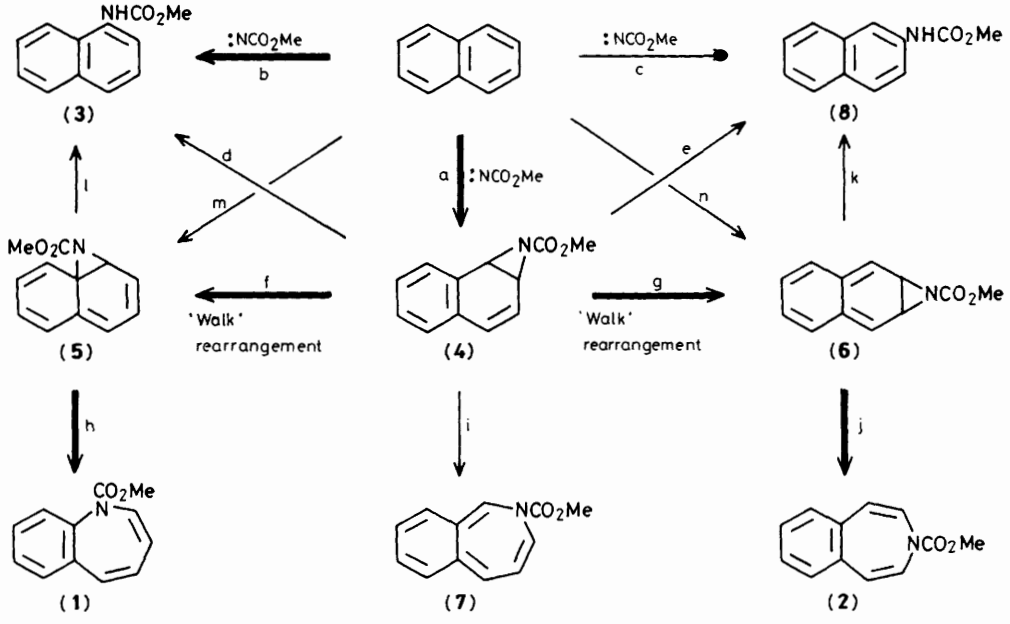
Reinvestigation of the Reaction of Nitrenes with Naphthalene. Formation of 1*H*-1-Benzazepine and 3*H*-3-Benzazepine

Kyosuke Satake,* Hiroshi Mizushima, Masaru Kimura, and Shiro Morosawa

Department of Chemistry, Faculty of Science, Okayama University, Tsushima-Naka 3-1-1, Okayama 700, Japan

Thermally generated methoxycarbonylnitrene in naphthalene gave 1*H*-1-benzazepine and 3*H*-3-benzazepine derivatives, the yields of which increased with increased nitrogen pressure; formation of methyl 1-naphthyl-carbamate and the reaction path are also discussed.

The reactions of nitrenes with benzene derivatives have been studied as part of a brief synthesis of 1*H*-azepine derivatives, but their reaction with arenes has never resulted in the formation of condensed azepines. Hafner reported that the reaction of ethoxycarbonylnitrene, generated thermally from ethyl azidoformate in naphthalene, resulted in the exclusive



Scheme 1. Proposed mechanism for the reaction of methoxycarbonylnitrene with naphthalene.

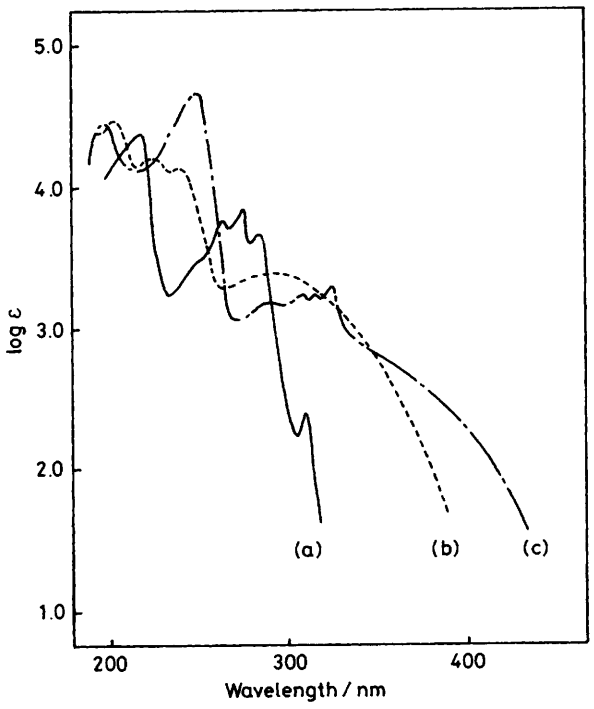


Figure 1. The electronic spectra of (a) naphthalene, (b) 1*H*-1-benzazepine (**1**), and (c) 3*H*-3-benzazepine (**2**) in cyclohexane.

formation of ethyl 1-naphthylcarbamate.[1] The reactions of arenes such as anthracene, phenanthrene, and pyrene with ethoxycarbonylnitrene gave only the corresponding carbamates.[2] We report here that the reaction of thermally generated methoxycarbonylnitrene in naphthalene gives not only methyl 1-naphthylcarbamate (**3**), but also methyl 1*H*-1-benzazepine-1-carboxylate (**1**), and methyl 3*H*-3-benzazepine-3-carboxylate (**2**). This is the first example of the synthesis of condensed azepines by the reaction of nitrenes with arenes. The multi-step synthesis of the 1*H*-1-benzazepine derivatives has been reported independently by Rautenstrauch,[3] Anastassiou,[4] and Ikeda,[5] and that of the 3*H*-3-benzazepine derivative by Swenton.[6]

