CHEMISTRY LETTERS, pp. 2261-2264, 1987.

Magnetic Field Effect as a Probe for Radical Pair Intermediates in the Photoreactions of Nitroaromatic Ethers

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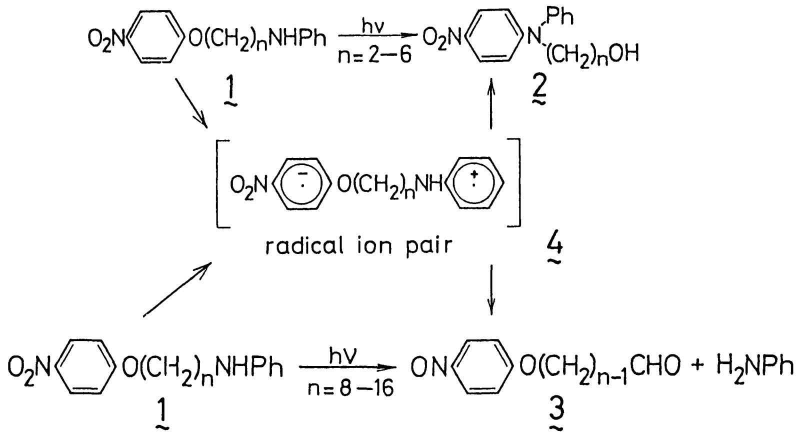
Intermediacy of a radical ion pair in the photo-Smiles rearrangement of N-[2-(4-nitro-1-naphthoxy)ethyl]aniline in CH_3CN was suggested on the basis of magnetic field effects on the photoreaction of its higher homolog.

Recently, the papers concerned with magnetic field effects are rapidly increasing.$^{1)}$ Considering that the effects are possibly observed in the organic reactions involving radiacal pairs produced by homolytic scission of single bonds, hydrogen abstraction$^{2)}$ or electron transfer,$^{3)}$ the effects should receive much more attention of organic chemists. We report here that the effects are useful for detection of radical pairs.

The lower homologs of p-$O_2NC_6H_4O(CH_2)_nNHPh$ (**1**, n=2-6) undergo the Smiles rearrangement, when irradiated in acetonitrile or methanol with a high-pressure Hg lamp, yielding **2** as a major product (Eq. 1).$^{4)}$ The next higher homolog with the polymethylene chain of n=7 shows practically no photoreaction. However, on further extension of the chain (n=8 -16), a new type photoreaction is observed; an intramolecular redox reaction, producing nitrosoaldehyde (**3**) and aniline (Eq. 2).$^{5)}$ The rate of this photoredox reaction increases with n and reaches a limit at n=12-16. Laser flash study of the n=2 and 12 homologs in acetonitrile, each representing these two types of photoreactions, has revealed that a radical ion pair **4** is a common intermediate formed by electron transfer from the anilino to the nitrophenoxyl moieties in this solvent.$^{5,6)}$ Evidently, this reaction-switching process, which should follow the formation of **4**, is strongly dependent on the conformation of the polymethylene chain.



(1)

(2)

Another noteworthy feature of the behavior of **4** is that the rate of the redox reaction was affected by an external magnetic field;$^{7)}$ the apparent rate of the production of the nitrosoaldehyde was remarkably retarded under the influence of a strong magnetic field (Fig. 1).8) This effect was peculiarly confined to the photoredox reaction, that is, to the reactions of the higher homologs (n=8), and not observed in the lower homologs, though the effect itself is possibly one of the characteristics of the reactions involving radical pairs.

