PHOTOCHEMISTRY OF 1-AZATRIPTYCENE

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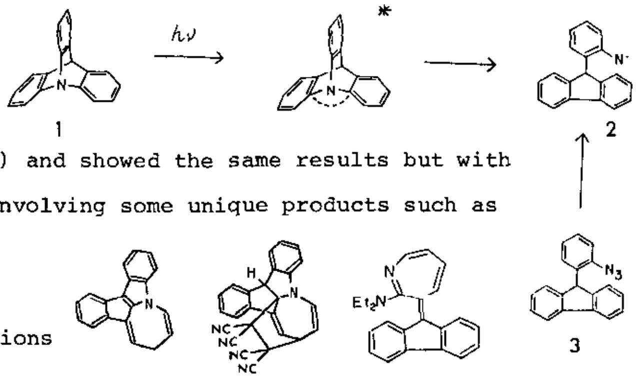
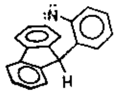
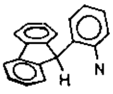
Photolysis of 1-azatriptycne (1) under neutral or basic conditions gave a number of azepine derivatives (eg. 4, 5), suggesting the intermediacy of o-(9-fluorenyl)phenylnitrene (2) which was formed through an extrusion of the bridgehead atom at the nitrogen end in high selectivity. Nitrene 2 was authentically generated from o-(9-fluorenyl)phenyl azide (3) and showed the same results but with slightly different product ratio, involving some unique products such as heptafluvene type compound (14). The difference was explained by the presence of the different conformations (ap- and sp-rotamers) of the immature nitrene 2 generated from two precurssors 1 and 3.



1 2 3 4 5 14


2a



2b

The intermediacy of 2 was unambiguously verified by the detection of triplet nitrene 2 by ESR spectroscopy at 4 K. Nitrene 2a from 1 showed an intense XY transition at 6820 G, while nitrene 2b from 3 showed the transition at 6837 G.$^{1)}$

The difference in the behavior between 2a and 2b was also recognized by absorption spectroscopy at cryogenic temperatures.$^{2)}$ Some of the important rate constants concerning to the reactivity of ap-nitrene was obtained by time-resolved spectroscopy.

The unique reactivity of the singlet excited state of 1 was rationalized on the basis of the chemical consequence of the excitonic interaction of the triply degenerated chromophoric system of the triptycene skeleton.

References

1) T. Sugawara, H. Iwamura, JACS, 1980, 102, 7134.
2) T. Sugawara, N. Nakashima, K. Yoshihara, H. Iwamura, JACS, 1983, 105, 858.
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