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Unprecedented photoinduced insertion reactions of *N*-methyl-1,2-naphthalenedicarboximide with phenylacetylene

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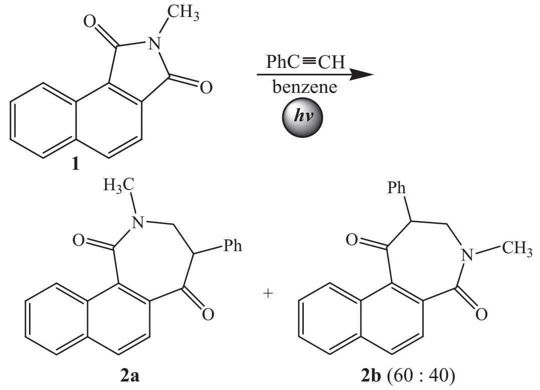
Irradiation of *N*-methyl-1,2-naphthalendicarboximide **1** together with phenylacetylene in benzene afforded unprecedented reductive insertion products dihydronaphthazepinediones **2a** and **2b**, which were characterised by NMR spectroscopy (^{1}H, ^{13}C), IR spectroscopy, MS, elemental analysis and assignments confirmed by X-ray crystallographic analysis.

Keywords: photochemical reaction, *N*-methyl-1,2-naphthalenedicarboximide, phenylacetylene

The photochemistry of naphthalenedicarboximides with alkenes has been intensively investigated.[1-7] The main reaction mode in the photoinduced reactions of *N*-methyl-1,2-naphthalenedicarboximide **1** with alkenes is the insertion of the alkenes between the C(=O)–N bond of the imide moiety to give dihydronaphthazepinedione products.[1,3]

In the studies of photochemistry of naphthalenedicarboximides with alkynes, it was found that the photoinduced cycloadditions of *N*-methyl-1,8-naphthalenedicarboximide with alkynes followed the pathway of *N*-methyl-1,8-naphthalenedicarboximide with alkenes.[8] But that is not the case for **1**. Irradiation of **1** with phenylacetylene in benzene solution afforded unprecedented novel reductive insertion products, dihydronaphthazepinediones **2a** and **2b** (Scheme 1).



Scheme 1

The structures of **2a** and **2b** were fully established by NMR (^{1}H, ^{13}C), MS, IR spectroscopy and elemental analysis. 2-Methyl-4-phenyl-3,4-dihydro-1*H*-naphth[1,2-*c*]azepine-1,5(2*H*)-dione **2a**: colourless crystals from petroleum ether-ethyl acetate, m.p. 161–162°C; δ_H (300 MHz) 8.50–8.47 (1H, d, J = 6.9 Hz), 8.02 (1H, d, J = 8.4 Hz), 7.95–7.92 (1H, dd, J = 9.6 and 4.0 Hz), 7.68–7.63 (2H, m), 7.42 (1H, d, J = 7.2 Hz), 7.31 (3H, m, br.), 7.10 (2H, s, br.), 4.42–4.33 (2H, m), 3.49 (1H, m), 3.39 (3H, s) ppm; δ_C (75 MHz) 205.2, 167.4, 135.8, 133.8, 132.0, 131.9, 130.8, 129.7, 129.6, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 123.9, 60.2, 52.8, 34.6 ppm; ν_{max}: 1684 (imide), 1650 (imide), 1459, 1398, 1258, 775 cm^{-1}; *m/z* 315(M$^+$, 6), 272(24), 211(39), 167(38), 126(47), 104(100). Found: C 80.25, H 5.3, N 4.6; Calcd. for $C_{21}H_{17}NO_2$: C 79.98, H 5.43, N 4.44.

4-Methyl-2-phenyl-3,4-dihydro-1*H*-naphth[2,1-*c*]azepine-1,5(2*H*)-dione **2b**: Colourless crystals from petroleum ether-ethyl acetate, m.p. 144–146°C. δ_H (300 MHz) 8.08 (1H, d, J = 8.4 Hz), 7.93 (1H, d, J = 8.6 Hz), 7.90 (1H, d, J = 8.4 Hz), 7.58–7.53 (1H, m), 7.44–7.41 (2H, m), 7.31–7.25 (3H, m), 7.15–7.12 (2H, m), 4.47 (1 H, dd, J = 11.8 and 3.9), 4.31 (1H, dd, J = 14.6 and 11.8) and 3.60 (1 H, dd, J = 14.6 and 3.9), 3.28 (3H, s) ppm; δ_C (75 MHz) 203.5, 169.3, 135.3, 135.1, 134.3, 132.7, 132.1, 131.3, 130.1, 129.6, 129.2, 128.7, 128.5, 128.2, 126.6, 125.6, 63.3, 52.5, 35.6 ppm; ν_{max}: 1694 (imide), 1645 (imide), 1482, 1397, 1253, 763 cm^{-1}; *m/z* 315(M$^+$, 23), 272(38), 211(46), 167(42), 126(43), 104(100). Found: C 80.35, H 5.5, N 4.3; Calcd. for $C_{21}H_{17}NO_2$: C 79.98, H 5.43, N 4.44.

