

2-SUBSTITUTED ACENAPHTHO[1,2-d]OXAZOLES¹

Otohiko Tsuge* and Masahiro Koga

Research Institute of Industrial Science, Kyushu University 86,
 Hakozaki, Higashi-ku, Fukuoka 812, Japan

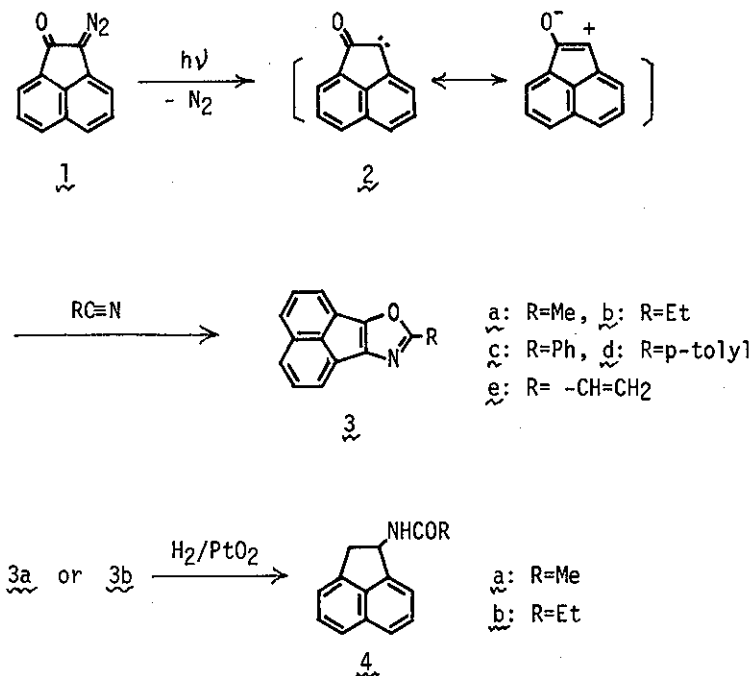
Irradiation of 2-diazoacenaphthenone (1) in nitriles such as acetonitrile, propionitrile, benzonitrile, p-tolunitrile, and acrylonitrile afforded the corresponding 2-substituted acenaphtho[1,2-d]oxazoles (3). In pyrolysis of 1 in benzonitrile 2-phenyloxazole derivative 3c was formed, together with traces of 2,2'-diacenaphthylidene-1,1'-dione.

Huisgen and his co-workers² first reported the 1,3-dipolar cycloaddition reaction of benzonitrile with the ketocarbene generated from uncatalyzed and copper-catalyzed pyrolysis of diazoacetophenone. Ketocarbenes not undergoing Wolff rearrangement are suitable for 1,3-dipolar cycloaddition. It has been reported that decomposition of 4,7-dimethyl-2-diazo-1-indanone in benzonitrile in the absence and presence of copper catalyst afforded the corresponding oxazole derivative in 11 and 34% yields respectively.³

2-Diazoacenaphthenone (1)⁴ is one of few diazo ketones where Wolff rearrangement could not be achieved.⁵ Thus it is expected that the ketocarbene 2 generated from 1 would behave as a 1,3-dipole. Our attention was focused on the investigation on the 1,3-dipolar cycloaddition of 2 to nitriles, which is

the subject of the present communication.

A solution of 1 (0.78 g, 4 mmol) in acetonitrile (200 ml) was irradiated by Pyrex-filtered light from a 100W high-pressure mercury lamp at room temperature for 12 hr. The nitrile was evaporated in vacuo, and the residue was chromatographed on alumina using benzene as an eluent to give 0.29 g (35%) of 2-methylacenaphtho[1,2-d]oxazole (3a).



Similarly, photolysis of 1 in propionitrile, benzonitrile, and p-toluenitrile gave the corresponding oxazole derivatives, 3b-3d. Previously, we reported that the reaction of 1 with acrylonitrile in boiling benzene afforded a mixture of two stereoisomeric 2'-cyanospiro[acenaphthenone-2,1'-cyclopropanes].⁶ In the irradiation of 1 with acrylonitrile, however, the corresponding oxazole derivative 3e was formed.

The yields, physical and spectral data of 3 are shown in Table I. Struc-

Table I

<u>3</u>	R	Yield %	Mp., °C	Appearance	Nmr(CDCl ₃) δ	M ⁺ (m/e)
<u>a</u>	Me	35	115-116	yellow prisms	2.64(3H, s), 7.3-7.9 (6H, m)	207
<u>b</u>	Et	40	68-69	yellow prisms	1.4(3H, t, J=7.5 Hz), 2.59 (2H, q, J=7.5 Hz), 7.2-7.9 (6H, m)	221
<u>c</u>	Ph	24	217-218	orange needles		269
<u>d</u>	p-tolyl	14	218-220	orange prisms		283
<u>e</u>	CH=CH ₂	11	135-136	orange prisms	3.5(2H, dd, =CH ₂ , J=7.5, 9 Hz), 5.85(1H, dd, =CH, J=7.5, 9 Hz), 7.2-7.9 (6H, m)	219

Satisfactory elemental analyses have been obtained for all 3. Ir spectra of all 3 showed no bands ascribable to NH, C≡N, and C=O absorptions.

tural elucidation of 3 was accomplished on the basis of spectral data (Table I) and of chemical conversion.

Hydrogenolysis of 3a and 3b over PtO₂ in dioxane at room temperature gave the corresponding 1-acylaminoacenaphthenes, 4a and 4b, in excellent yields respectively.

4a: yield 85%; colorless needles, mp 204-205°C (lit.⁷ mp 205°C); ir (KBr) 3300 (NH), 1643 cm⁻¹ (C=O); nmr (CDCl₃) δ 1.98 (3H, s, CH₃), 3.05, 3.75 (each 1H, m, CH₂), 6.0 (2H, m, CH and NH), 7.2-7.9 (6H, m, ArH); mass spectrum m/e 211 (M⁺).

4b: yield 85%; colorless needles, mp 198-199°C; ir (KBr) 3300 (NH), 1643 cm⁻¹ (C=O); nmr (CDCl₃) δ 1.15 (3H, t, CH₃, J=7.2 Hz), 2.25 (2H, q, CH₂Me, J=7.2 Hz), 3.1, 3.8 (each 1H, m, CH₂), 6.0 (2H, br, CH and NH), 7.2-7.9 (6H, m, ArH); mass spectrum m/e 225 (M⁺).

No thermal decomposition of 1 occurred in boiling benzene or toluene for a

long while.⁶ When a solution of 1 in benzonitrile was heated at 150°C for 2.5 hr, oxazole derivative 3c was obtained in 8% yield, together with traces of 2,2'-diacenaphthylidene-1,1'-dione and recovery of 1 (53%).

Thus, it is clear that 2 generated from 1 by photolysis and thermolysis behaves as a 1,3-dipole toward nitriles.

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