

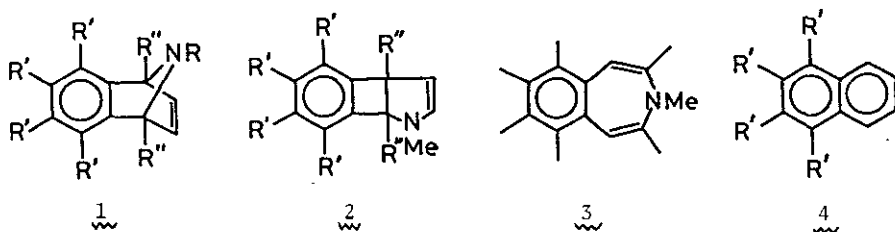
THE PHOTOCHEMICAL REACTION OF N-ALKYL-7-AZABENZONORBORNADIENES

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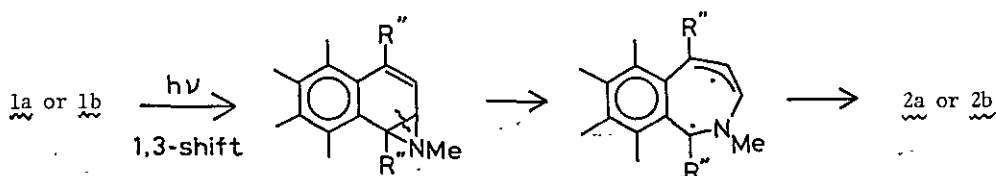
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7-Azabenzonornbornadienes with an electron-withdrawing substituent on nitrogen are known to give 3-benzazepine derivatives via a quadricyclene-type intermediate on irradiation of UV-light in cyclohexane, while in acetone-sensitized reactions the major 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 ($R'=Me$, $R''=H$) 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.



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.

- 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)