Preparation of Benz[*cd*]indazole by Excimer Laser Photolysis

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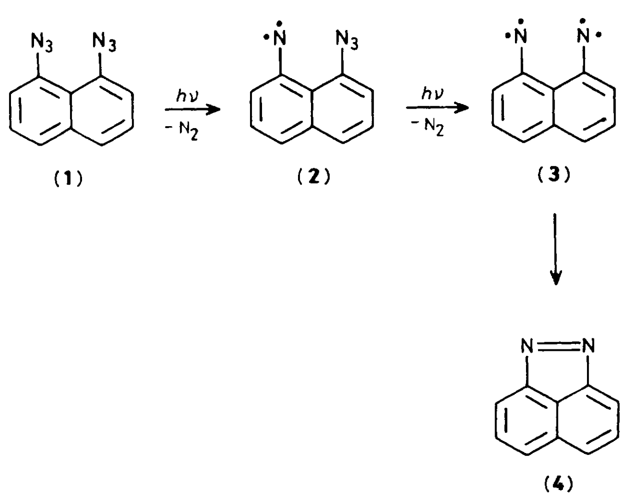
Benz[*cd*]indazole was prepared by KrF pulsed-excimer laser photolysis of 1,8-diazidonaphthalene, *via* a two-photon process.

U.v.–visible pulsed-laser photolysis is well established as an important technique for investigating dynamic processes in photochemistry. Recently however, there has been considerable interest in the organic photochemistry of 'the laser *vs.* the lamp'[1] and several novel reactions induced by excimer laser photolysis have been reported.[2] Herein we report a new use of u.v.–visible pulsed-lasers in organic synthesis.

Benz[*cd*]indazole (**4**), an aza-analogue of acenaphthylene, was the subject of many unsuccessful synthetic attempts before we succeeded producing it by low temperature photolysis of 1,8-diazidonaphthalene (**1**) in a glassy organic solvent at 77 K (Scheme 1).[3] Conventional photolysis (sensitized or unsensitized) of (**1**), had not led to (**4**).[4]

Although the formation of an N=N bond by a simple



Scheme 1

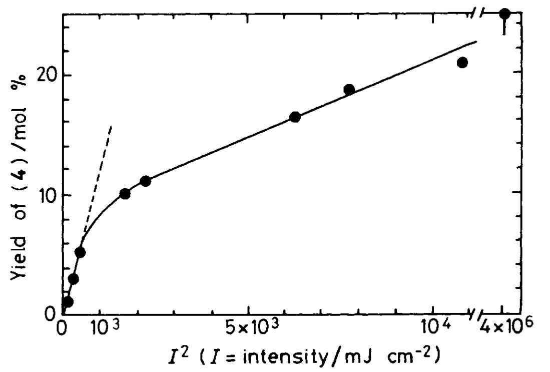


Figure 1. Dependence of the yield of (**4**) on the light intensity. Hexane solutions of (**1**) (2.50 × 10^{-5} M) were photolysed by a single KrF laser pulse at 20 °C.

intramolecular coupling of nitreno groups might be expected, under usual conditions this is precluded by the high reactivity of the nitreno group. However, given the clear-cut mechanism of the low temperature photolysis in a rigid matrix, we expected the excimer laser photolysis of (**1**) to produce (**4**) in fluid organic solvents at ordinary temperatures.

Laser photolyses were carried out in quartz cubic cells with 10 mm optical path. Hexane solutions of (**4**) (0.5—2 ml) were irradiated with a single pulse (max 75 mJ, 8 ns) of the 248 nm line (KrF) from an excimer laser (Lambda Physik: Model EMG-50). The laser beam (5 × 16 mm) was focused or unfocused into the sample through a quartz lens for the irradiations with different intensities (fluences). The formation of (**4**) was confirmed by comparison of its electronic absorption spectrum with that of the authentic sample. The constituents of photolysed solutions were determined by h.p.l.c. analysis (silica gel). Table 1 gives % conversion of (**1**) and the % yield of (**4**) after a single shot of KrF laser.

