Reaction of Benzonitrile Oxides with Conjugated Nitroalkenes

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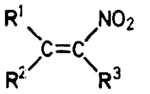
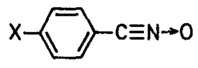
It is known that nitroalkenes react as dipolarophiles in cycloaddition reactions[1]. In a previous communication[2], we described the 1,3-dipolar cycloaddition of unconjugated nitroalkenes with aliphatic and aromatic nitrile oxides. It was found that this reaction affords only 5-nitroalkyl-4,5-dihydro-1,2-oxazoles. We report now the first examples of the use of conjugated nitroalkenes (1-nitroalkenes, **1**) as dipolarophiles in the cycloaddition with aromatic *N*-oxides (**2**).





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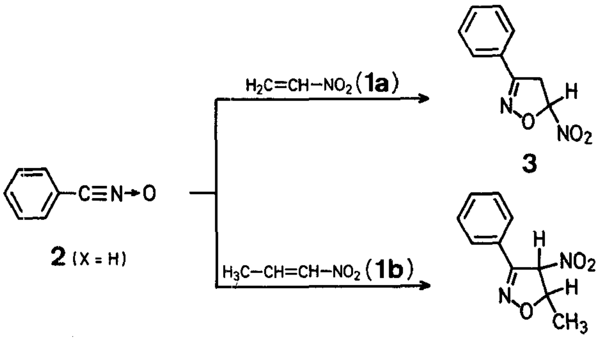
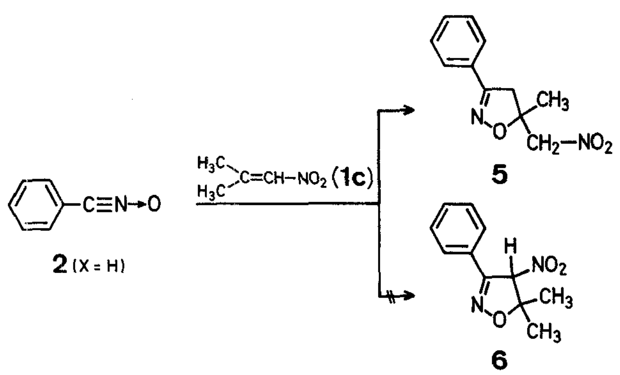
1	R¹	R²	R³
a	H	H	H
b	H	CH_3	H
c	CH_3	CH_3	H
d	H	H	CH_3
e	H	CH_3	CH_3

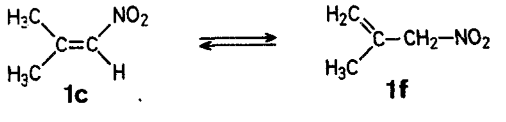
The course of the cycloaddition depends on the structure of the nitroalkenes **1** and the products are 4- or 5-nitro-4,5-dihydro-1,2-oxazoles, or 1,2-oxazoles not containing a nitro group. Thus, the reaction of benzonitrile oxide (**2**, X = H) with nitroethylene (**1a**) in ether at room temperature yields 5-nitro-3-phenyl-4,5-dihydro-1,2-oxazole (**3**) whereas the analogous reaction with 1-nitro-1-propene (**1b**) leads to 5-methyl-4-nitro-3-phenyl-4,5-dihydro-1,2-oxazole (**4**).



Under the same conditions, 2-methyl-1-nitropropene (**1c**) adds to benzonitrile oxide (**2**, X = H) to give 5-methyl-5-nitromethyl-3-phenyl-4,5-dihydro-1,2-oxazole (**5**) instead of the expected product **6** of a 1,3-dipolar cycloaddition.



This result can be explained by assuming that under the reaction conditions 2-methyl-1-nitropropene (**1c**) isomerizes partially to 2-methyl-3-nitropropene (**1f**) by hydrogen shift.



The possibility of the isomerization **1c**→**1f** has already been reported by Descotes et al.[3]. Further, it is known that disubstituted ethylenes react much faster than trisubstituted ethylenes in 1,3-dipolar cycloadditions[4].

