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THE EFFECT OF EXTERNAL MAGNETIC FIELD ON THE PHOTOCHEMICAL REACTION OF ISOQUINOLINE N-OXIDE

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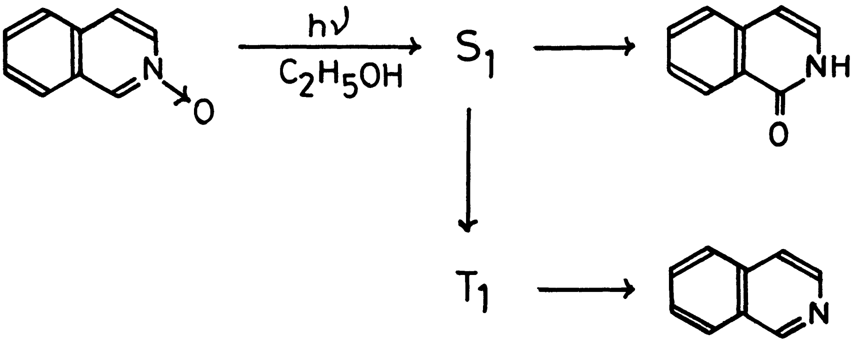
It was found that the magnetic field affected the photochemical isomerization of isoquinoline N-oxide to lactam in ethanol to cause an interesting variation in the yield of lactam. The results appear to indicate that there occurs a remarkable enhancement of the intersystem crossing from the excited singlet state of isoquinoline N-oxide by the magnetic field of approximately 10 kG.

It is one of the most important and interesting problems in molecular photochemistry to investigate whether or not photochemical reactions are influenced by a magnetic field. In 1972 Gupta and Hammond have reported that the photosensitized isomerization of stilbene or piperylene was affected by the magnetic field.1) The results have been discussed by Atkins in terms of a theory related to chemically induced dynamic nuclear polarization (CIDNP); the magnetic field was assumed to induce singlet-triplet mixing in the exciplex which would be formed between a triplet sensitizer molecule and an olefinic molecule by virtue of the different g-values of the doublet components of the states.2) On the other hand, Sakuragi et al. have described that application of external magnetic field (0 to 14 kG) on the singlet or triplet sensitized photolysis of dibenzoyl peroxide scarcely affected the yield of phenyl benzoate resulting from cage recombination between benzoxyl and phenyl radicals.3,4)

Very recently, Matsuzaki and Nagakura have found that fluorescence from the excited singlet state of carbon disulfide or glyoxal was quenched and intersystem crossing was enhanced in the presence of a magnetic field.5) It is therefore probable that in certain cases the yield of product arising from the excited singlet state would be diminished by application of an external magnetic field. As is well known, the ultraviolet irradiation of isoquinoline N-oxide in ethanol leads to isomerization through the lowest excited singlet state (S_1) to give rise to lactam (isocarbostyril) in ca. 67% yield, whereas the deoxygenation reaction occurs from the lowest triplet state (T_1) to give isoquinoline in a few percent yield (Scheme 1).6,7) In the present investigation, therefore, the photochemical reaction of isoquinoline N-oxide in ethanol was carried out in the absence and in the presence of a magnetic field (0 to 17 kG) and the yield of lactam was determined as a function of the field strength.

Scheme 1



A 50 ml of ethanol solution containing 50 mg of isoquinoline N-oxide in a quartz vessel was placed in an electromagnet (EEO-1815) supplied by Maezumi Electric Company and was illuminated with a 500W Ushio high-pressure mercury lamp (USH-500D) equipped with a Toshiba filter UV-31 for 30 min while nitrogen was bubbled in (conversion : ca. 30%). The amounts of lactam and unreacted N-oxide were measured by means of a chromatographic separation[8)] combined with a spectroscopic determination.