Naphthalene (0.20 mol) and methyl azidoformate (0.1 mol) were placed in a stainless steel reaction vessel without solvent, and nitrogen was introduced (58 kg cm^{-2}).[7] The mixture was stirred for 3 h at 125 °C, cooled, and the pale yellow oil obtained after removal of the unreacted naphthalene by treatment with cold methanol was chromatographed on silica gel (Wako C-200) using hexane–ethyl acetate (1:1 v/v). Further purification by medium pressure liquid chromatography (m.p.l.c.)† using hexane–ethyl acetate (4:1 v/v) gave the following four fractions: a small amount of naphthalene, the 3*H*-3-benzazepine derivative (**2**) as a yellow oil, the 1*H*-1-benzazepine derivative (**1**) as a colourless oil, and the 1-naphthylcarbamate (**3**) as colourless needles (m.p. 121—122 °C). The structures of the benzazepines obtained were ascertained by comparison of the ^{1}H n.m.r. [(**1**): δ 3.65 (s, 3H), 5.63 (dd, *J* 7.5, 6.0 Hz, 1H), 6.09 (dd, *J* 11.0, 6.0 Hz, 1H), 6.22 (d, *J* 7.5 Hz, 1H), 6.75 (d, *J* 11.0 Hz, 1H), 6.6—7.5 (m, aromatic 4H); (**2**): δ 3.75 (s, 3H), 5.38 (d, *J* 10.0 Hz, 2H), 6.15 (d, 10.0 Hz, 2H), 6.6—7.1 (m, aromatic 4H)] and the electronic spectra (Figure 1) with those in the literature.[3—6] The benzazepines (**1**) and (**2**) were also obtained in lower yield from reactions without nitrogen or of the nitrene generated by the base-catalysed reaction of methyl (*p*-tolylsulphonyloxy)-carbamate at 5 °C with an equimolar amount of naphthalene. The isolated yields of (**1**), (**2**), and (**3**) are shown in Table 1.

† Preparative m.p.l.c. was carried out on an apparatus consisting of an FMI-Lab pump, an ALTEX-MS u.v.-detector (254 nm), a TOA EPR-10B chart recorder, and a column (22 × 500 mm) packed with silica gel (Woelm 32–63).

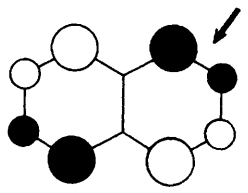


Figure 2. The orbital coefficients of the HOMO of naphthalene.

Table 1. Isolated yields of the products of the reaction of methoxycarbonylnitrene with naphthalene (based on consumed naphthalene).

	Isolated yield (%)		
Conditions	(**1**)	(**2**)	(**3**)
N_3CO_2Me (0.5 equiv.) 125 °C, 3 h	1	1	32
N_3CO_2Me (0.5 equiv.) 125 °C, 3 h, N_2	3	2.5	35
$TsONHCO_2Me$ (1 equiv.) Et_3N, 5 °C[a]	0.5	0.5	13

[a] Ts = *p*-$MeC_6H_4SO_2$.

A mechanism is proposed for the above reaction in Scheme 1. Recently, Barlow *et al.* isolated the adduct of ethoxycarbonylnitrene with perfluoronapthalene,[8] which was stabilized by so called 'perfluoroalkyl effects'. On the basis of this result, direct addition to give the intermediates (**5**) (path m) and (**6**) (path n) is unlikely. Consequently, addition of the nitrene occurs selectively at the C(1)–C(2) bond of naphthalene (path a) to form intermediate (**4**). This selectivity is also suggested by frontier molecular orbital (FMO) considerations, *i.e.* the preferred site in the HOMO of naphthalene for approach of the singlet nitrene's LUMO is the C(1)–C(2) bond (Figure 2, arrowed). Insertion of the nitrene into a C–H bond and opening of the aziridine ring of intermediates (**4**), (**5**), and (**6**) leads to naphthylcarbamates (**3**) and (**8**). The complete absence of 2-naphthylcarbamate (**8**) in the products of the present reaction indicates that insertion into the C(2)–H bond (path c) and aziridine ring-opening of (**4**) (path e) and (**6**) (path k) are negligible. Paths d and l should also be negligible since there is no significant difference in ease of the ring-opening reaction between paths e,k and d,l. Formation of the 1-naphthylcarbamate must therefore occur *via* path b exclusively. The formation of benzazepines (**1**) and (**2**) can be explained by a thermodynamically controlled isomerization of intermediates (**5**) and (**6**) (paths h and j), which appear to be formed by the 'walk' rearrangement of the aziridine ring in intermediate (**4**) (paths f and g) as observed in the case of the cyclopropane ring.[9] In contrast, the absence of benzazepine (**7**) suggests that path i is an unfavourable process because of the loss of the resonance energy of the benzene moiety. It was thus concluded that in the present reaction nitrene insertion into the C(1)–H bond competes with addition to the C(1)–C(2) bond, leading to the subsequent 'walk' rearrangement

paths, finally giving methyl 1-naphthylcarbamate (**3**) and benzazepines (**1**) and (**2**).

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