone (13 per cent), 10,10'-bianthrone (48 per cent) and anthraquinone mono-oxime (XIII, 30 per cent). The isolation of anthraquinone mono-oxime is of particular significance in mechanistic considerations.

The exit gases were passed through two Dry Ice-acetone traps and then through a liquid nitrogen trap. Nitrogen dioxide was sought but not found in this experiment. Irradiation of 9-nitroanthracene with nitrogen(II) oxide



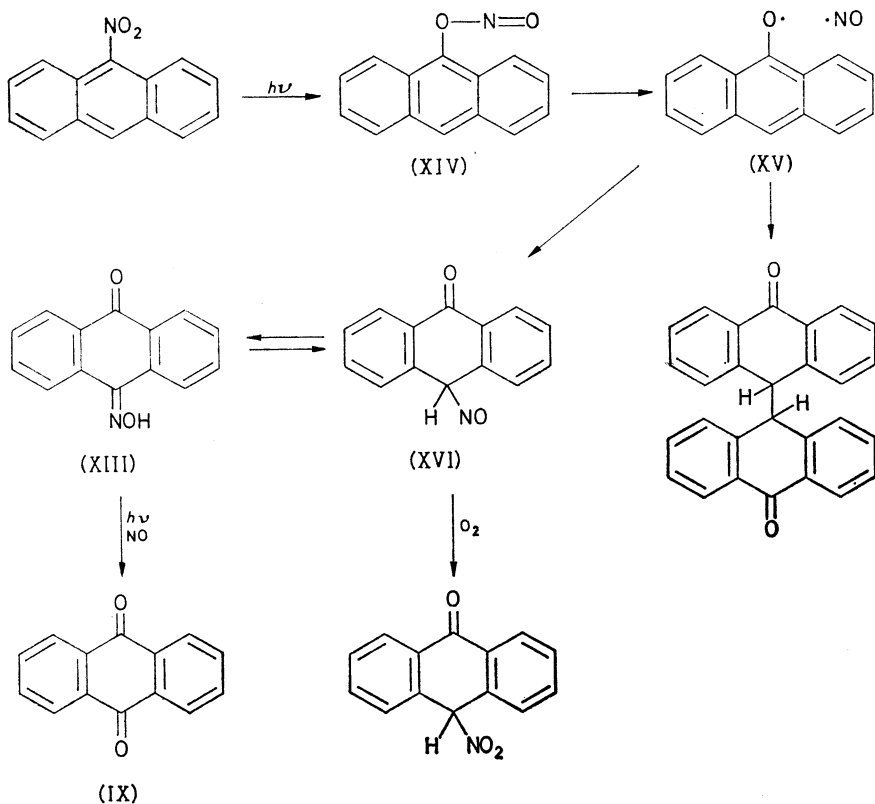
bubbling through the solution gave a substantially larger yield (77 per cent) of anthraquinone at the expense of 10,10'-bianthrone (9 per cent).

These results described above can be understood in terms of the following mechanistic path. Photoisomerization of the nitro compound gives the nitrite ester which can decompose thermally or photochemically to the 9-anthroxy radical (XV) and nitrogen(II) oxide. Dimerization of two 9-anthroxy radicals would give 10,10'-bianthrone, while addition of nitrogen(II) oxide to (XV) would give the nitroso-ketone (XVI). Oxidation of (XVI) (in experiments in which oxygen is present) could give the nitro-anthrone reported by Dufraisse<sup>2</sup>. Isomerization of the nitroso-ketone would give anthraquinone mono-oxime (XIII). Irradiation of the mono-oxime gives anthraquinone<sup>5</sup>. We have found that the yield of anthraquinone from this irradiation is increased substantially if nitrogen(II) oxide is present during the irradiation.