The experimental results are shown in Fig.1. As can be seen from the figure, the yield of lactam was 65 to 68% at the magnetic field below 5 kG, but it decreased steeply with increasing field strength to be ca. 52% at about 10 kG. Further increase in the magnetic field, interestingly, resulted in a steep increase in the yield to approach approximately a constant value (ca. 65%).

The results described above seem to indicate that the intersystem crossing from the S_1 state of isoquinoline N-oxide is enhanced by a characteristic magnetic field (∼10 kG). In order to confirm this it is necessary to examine the field dependence of the yield of isoquinoline arising from the T_1 state, although the exact and reliable data is quite difficult to obtain because of a very low yield of isoquinoline. Meanwhile, the photochemical isomerization of isoquinoline N-oxide to lactam in ethanol has been assumed to proceed via a heterolytic cleavage of the oxaziridine intermediate formed as a primary photoproduct, followed by the formation of a zwitterion or a carbonium ion which can then be rearranged to the lactam (cf. Schemes 1 and 2 in Ref.6). Very recently, however, the photochemical isomerization has been demonstrated not to involve the oxaziridine intermediate, but proceed via a protonation of the N→O group through hydrogen-bonding interaction between the N-oxide oxygen atom and ethanol molecule in the S_1 state (Scheme 2).[9)] Thus it is almost certain that a radical pair which may be sensitive to a magnetic field does not participate in this reaction. For this reason, it seems reasonable to consider that the observed field dependence of the photochemical reaction of isoquinoline N-oxide is most likely due to a magnetic perturbation for the intersystem crossing from the S_1 state, but not for the chemical process. If it is the case, the fact that the yield of lactam shows a minimum value at approximately 10 kG (Fig.1) strongly suggests that there exists a characteristic magnetic field responsible for the enhancement of intersystem crossing from the S_1 state of isoquinoline N-oxide. So far the existence of such a characteristic magnetic field has never been known and predicted in the literature.

The magnetic field effect found in the present investigation, although the origin is quite ambiguous at present, seems to be employed as a useful method of elucidating a primary photochemical process and also provide important informations on the nature of the intersystem crossing. Further studies are now in progress.