The formation of (**4**) can be tentatively explained by a two-photon process within the pulse duration of 8 ns. After the nitrenoazide (**2**) is formed by the absorption of the first photon, photolysis of (**2**) by a second photon is required for the formation of (**3**) before the competitive nitrene reactions (hydrogen abstraction from solvents, coupling reactions, and so on) can occur. Reiser and co-workers have reported that the half-life of 1-nitrenonaphthalene in hexane is *ca.* 5 μs.[5] The simultaneous or rapidly sequential two-photon process induced by pulsed-laser photolysis should be an effective method for preparing (**4**) *via* the short-lived intermediate (**2**); the yield of (**4**) should be proportional to the square of light intensity. Figure 1 shows a relationship suggesting the two-photon mechanism for low intensities (4, 14, and 24 mJ cm^{-2}). The lower-than-predicted achieved yields at higher intensities may be explained by the decomposition of (**4**) by the additional photons; the h.p.l.c. analysis showed additional unidentified peaks. This is similar to the case of high intensity irradiation in the diluted solutions as given in Table 1.

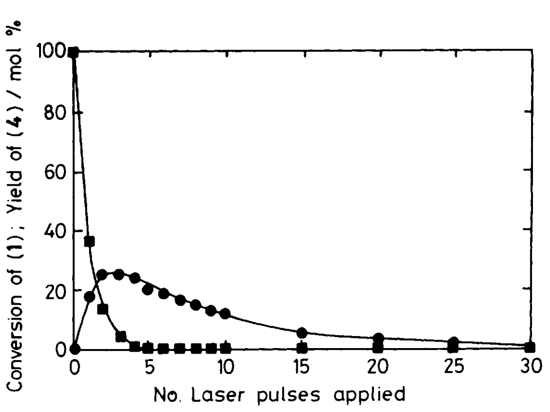


Figure 2. Repeated KrF pulsed-excimer laser photolyses (fluence 88 mJ/cm^{-2}) of (**1**) (2.50 × 10^{-5} M) in N_2-bubbled hexane solution at 20 °C; yield of (**4**) (●) and conversion of (**1**) (■) *vs.* number of laser pulses applied.

Table 1. Yield and selectivity of benz[*cd*]indazole (**4**) produced from 1,8-diazidonaphthalene (**1**) in hexane at 20 °C by a single pulse of KrF excimer laser.

Concentration of (**1**)/ M	Laser fluence/ mJ cm^{-2}	Conversion of (**1**)/ %	Yield of (**4**)/ %	Selectivity for (**4**)/ %
2.50 × 10^{-6}	4	22.8	2.6	11.4
	88	68.5	19.1	27.9
	2000	97.3	26.0	26.7
2.50 × 10^{-5}	4	16.2	2.3	14.2
	88	64.9	18.7	28.8
	2000	87.8	24.5	27.9
2.50 × 10^{-4}	4	11.5	1.0	8.7
	88	33.5	9.7	29.0
	2000	48.6	14.6	30.0

The dependence of the yield of (**4**) upon the number of laser pulses applied is shown in Figure 2. It is noteworthy that (**4**) is photolabile and decomposed by more than two laser shots.† This is one reason why (**4**) was not accessible by photolysis using conventional low-intensity continuous-light sources in fluid solution at room temperature. Even the laser-pulse duration of 8 ns may be too long, compared with the dynamic time-scale for bond cleavage to eliminate N_2 and the intramolecular coupling to form the N=N bond, *i.e.* (**4**) may decompose by additional photons within a single pulse. The proposed mechanism involving the intermediates (**2**) and (**3**)

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† Although (**4**) is photolabile in fluid solution at room temperature, it survives irradiation with a conventional lamp or a laser in a rigid matrix at low temperature.

has still to be confirmed by ultrashort time-resolved spectroscopy.

In conclusion, u.v.–visible pulsed-excimer laser with high light intensity and short pulse time was effective in the preparation of (**4**), previously unattainable by conventional lamp photolysis.

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