A Facile Method for the Preparation of Nitroenamines

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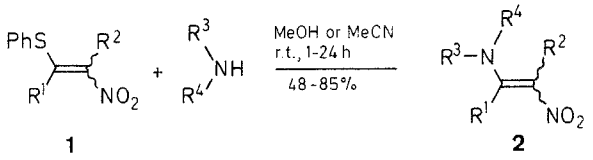
Various kinds of nitroenamines are readily prepared by the reaction of 1-nitro-2-phenylthioalkenes with amines.

The chemistry of nitroenamines has been extensively investigated and their potential utility for organic synthesis has been well established.[1] The following methods have been used for their preparation: condensation of dimethylformamide acetals with nitroalkanes,[2,3] condensation of triethyl orthoformate with nitromethane in the presence of secondary amines,[4] and transamination of 1-dimethylamino-2-nitroethene.[5,6] We here report a new general method for the preparation of nitroenamines **2** from 1-nitro-2-phenylthioalkenes **1** and aliphatic amines in methanol or aromatic amines in acetonitrile at room temperature. The 1-nitro-2-phenylthioalkenes **1** are available from nitroalkanes, aldehydes, and thiols.[7]



1 **2**

2	R^1	R^2	R^3	R^4
a	H	H	$(CH_2)_4$	
b	CH_3	H	$(CH_2)_4$	
c	H	CH_3	$(CH_2)_4$	
d	H	H	CH_3	CH_3
e	H	H	t-C_4H_9	H
f	H	H	C_6H_5	CH_3
g	H	H	$H_2C{=}CHCH_2$	$H_2C{=}CHCH_2$

Table 1. Preparation of Nitroenamines **2**

Product	Solvent, Reaction Time (h)	Yield[a] (%)	mp (°C)	Molecular Formula[b] or Lit. Data
2a	MeOH, 2	85	78	77–78[5]
2b	MeOH, 12	64	113–114	$C_7H_{12}N_2O_2$ (156.2)
2c	MeOH, 6	78	91	93–94[6]
2d	MeOH, 1	74	104–105	104[2]
2e	MeOH, 12	48	80–81	81–82[8]
2f	MeCN, 24	80	94–95	94[4]
2g	MeOH, 12	80	oil	$C_8H_{12}N_2O_2$ (168.2)

[a] Yield of isolated product.
[b] Satisfactory microanalyses: C ±0.40, H ±0.15, N ±0.39.

Table 2. Spectral Data of Nitroenamines **2**

Compound	IR ($CHCl_3$) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)
2a	1630	8.35 (d, J = 10, 1H); 6.63 (d, J = 10, 1H); 3.68 (t, J = 6, 2H); 3.20 (t, J = 6, 2H); 2.16–1.92 (m, 4H)
2b	1630	6.76 (s, 1H); 3.72–3.56 (m, 2H); 3.36 (m, 2H); 2.64 (s, 3H); 2.10–1.96 (m, 4H)
2c	1630	8.52 (s, 1H); 3.76–3.60 (m, 4H); 2.32 (s, 3H); 2.06–1.91 (m, 4H)
2d	1630	8.15 (d, J = 10, 1H); 6.66 (d, J = 12, 1H); 3.21 (s, 3H); 2.87 (s, 3H)
2e	3250, 1630	8.8–8.2 (br, 1H); 6.96 (d, d, J = 5, 14, 1H); 6.52 (d, J = 6, 1H); 1.36 (s, 9H)
2f	1630	8.48 (d, J = 10, 1H); 7.58–7.16 (m, 5H); 6.88 (d, J = 10, 1H); 3.35 (s, 3H)
2g	1630	8.14 (d, J = 10, 1H); 6.76 (d, J = 10, 1H); 6.00–5.60 (m, 2H); 5.42–5.16 (m, 4H); 4.00–3.70 (m, 4H)

1-Pyrrolidino-2-nitroethylene (2a); Typical Procedure:

A mixture of 1-nitro-2-phenylthioethylene (**1**; $R^1 = R^2 = H$; 0.18 g, 1 mmol) and pyrrolidine (0.14 g, 2 mmol) in MeOH (5 mL) is stirred at room temperature for 3 h. The solvent is evaporated under reduced pressure and the residue is subjected to column chromatography (silica gel, hexane/EtOAc) to give **2a**; yield: 0.12 g (85%); mp 78 °C (Lit.[5] mp 77–78 °C).

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