

PHOTOCHEMISTRY OF 1-AZATRIPTYCENE

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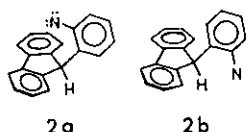
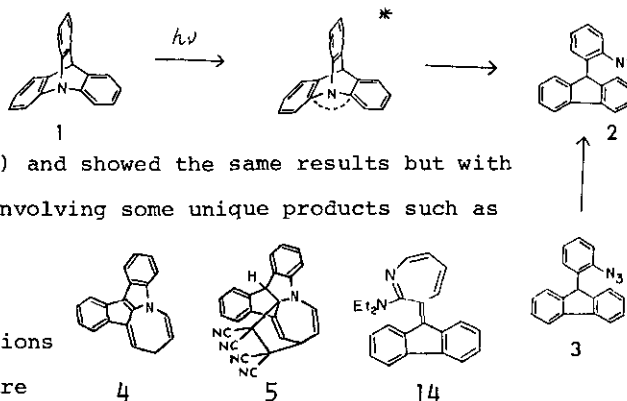
Photolysis of 1-azatriptycene (**1**) under neutral or basic conditions gave a number of azepine derivatives (eg. **4**, **5**), suggesting the intermediacy of o-(9-fluorenyl)phenylnitrene (**2**) which was formed through an extrusion of the bridgehead atom at the nitrogen

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 precursors **1** and **3**.

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.
- S. Murata, T. Sugawara, H. Iwamura, JACS, in press.