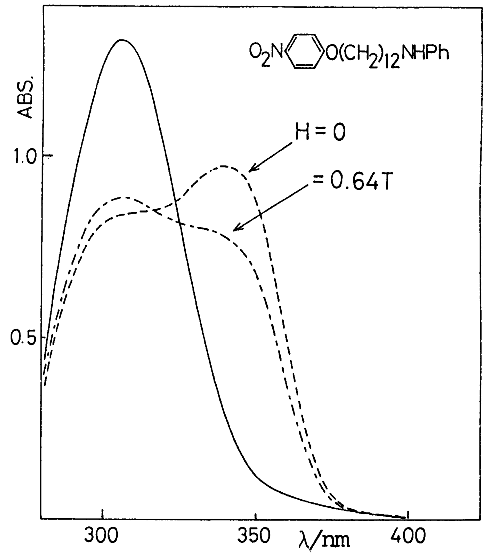
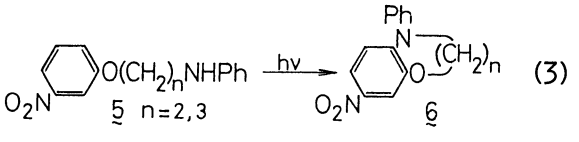


Fig. 1. UV Absorption spectra of the solutions of **1** (n=12) in $C_6H_6$8) (ca. 10^{-4} mol/dm^3) before (solid line) and after (broken line) 16 min of irradiation in the presence and absence of external magnetic field (0.64 T).

Thus it may safely be said that if the lower members of a homologous series of compounds in polar solvents show a photo-Smiles type substitution and the higher ones a redox type photoreaction, and if an external magnetic field exerts rate retarding effect on the latter reaction, the former substitution reaction proceeds, even if the effect is not observed, through a radical ion pair. This supposition implies that electron-transfer process is strongly dependent on the distance of a donor-acceptor pair, generally far more favorable for the lower homologs.

In order to examine the validity of this supposition, we studied the photoreaction of m-$O_2NC_6H_4O(CH_2)_nNHPh$ (**5**), the lower homologs (n=2 and 3) of which have been found to yield **6** as a product of an apparently nucleophilic type photosubstitution.9) Laser flash study suggests the intermediacy of a radical ion pair similar to **4** in acetonitrile. As shown in Fig. 2, the n=12 homolog of the meta series clearly suffers a small but definite magnetic field effect. Thus the formation of the radical ion pair in the photosubstitution (Eq. 3) is again confirmed.



5 n=2,3 **6** (3)

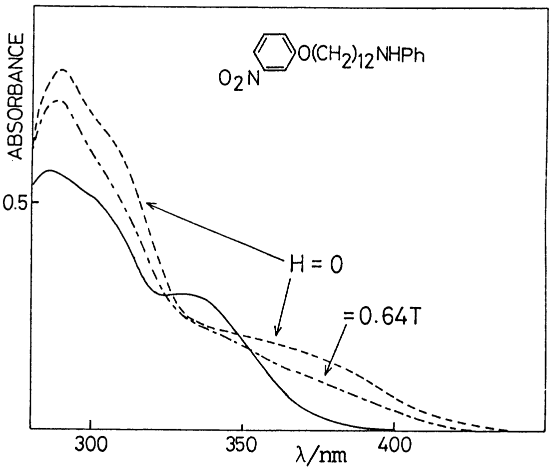
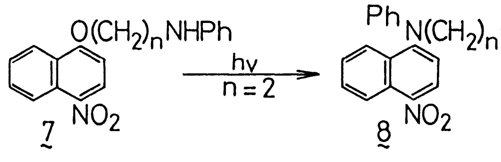


Fig. 2. UV Absroption spectra of the solutions of **5** (n=12) in $C_6H_6$8) (ca. 10^{-4} mol/dm^3) before (solid line) and after (broken line) 16 min of irradiation in the presence and absence of external magnetid field (0.64T).

Another example is the photo-Smiles rearrangement of N-[2-(4-nitro-1-naphthoxy)ethyl]aniline (**7**) (Eq. 4).10) Although the reaction pattern providing **8** as well as other characteristics of the reaction suggests a similar reaction mechanism to that of **1**, the laser flash study was fruitless because the fluorescence from the naphthalene moiety overlaps the region corresponding to the absorption of the corresponding radical ions. Therefore, magnetic field effect was expected to provide valuable information on the transient species.