In the case of the addition of 2-nitropropene (**1d**) and 2-nitro-2-butene (**1e**) to benzonitrile oxide (**2**, X=H), the reaction proceeds beyond the 1,2-oxazoline stage to give the corresponding 1,2-oxazoles (**7**, **8**) with elimination of nitrous acid. Compound **7** was also synthesized by dehydronitration of 5-methyl-4-nitro-3-phenyl-4,5-dihydro-1,2-oxazole (**4**) in boiling xylene. 5-Nitro-3-phenyl-1,5-dihydro-1,2-oxazole (**3**) under similar conditions (boiling toluene) gives 3-phenyl-1,2-oxazole (**9**).

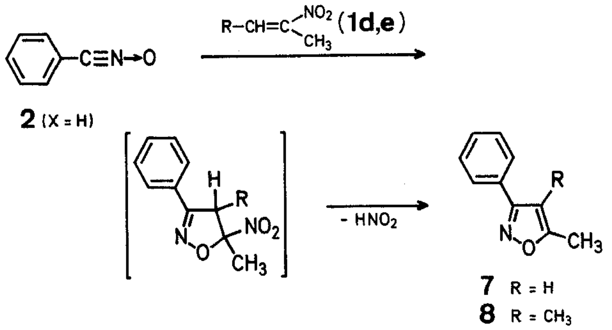
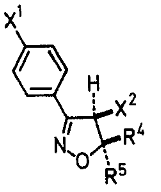


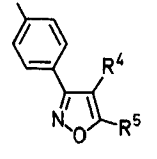
Table 1. 3-Phenyl-4,5-dihydro-1,2-oxazoles prepared



X^1	X^2	R^4	R^5	Yield [%]	m.p. (Solvent)	Brutto formula[a]	^{1}H-N.M.R. (CDCl$_3$ and acetone-d_6) δ [ppm]
H	H	H	NO$_2$	90	79–80° (ethanol)	$C_9H_8N_2O_3$ (192.2)	3.93 (d, 2H, J=4.6 Hz); 6.17 (q, 1H, J=4.6 Hz)
NO$_2$	H	H	NO$_2$	98	139–140° (methanol)	$C_9H_7N_3O_5$ (237.2)	4.34 (d, 2H, J=4.6 Hz); 6.69 (q, 1H, J=4.6 Hz)
H$_3$CO—	H	H	NO$_2$	93	124–126° (methanol)	$C_{10}H_{10}N_2O_4$ (222.2)	4.30 (d, 2H, J=4.6 Hz); 6.54 (q, 2H, J=4.6 Hz)
H	NO$_2$	H	CH$_3$	68	88–89° (ethanol)	$C_{10}H_{10}N_2O_3$ (206.2)	1.50 (d, 3H, J=6.9 Hz); 5.32 (o, 1H, J=6.9 Hz, J=3.5 Hz); 5.92 (d, 1H, J=3.5 Hz)
NO$_2$	NO$_2$	H	CH$_3$	60	168–170° (methanol)	$C_{10}H_9N_3O_5$ (251.2)	
H	H	CH$_3$	—CH$_2$—NO$_2$	10	82–83° (propanol)	$C_{11}H_{12}N_2O_3$ (220.2)	3.12 (d, 1H, J=17.2 Hz); 3.66 (d, 1H, J=17.2 Hz); 4.50 (s, 3H); 1.60 (s, 3H)
NO$_2$	H	CH$_3$	—CH$_2$—NO$_2$	18	99–101° (ethanol)	$C_{11}H_{11}N_3O_5$ (265.2)	1.60 (s, 3H); 3.42 (d, 1H, J=17.4 Hz); 3.84 (d, 1H, J=17.4 Hz); 4.88 (s, 2H)

[a] The elemental analyses showed the following maximum deviations from the calculated values: C, ±0.49; H, ±0.20; N, ±0.32.

