A One-Pot Synthesis of Nitroenamines

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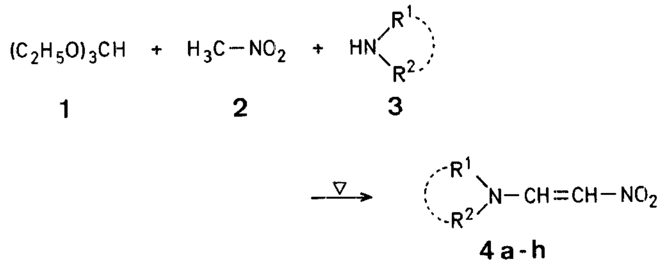
Nitroenamines can be prepared from dimethylformamide acetal or from dimethylformamide mercaptal and nitromethane[1,2], from 1,1-dichloro-2-nitroethane or 1-chloro-2-nitroethene and secondary amines[3,4], and by transamination of 1-dimethylamino-2-nitroethene[5].

We found that boiling a mixture of triethyl orthoformate (**1**), nitromethane (**2**), and secondary amine **3** produces nitroenamines **4** in one step.



Reactions of highter nitroalkanes result in such low yields that a preparative work-up is of no interest. We found also that gaseous dimethylamine can be replaced by dimethylformamide (**5**). However, reactions of higher formamides also give very poor yields of the nitroenamines **4**.

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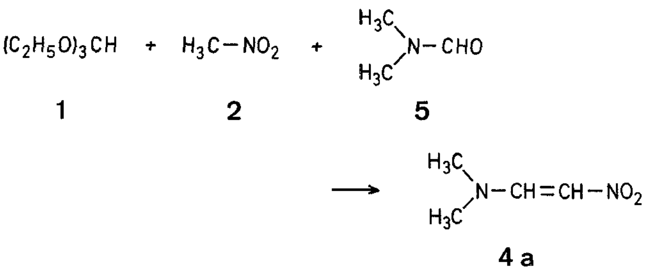
Table. Nitroenamines **4a–h** from Secondary Amines **3**

Product No.	R^1	R^2	Yield[a] [%]	Time [h]	m.p. [°C] (solvent)	Molecular formula or Lit. m.p. [°C]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
4a	CH_3	CH_3	35[b]	3	104° (ethanol)	104°[1], 103–104°[2]	3.10 (d, 6H); 6.70 (d, 1H, $J=11$ Hz); 8.20 (d, 1H)
4b	C_2H_5	C_2H_5	9	7	36° (PE)	102–103°[4]	1.30 (t, 6H); 3.35 (m, 4H); 6.75 (d, 1H, $J=11$ Hz); 8.20 (d, 1H)
4c	$—(CH_2)_4—$		20	1	77° (PE)	77–78°[5]	2.5 (m, 4H); 3.2 (m, 2H); 3.65 (m, 2H); 6.60 (d, 1H, $J=11$ Hz); 8.35 (d, 1H)
4d	$—(CH_2)_5—$		25	15	97° (PE)	96–97°[5]	1.7 (m, 4H); 3.4 (m, 6H); 6.75 (d, 1H, $J=11$ Hz); 8.10 (d, 1H)
4e	$—(CH_2)_2—O—(CH_2)_2—$		70	1	140° (ethanol)	144°[3], 140–141°[5]	3.3 (m, 4H); 3.7 (m, 4H); 6.70 (d, 1H, $J=11$ Hz); 8.10 (d, 1H)
4f	C_6H_{11}	CH_3	15	1	95° (PE)	$C_9H_{16}N_2O_2$[c] (184.2)	1.6 (m, 10H); 2.85 (s, 3H); 3.1 (m, 1H); 6.70 (d, 1H, $J=11$ Hz); 8.30 (d, 1H)
4g	C_6H_5	CH_3	67	7	94° (toluene/cyclohexane)	91–92°[3]	3.40 (s, 3H); 6.90 (d, 1H, $J=11$ Hz); 7.3 (m, 5H); 8.55 (d, 1H)
4h	C_6H_5	C_6H_5	16	15	77° (PE)	$C_{14}H_{12}N_2O_2$[d] (240.3)	6.60 (d, 1H, $J=11$ Hz); 7.3 (m, 10H); 8.25 (d, 1H)

[a] Yield of pure isolated product; purity checked by T.L.C. on silica gel (chloroform as solvent, chloroform/ethyl acetate, 95:5 as developer) and ^{1}H-N.M.R. spectrometry.

[b] Gaseous dimethylamine (0.2 mol) is injected during the reaction.

[c] calc.	C 58.67	H 8.75	N 15.21
found	58.59	8.65	15.10
[d] calc.	C 69.99	H 5.03	N 11.66
found	69.85	5.10	11.58



Nitroenamines 4; General Procedure:

A mixture of nitromethane (**2**; 0.5 mol), triethyl orthoformate (**1**; 0.2 mol), secondary amine **3** (0.1 mol) and *p*-toluenesulfonic acid (0.5 g) is heated under reflux for the time reported in the Table. The mixture is dried under vacuo, the crude residue diluted with dichloromethane, and purified through an alumina column (30 × 2.5 cm) using dichloromethane as eluting agent. Nitroenamines **4** are then recrystallized as shown in the Table.

1-Dimethylamino-2-nitroethene (4a) from Dimethylformamide (5):

A flask fitted with a 20 cm column is charged with a mixture of dimethylformamide (**5**; 0.5 mol), triethyl orthoformate (**1**; 0.1 mol), nitromethane (**2**; 0.1 mol) and *p*-toluenesulfonic acid (0.5 g). The stirring mixture is heated in an oil bath and the temperature increased until the distillation of ethanol is ended. Then the mixture is dried under vacuo and the residue treated as above; yield: 52%. If the reaction is performed under reflux without separation of ethanol, the yield is only 34%.

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