(4)

In Fig. 3 is illustrated the sectral change with time of the solutions of the n=12 homolog of 7 irradiated in the presence and absence of an external magnetic field. Retardation of the photoreaction in the field is obvious. The series of the sepctral curves show no isosbetic point, suggesing the occurence of a secondary photoprocess of decomposition of the products.

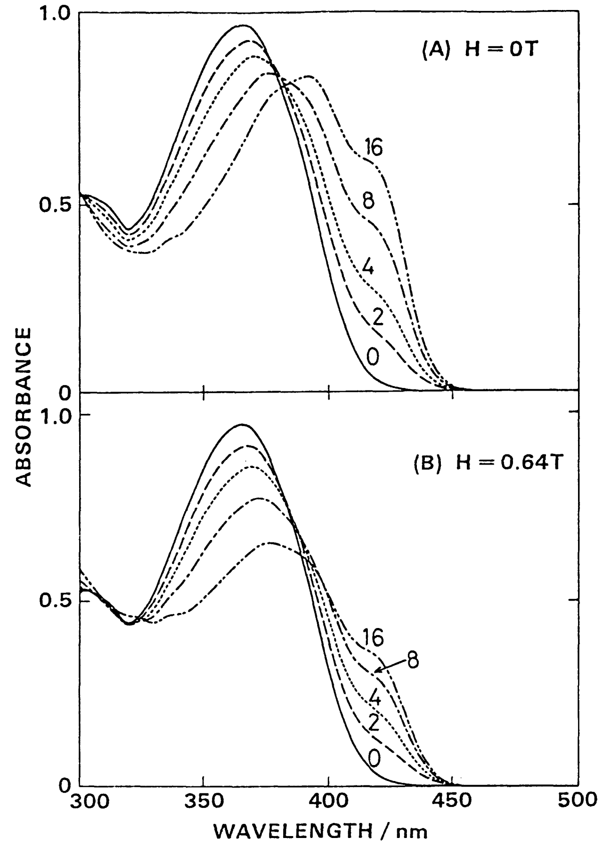


Fig. 3. UV Absorption spectra of the solutions of the n=12 homolog of 7 in $C_6H_6$8) (ca. 10^{-4} mol/dm^3); (A) in the absence of, and (B) in the presence of external magnetic field (0.64 T). The numerals attached to the curves denote the irradiation time in min.

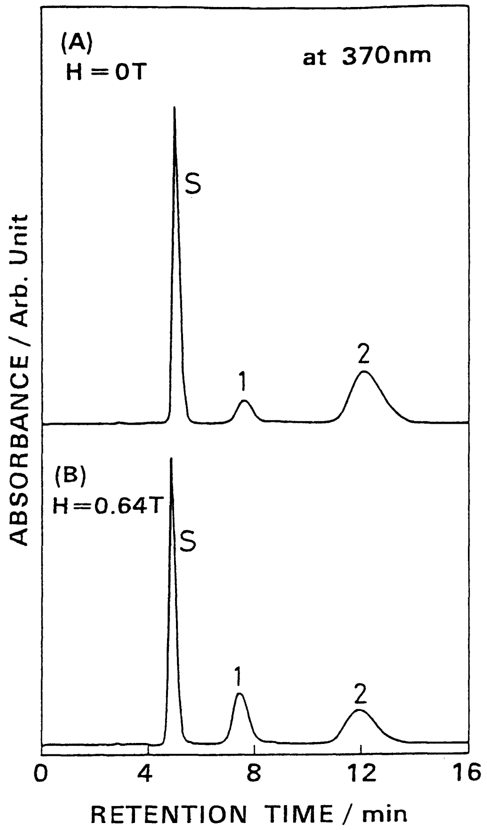


Fig. 4. High performance liquid chromatograms, monitored at 370 nm, of the reaction mixtures of the n=12 homolog of 7, irradiated for 16 min in benzene. Peaks S, 1, and 2 denote the starting materias, nitronaphthoxyl and nitrosonaphthoxyl derivatives, respectively.