Table 2. 3-Phenyl-1,2-oxazoles prepared



X	R^4	R^5	Yield [%]	m.p. Solvent	Brutto formula[g]	^{1}H-N.M.R. (CDCl$_3$ and acetone-d_6) δ [ppm]
H	H	H	77[a]	b.p. 97–98°/4 torr[b]	C_9H_7NO (145.2)	
NO$_2$	H	H	77[a]	181–183°[c] (ethanol)	$C_9H_6N_2O_3$ (190.2)	
H$_3$CO	H	H	61[a]	46–47° (hexane)	$C_{10}H_9NO_2$ (175.2)	3.82 (s, 3H); 6.56 (d, 1H, J≈2 Hz); 8.38 (d, 1H, J≈2 Hz)
H	H	CH$_3$	56; 43[d]	41–42°[e] (hexane)	$C_{10}H_9NO$ (159.2)	2.30 (s, 3H); 6.12 (s, 1H)
NO$_2$	H	CH$_3$	72; 50[d]	154–155° (dioxan)	$C_{10}H_8N_2O_3$ (204.2)	2.45 (s, 3H); 6.38 (s, 1H)
H$_3$CO	H	CH$_3$	53	92–93° (ethanol)	$C_{11}H_{11}NO_2$ (189.2)	2.43 (s, 3H); 3.82 (s, 3H); 6.28 (s, 1H)
H	CH$_3$	CH$_3$	30	b.p. 101–102°/1 torr[f]	$C_{11}H_{11}NO$ (173.2)	1.93 (s, 3H); 2.23 (s, 3H)

[a] From the corresponding 3-aryl-5-nitro-4,5-dihydro-1,2-oxazole.

[b] n_D^{20}: 1.5616; d_4^{20}: 1.1386. Ref.[5], b.p. 145°/30 torr; n_D^{20}: 1.5625; d_4^{20}: 1.1378.

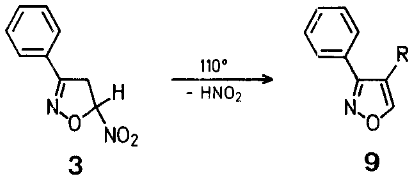
[c] M.S.: m/e=190 (M$^+$), 189, 160, 143, 118. Ref.[6], m.p. 182–183°.

[d] From the corresponding 3-aryl-5-methyl-4-nitro-4,5-dihydro-1,2-oxazole.

[e] Ref.[7], m.p. 42°.

[f] n_D^{20}: 1.5646.

[g] The N analyses showed a maximum deviation of ±0.27 from the calculated values.



The melting points were determined using a Boëtius apparatus and are uncorrected. The ^{1}H-N.M.R. spectra were recorded on a Tesla apparatus BS-478 (80 Hz) in $CDCl_3$ and also in acetone-d_6 using hexamethyldisilazane (HMDS, $\delta = 0.05$ ppm) as an internal standard.

Reaction of Benzonitrile Oxides with Nitroalkenes; General Procedure:

A solution of the nitroalkene[8] (**1**; 0.02 mol) in dry ether (20 ml) is added dropwise to a vigorously stirred solution of the benzonitrile oxide[4] (**2**; 0.01 mol) in dry ether (80 ml) at 0°. Stirring is continued for 12 h at room temperature. The mixture is then refluxed for 2 h, the ether is evaporated in vacuo, and the residue is distilled in vacuo or recrystallized from a suitable solvent (Table 1).

Dehydronitration of 3-Aryl-5-nitro-4,5-dihydro-1,2-oxazoles; General Procedure:

A solution of the 3-aryl-5-nitro-4,5-dihydro-1,2-oxazole (0.01 mol) in dry toluene (50 ml) is refluxed for 2 h on the oil bath. The solvent is then evaporated in vacuo and the residue is distilled in vacuo or recrystallzed (Table 2).

Dehydronitration of 3-Aryl-5-methyl-4-nitro-4,5-dihydro-1,2-oxazoles; General Procedure:

A solution of the 3-aryl-5-methyl-4-nitro-4,5-dihydro-1,2-oxazole (0.01 mol) in dry *p*-xylene (50 ml) is refluxed for 6 h on the oil bath. The solvent is then evaporated and the residue is recrystallized (Table 2).

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