The structure of **2a** has also been determined and confirmed by single crystal X-ray crystallographic analysis (Fig. 1), which unambiguously differentiated the two regioisomers **2a** and **2b** which were incorrectly assigned before.[3] Crystal data for **2a**: $C_{21}H_{17}NO_2$, M = 315.37, *monoclinic*, a = 37.890(8), b = 11.820(2), c = 15.020(3) Å, V = 6592(2) Å^3, T = 293(2) K, space group *C2/c*, Z = 16, 5884 reflections measured, 5792 unique (R_{int} = 0.025), which were used in all calculations. The final wR (F_2) was 0.257 (all data).

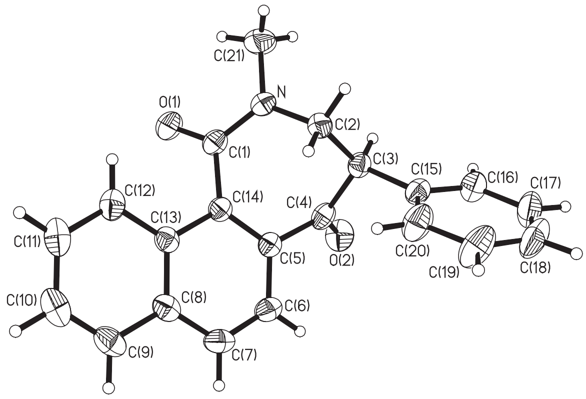
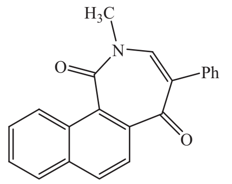
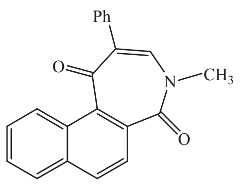


Fig. 1 The X-ray crystal structure ORTEP diagram of **2a**.

It may be rationalised that **2a** and **2b** resulted from reduction of primary products **3a** and **3b** which were the insertion products of phenylacetylene between the C(=O)–N bond of the imide moiety. A similar observation has also been made for the photoinduced reaction of **1** with *t*-butylacetylene.[9] Alibés *et al.*[10] reported that the photocycloaddition of acetylene and furanones gave rise to cyclobutanes and not the expected cyclobutenes. The mechanisms of the C=C bond reduction in the naphthazepinediones need to be further investigated.



3a



3b

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Experimental

Melting points are uncorrected. ^{1}H NMR spectra were measured on a Bruker DPX 300 spectrometer at 300 MHz or 500 MHz with $CDCl_3$ as solvent. ^{13}C NMR spectra were measured on a Bruker Avance 300 spectrometer at 100 MHz with $CDCl_3$ as solvent. IR spectra were recorded with a Shimadzu IR 440 spectrometer in KBr pellets. Mass spectra were taken on a VG ZAB-HS spectrometer in the electron impact ionisation mode. Elemental analyses were performed with a Perkin-Elmer 240 C analyser.

A solution of *N*-methyl-1, 2-naphthalenedicarboximide **1** (633 mg, 3.0 mmol) and phenylacetylene (2.04 g, 20 mmol) in benzene (100 ml) was irradiated with UV light of $\lambda > 330$ nm using a medium-pressure mercury lamp (500 W) for 12 h. After evaporation of the solvents under reduced pressure, the residue was subjected to flash chromatography on a silica gel (300–400 mesh) column to afford **2a** (458 mg, 57%) and **2b** (305 mg, 38%), and recovered **1** (95 mg, 85% conversion).

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Supporting Information (SI) available

^{1}H NMR spectra of compounds **2a** and **2b** are available from the author; CCDC 260171 for compound **2a** contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

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