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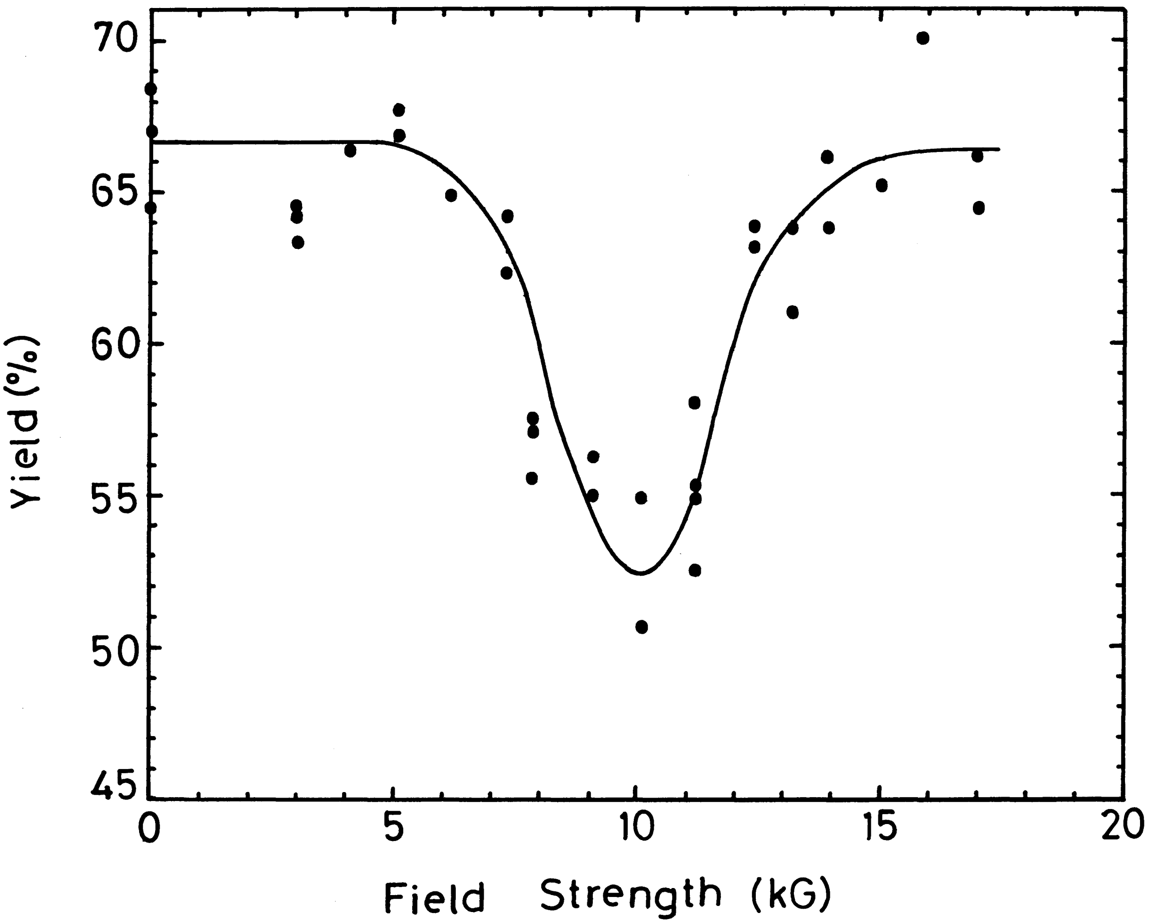
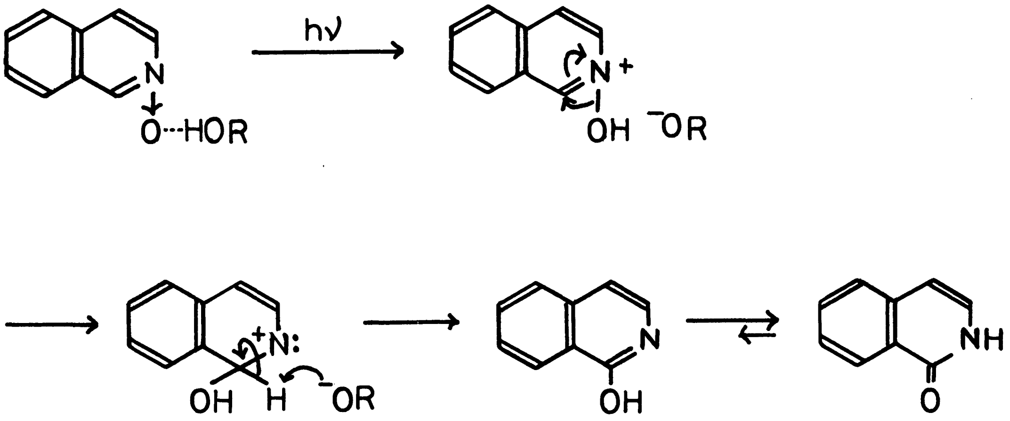


Fig.1. The Effect of Magnetic Field on the Yield of Lactam (Isocarbostyril) in the Photochemical Reaction of Isoquinoline N-Oxide in Ethanol.

Scheme 2



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4) Very recently, however, the singlet sensitized reaction of dibenzoyl peroxide has been observed to be affected by the magnetic field of 42 kG. Y.Tanimoto, H.Hayashi, H.Sakuragi, K.Tokumaru, and S.Nagakura, Annual meeting of the Chemical Society of Japan, Hiratsuka, April, 1976.
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8) The irradiated solution was concentrated in vacuo and subsequently chromatographed on an alumina column by elution with chloroform-diethyl ether (1 : 1), chloroform-ethanol (40 : 1) or chloroform-ethanol (20 : 1) to separate the isoquinoline, isoquinoline N-oxide or isocarbostyril.
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