THE PHOTOCHEMICAL REACTION OF N-ALKYL-7-AZABENZONORBORNADIENES

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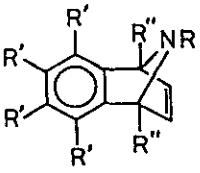
7-Azabenzonorbornadienes with an electron-withdrawing substituent on nitrogen are known to give 3-benzazepine derivatives via a quadricyclene-type intermediate on irradiation of UV-light in cyclohexane, while in acetone-sensitized reactions the major pathway is a di-π-methane rearrangement.1)

Irradiation of 1a (R=R'=R''=Me) in cyclohexane with a 100W medium-pressure Hg lamp under *nitrogen for 1.5 hr gave a tricyclic compound 2a (R'=R''=Me) in a 25% yield along with a small* amount of 3-benzazepine 3. 1b (R=R'=Me, R''=H) also gave 2b (R'=Me, R''=H) as well as a deaminated hydrocarbon 4 (R'=Me) in 10 and 14% yields respectively under similar conditions. 1c (R=Me, R'=R''=H) gave only naphthalene 4 (R'=H) in a 44% yield, but 1d (R=t-Bu, R'=R''=H) gave N-t-butyl-1-naphthylamine and naphthalene in 20 and 30% yields respectively. 1d is stable without light if treated carefully.



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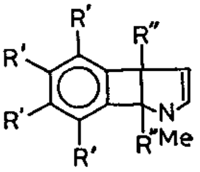

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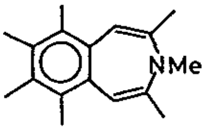

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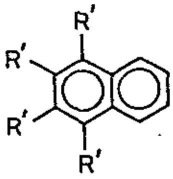

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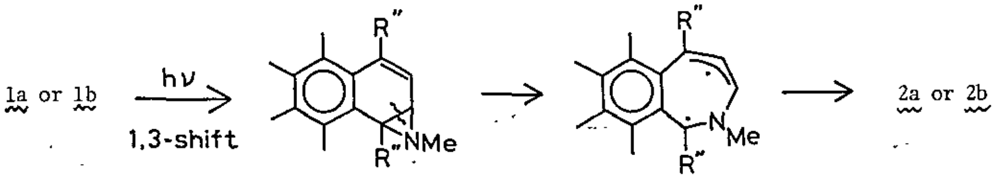
A plausible mechanism for the formation of 2 is shown in the scheme.



A formation of N-t-butyl-1-naphthylamine could be accounted for in terms of an intramolecular electron transfer from the nitrogen to the aromatic nucleus followed by the benzylic carbon-nitrogen bond cleavage and aromatization.

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1) G. Kaupp, J. Perrenton, R. Leute and H. Prinzbach, Chem. Ber., 103, 2288 (1970) ; R. S. Swenton, J. Oberdier and P. D. Rosso, J. Org. Chem., 39, 1038 (1974)