The photoisomerization of  $\beta$ -methyl- $\beta$ -nitrostyrene (V) to the keto-oxime (VI) mentioned earlier can be rationalized by means of a mechanistic

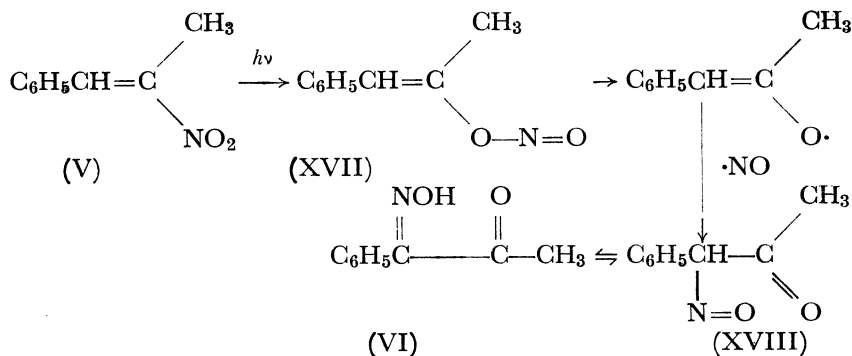
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sequence analogous to that given for the nitroaromatic compounds. Initial photoisomerization would give the nitrite (XIV). Thermal or photochemical cleavage of the nitrite followed by readdition of nitrogen(II)

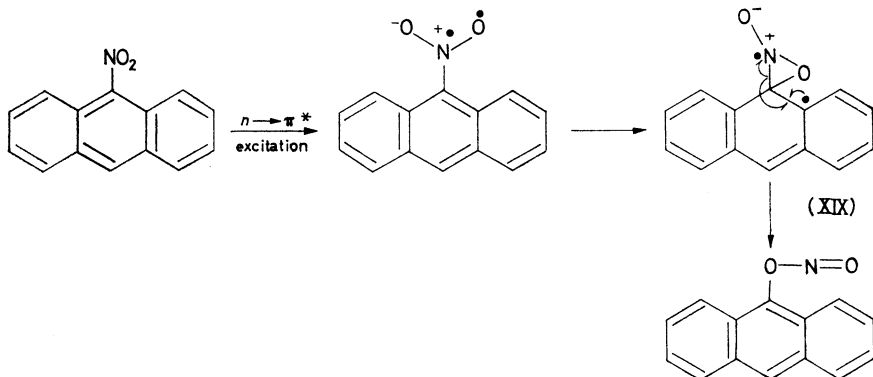


oxide at the  $\alpha$ -carbon would give the nitroso-ketone (XVIII) which could isomerize to the keto-oxime (VI).

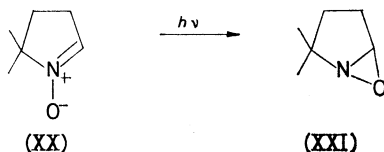
Two mechanisms must be considered for isomerization of the aryl nitro group to an aryl nitrite. First, one might imagine direct fission of the C-N



bond to a radical pair which could recombine to form the nitrite. This process would be analogous to the photochemical isomerization of nitromethane to methyl nitrite<sup>6</sup>. Nitrogen dioxide would be expected as a product from the direct cleavage of the C-N bond. Nitrogen dioxide is not observed as a product in our experiments. A second possibility exists for the aryl nitro compounds (but not for the nitroalkanes). This possibility would be



in accord with the observation that adjacent *peri* hydrogens or *ortho* substituents facilitate the photoisomerization. There is analogy for photoisomerization to the oxazirane ring (XIX). Irradiation of (XX) gives the oxazirane (XXI)<sup>7</sup>.



The wavelength dependence of dimerization and photoisomerization of 9-nitroanthracene may be explained by the suggestion of Yang that photoisomerization comes from an upper ( $n, \pi^*$ ) triplet state while dimerization comes from the low lying ( $\pi, \pi^*$ ) triplet state. If this explanation is correct this case is quite analogous to that of anthracene-9-carboxyaldehyde studied by Yang<sup>8</sup>.

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- 8 See accompanying paper by N. C. Yang. *Pure Appl. Chem.* **9**, 591 (1964).