Photochemical Ring Expansion of Diazidonaphthalenes: Formation of the First Examples of Azepinoazepines

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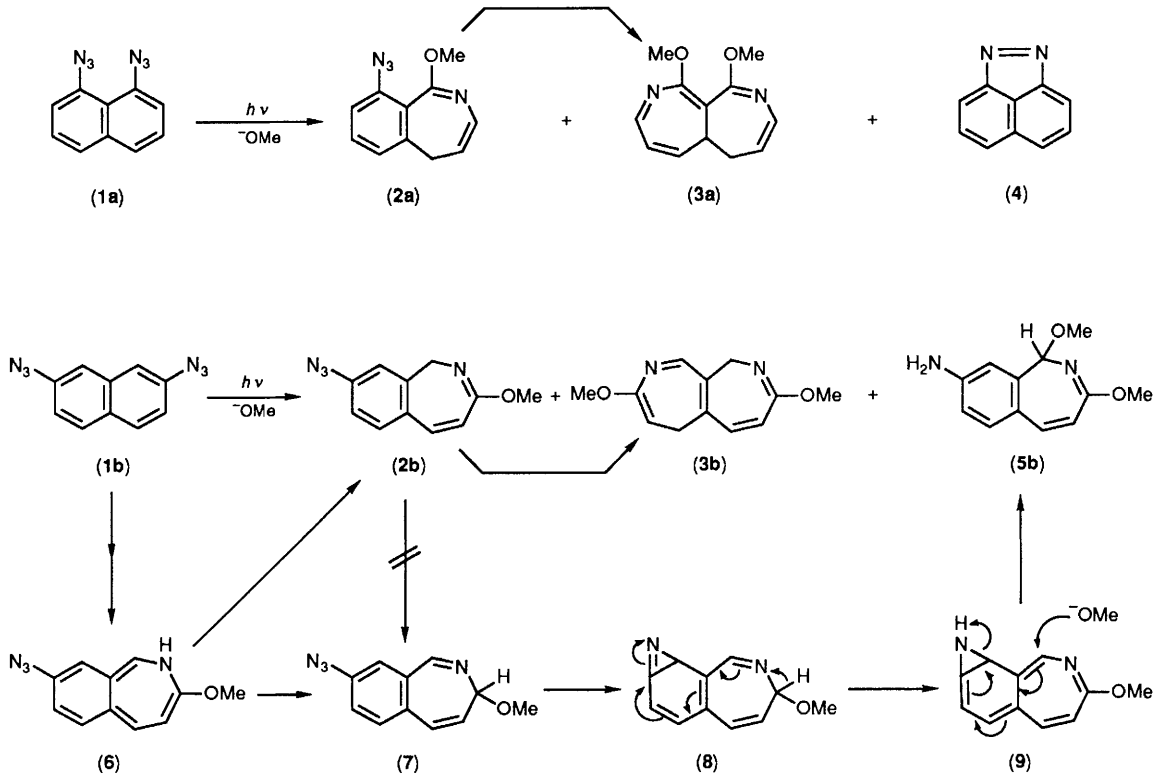
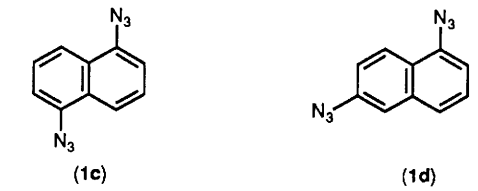
Photolysis of 1,5-, 1,6-, 1,8-, and 2,7-diazidonaphthalenes (**1**) results in ring expansion of both benzene rings to give the corresponding novel azepinoazepines (**3**) *via* the azidobenzazepines (**2**).

There have been several interesting reports on the thermal or photochemical decomposition of diazidonaphthalenes. 1,8-Diazidonaphthalene gives benz[*cd*]indazole,[1] while 1,2-[2] and 2,3-diazidonaphthalenes[3] undergo ring opening or rearrangements to form various nitrile compounds. On the other hand, phenyl,[4] pyridyl,[5] and benzopyridyl[6] azides are known to undergo ring expansion *via* nitrene and azirine intermediates giving rise to seven-membered nitrogen heterocycles, upon photolysis or thermolysis in the presence of nucleophiles. However, there have been no reports

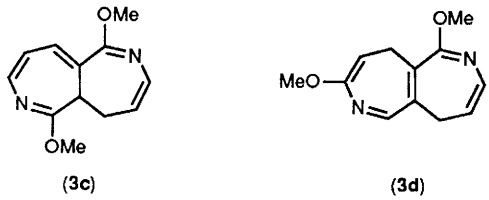


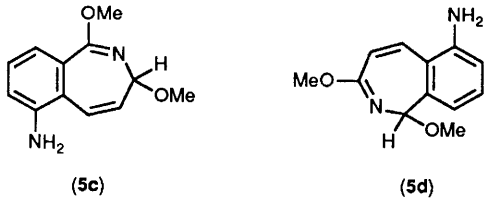
Scheme 1



concerning the ring expansion of diazidonaphthalenes and, in particular, the simultaneous expansion of both rings of condensed bicyclic compounds. We report here that the diazidonaphthalenes (**1**) underwent photochemical ring expansion of both rings to give the novel heterocycles (**3**) which are the first examples of azepinoazepine ring systems.