In order to confirm that the magnetic field effect is not on this secondary process but on the product-determining process, the composition of the reaction mixture was analyzed by HPLC (Fig. 4). Two major products were found in the reaction mixture, in addition to the starting material (peak S). The peak with shorter retention time (peak 1) has 4-nitronaphthoxyl chromophore and the one with longer retention time (peak 2) has 4-nitrosonaphthoxyl chromophore. In the presence of the external magnetic field, an appreciable change in the areas of the latter two peaks was observed and, in CH_3CN, the relation of their peak areas latter two peaks was observed and, in CH_3CN, the relation of their peak areas changed even from (peak 1)<(peak 2) to (peak 1)>(peak 2). This remarkable effect is reasonably explained$^{7)}$ if the radical pair, originally in the ground triplet state, has two competitive routes of decompotition; that is, one is production of the nitrosonaphthoxyaldehyde and the other yielding the nitronaphthoxyl derivative (the complete structure of the latter compound has not yet been determined). The nitroso derivative is produced from the radical pair in the singlet state derived by intersystem crossing, while the nitro derivative is produced from an escape process involving the triplet state. The magnetic field affects the process of the intersystem crossing by separating the degenerate triplet levels into three, from which only one level is allowed to cross to the singlet, thus narrowing the reaction pathway through this process to reduce the production rate of the nitroso derivative. These results strongly support the intermediacy of a radical ion pair in the rearrangement of **7** in polar solvents.

All these examples suggest that magnetic field effects can be a useful tool for detecting radical pair intermediates as well as CIDNP and CIDEP. The advantage of this method over the latter two lies in that it requires no special apparatus other than a magnet.

This study was supported by the Ministry of Education, Science and Culture (Scientific Research Grant-in-Aid No.61540364 and 61134038), and by the Joint Studies Program (1986) of the Institute for Molecular Science.

References

1) For leading references, see: I. R. Gould, N, J. Turro, and M. B. Zimmt, Adv. Phys. Org. Chem., 20, 1, (1984). "Spin Polarization and Magnetic Field Effects in Radical Reactions," ed by Yu. N. Molin, Elsevier, Amsterdam, 1984.
2) Y. Tanimoto, E. Shimada, and M. Itoh, Bull. Chem. Soc. Jpn., 59, 3039 (1986). and references therein.
3) H. Sakuragi, R. Nakagaki, T. Oguchi, T. Arai, K. Tokumaru, and S. Nagakura, Chem. Phys. Lett., 135, 325 (1987), and references therein; H. Nakamura, A. Uehata, A. Motonaga, T. Ogata, and T. Matsuo, Chem. Lett., 1987, 543.
4) K. Mutai and K. Kobayashi, Bull. Chem. Soc. Jpn., 54, 462 (1981).
5) R. Nakagaki, M. Hiramatsu, K. Mutai, and S. Nagakura, Chem. Phys. Lett., 121, 262 (1985).
6) K. Yokoyama, R. Nakagaki, J. Nakamura, K. Mutai, and S. Nagakura, Bull. Chem. Soc. Jpn., 53, 2472 (1980).
7) R. Nakagaki, M. Hiramatsu, K. Mutai, Y. Tanimoto, and S. Nagakura, Chem. Phys. Lett., 134, 171 (1987).
8) The magnetific field effects on the production rate of the nitroso derivative were noted in several solvents (acetonitrile, benzene, ethyl acetate, THF, etc). Here the results in benzene were shown because the effects are spectroscopically most typical in this solvent.
9) K. Mutai, K. Kobayashi, and K. Yokoyama, Tetrahedron, 40, 1755 (1984).
10) K. Mutai and R. Nakagaki, Bull. Chem. Soc. Jpn., 58, 3663 (1985).

(Received August 12, 1987)