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

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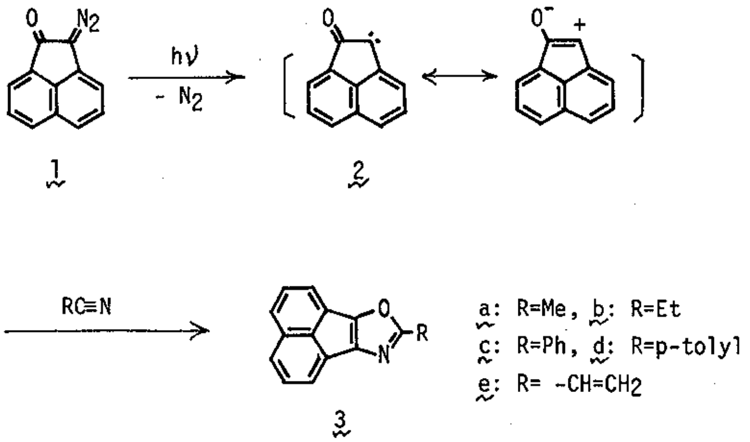
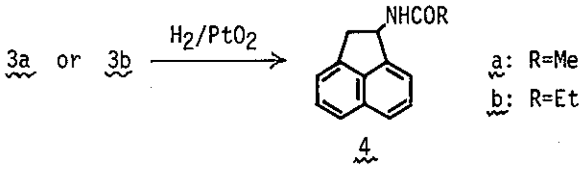
Irradiation of 2-diazoacenaphthenone (**1**) in nitriles such as acetonitrile, propionitrile, benzonitrile, p-tolunitrile, and acrylonitrile afforded the corresponding 2-substituted acenaphtho-[1,2-d]oxazoles (**3**). In pyrolysis of **1** in benzonitrile 2-phenyloxazole derivative **3c** was formed,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

Huisgen and his co-workers[2] 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-tolunitrile 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. Structural elucidation of **3** was accomplished on the basis of spectral data (Table I) and of chemical conversion.

Table I

3	R	Yield %	Mp., ^{o}C	Appearance	Nmr($CDCl_3$) δ	M^+ (m/e)
a	Me	35	115-116	yellow prisms	2.64(3H, s), 7.3-7.9 (6H, m)	207
b	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
c	Ph	24	217-218	orange needles		269
d	p-tolyl	14	218-220	orange prisms		283
e	$CH=CH_2$	11	135-136	orange prisms	3.5(2H, dd, =C$\underline{H}_2$, J=7.5, 9 Hz), 5.85(1H, dd, =C$\underline{H}$, 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.

Hydrogenolysis of **3a** and **3b** over PtO_2 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 ($CDCl_3$) δ 1.98 (3H, s, C$\underline{H}_3$), 3.05, 3.75 (each 1H, m, C$\underline{H}_2$), 6.0 (2H, m, C$\underline{H}$ and N$\underline{H}$), 7.2-7.9 (6H, m, Ar$\underline{H}$); 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 ($CDCl_3$) δ 1.15 (3H, t, C$\underline{H}_3$, J=7.2 Hz), 2.25 (2H, q, C$\underline{H}_2$Me, J=7.2 Hz), 3.1, 3.8 (each 1H, m, C$\underline{H}_2$), 6.0 (2H, br, C$\underline{H}$ and N$\underline{H}$), 7.2-7.9 (6H, m, Ar$\underline{H}$); 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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