Photolysis (400 W, high-pressure Hg lamp; Pyrex filter) of the diazidonaphthalene (**1a—d**) was carried out in methanol–dioxane (1 : 1) containing a large excess of sodium methoxide with ice cooling until almost all the starting azides had been consumed (for 20—40 min).† 1,8-Diazidonaphthalene (**1a**) gave the 9-azido-5*H*-2-benzazepine (**2a**) (15—20%) and the 1,10-dimethoxyazepino[3,4-*c*]azepine (**3a**) (10—15%),‡ together with benz[*cd*]indazole (**4**) (*ca.* 40%). 2,7-Diazidonaphthalene (**1b**) also afforded two ring-expansion products





† Irradiation times longer than 20—40 min resulted in a decrease in the amounts of products, especially (**3**).

‡ Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds reported. *Selected ^1H NMR data* ($CDCl_3$): (**2a**) (m.p. 45 °C) δ 2.92 (2H, d, 5-H_2), 5.30 (1H, dt, 4-H), and 6.52 (1H, d, 3-H), $J_{3,4}$ 7 and $J_{4,5}$ 8 Hz; (**2b**) (m.p. 93—94 °C) δ 4.20 (2H, s, 1-H_2), 6.20 (1H, d, 4-H), and 7.08 (1H, d, 5-H), $J_{4,5}$ 12 Hz; (**3a**) (m.p. 56—58 °C) δ 2.68 (1H, dd, 5-H), 2.86 (1H, d, 5a-H), 3.1—3.4 (1H, m, 5-H'), 3.66 and 3.72 (each 3H, s, OMe), 5.12 (1H, ddd, 4-H), 5.8—6.0 (2H, m, 6- and 7-H), 6.24 (1H, dd, 3-H), and 6.86 (1H, dd, 8-H), $J_{3,4}$ 8, $J_{3,5'}$ 2, $J_{4,5}$ 8, $J_{4,5'}$ 6, $J_{5,5'}$ 14, $J_{5',5a}$ 2, $J_{6,7}$ 8, $J_{6,8}$ 2, and $J_{7,8}$ 8 Hz; (**3b**) (m.p. 68—69 °C) δ 2.56 (2H, d, 6-H_2), 3.62 and 3.66 (each 3H, s, OMe), 3.88 (2H, s, 1-H_2), 5.36 (1H, t, 7-H), 5.64 (1H, d, 4-H), 6.40 (1H, d, 5-H), and 6.80 (1H, s, 10-H), $J_{4,5}$ 11 and $J_{6,7}$ 7 Hz. The locations of the sp^3 carbon atoms in the azepine rings of (**3**) were confirmed by ^{13}C NMR spectroscopy: (**3a**) δ 32.36 (t, C-5) and 53.60 (d, C-5a); (**3b**) δ 33.65 (t, C-6) and 51.24 (t, C-1); (**3c**) δ 33.59 (t, C-5) and 54.12 (d, C-5a); (**3d**) δ 31.18 and 33.36 (each t, C-5 and -10).

(**2b**) and (**3b**) in similar yields, as well as the unexpected aminobenzazepine (**5b**) (40—50%) having two methoxy groups in the azepine ring.§ The compounds (**2**) isolated were converted to (**3**) by further irradiation for 5—10 min under conditions similar to those for (**1**) in 30—40% yields.

A possible mechanism for the photolysis of (**1b**) is shown in Scheme 1. The unstable 2*H*-2-benzazepine (**6**) initially formed from (**1b**) may undergo a [1,7] hydrogen shift in the azepine ring to yield two tautomers (**2b**) and (**7**). The 1*H*-isomer (**2b**) gives only the azepinoazepine (**3b**) and no aminobenzazepine (**5b**), while the unisolable 3*H*-isomer (**7**) might be converted into (**5b**) *via* the intermediates (**8**) and (**9**).

Similarly, 1,5- (**1c**) and 1,6-diazidonaphthalene (**1d**) gave the azepinoazepines (**3c**) (15—20%) and (**3d**) (20—25%), and aminobenzazepines (**5c**) (5—10%) and (**5d**) (15—20%), respectively, as well as the corresponding azidobenzazepines (**2**). In the case of the unsymmetrical azide (**1d**), of course, two kinds of azidobenzazepines were obtained.

The compounds (**3**) reported are the first examples of azepinoazepines and considered to be aza-analogues of dihydroheptalenes. Heptalenes are typical non-aromatic cyclic compounds with twelve π electrons and can be prepared by oxidation of dihydroheptalenes,[7] but their aza-analogues are unknown. However, attempts to convert (**3**) into fully unsaturated diazaheptalenes have been unsuccessful.

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§ *Selected data* for (**5b**): m.p. 113—115 °C; ^{1}H NMR δ 3.64 and 3.76 (each 3H, s, OMe), 4.04 (2H, br., NH_2), 4.90 (1H, s, 1-H), 6.26 (1H, d, 4-H), 6.68 (1H, dd, 7-H), 7.24 (1H, d, 5-H), and 7.1—7.2 (2H, m, 6- and 9-H), $J_{4,5}$ 12, $J_{6,7}$ 8, and $J_{7,9}$ 2 Hz; ^{13}C NMR (sp^3-C) δ 51.7 (q), 53.3 (q), and 88.6 (d). The structures of (**5**) were also confirmed by chemical studies. Details including the results of several reactions of (**2**) and (**3**) will be published elsewhere.

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