

A Convenient Synthesis of 1-(2-Furyl)-2-nitroalk-1-enes on Alumina Surface without Solvent

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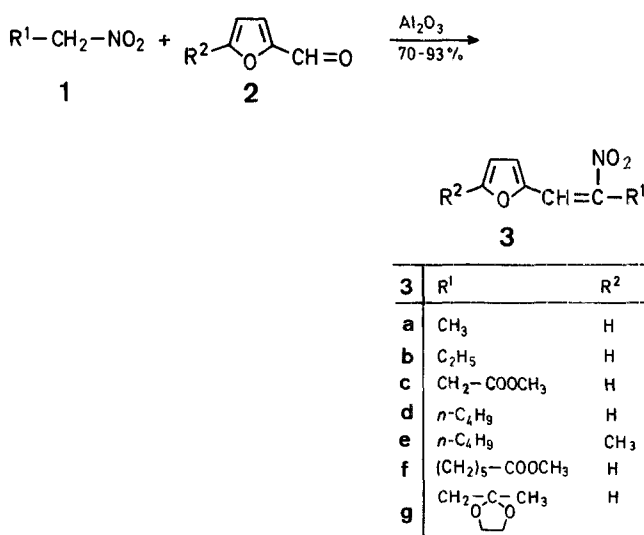
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Unsaturated nitro compounds are of importance because of their numerous uses as fungicides, insecticides, and pharmacologically active substances; moreover they are valuable monomers and form interesting, highly polymerized products¹. Even more important is the part played by unsaturated nitro compounds in organic synthesis². As highly active chemical substances, they can be utilized as starting materials in the synthesis of many classes of organic compounds¹⁻¹⁴.

In connection with our interest in the construction of carbocyclic structures by means of nitroalkane derivatives, we report here a mild, simple, and very convenient new heterogeneous method for an effective synthesis of the 1-(2-furyl)-2-nitroalk-1-enes **3a-g**. The starting compounds **1** and **2** are completely adsorbed by vigorous stirring with a sufficient amount of alumina (Carlo Erba RS chromatographic alumina, activity I according to Brockmann) without solvent. After standing for 24–36 h at room temperature, the products **3a-g** are isolated in high yield (Table) by washing with dichloromethane, filtration of the organic extracts, and evaporation of the solvent under reduced pressure. The reaction sequence probably involves the intermediacy of 2-nitroalkanols¹⁵ which suffer loss of water to give the corresponding nitroalkenes.

Table. 1-(2-Furyl)-2-nitroalk-1-enes **3a-g** prepared

3	Reaction time [h]	Yield ^a [%]	b.p. [°C]/torr or m.p. [°C] ^b	Molecular Formula ^c or Lit. data	I.R. (film) ν [cm ⁻¹] ^d		¹ H-N.M.R. (CDCl ₃ /TMS _{int}) ^e δ [ppm]
					C=C	NO ₂	
a	44	70	44–45°	m.p. 48–49° ¹⁶	1760	1520	1.73–2.16 (m, 2H); 2.58 (s, 3H); 7.6–7.94 (m, 2H)
b	40	78	128°/10	b.p. 124–5°/10 ¹⁶	1760	1510	1.18 (t, 3H, $J = 7.5$ Hz); 3.03 (q, 2H, $J = 7.5$ Hz); 6.53–6.67 (m, 1H); 6.75–6.90 (m, 1H); 7.56–7.80 (m, 2H)
c	30	93	95–96°	C ₉ H ₉ NO ₅ (211.2)	1650	1510	3.73 (s, 3H); 4.20 (s, 2H); 6.60–6.77 (m, 1H); 6.90–7.15 (m, 1H); 7.66 (s, 1H); 8.03 (s, 1H)
d	48	77	144°/10	C ₁₀ H ₁₃ NO ₃ (195.2)	1650	1510	0.95 (t, 3H, $J = 4.15$ Hz); 1.20–1.85 (m, 4H); 3.06 (t, 2H, $J = 7.5$ Hz); 6.53–6.70 (m, 1H); 6.8–6.93 (m, 1H); 7.6–7.9 (m, 2H)
e	31	85	oil ^f	C ₁₁ H ₁₅ NO ₃ (209.2)	1640	1520	0.83–1.10 (m, 3H); 1.21–1.80 (m, 4H); 2.49 (s, 3H); 2.93–3.15 (m, 2H); 6.16–6.30 (m, 1H); 6.7–6.82 (m, 1H); 7.73–7.83 (m, 1H)
f	46	78	oil ^f	C ₁₃ H ₁₇ NO ₅ (267.3)	1645	1510	1.23–1.96 (m, 6H); 2.24–2.48 (m, 2H); 2.95–3.23 (m, 2H); 3.64 (s, 3H); 6.55–6.68 (m, 1H); 6.80–6.93 (m, 1H); 7.65–7.77 (m, 1H); 7.83–7.9 (m, 1H)
g	27	75	oil ^f	C ₁₁ H ₁₃ NO ₅ (239.2)	1650	1510	1.38 (s, 3H); 3.57 (s, 2H); 3.9 (s, 4H); 6.53–6.67 (m, 1H); 6.90–7.04 (m, 1H); 7.62–7.73 (m, 1H); 7.82–7.95 (m, 1H)

^a Yield of pure, isolated product. At least 98% pure by G.L.C. analysis (experimental).^b Uncorrected.^c Satisfactory microanalyses obtained: C ± 0.18 , H ± 0.12 , N ± 0.17 .^d Recorded on a Perkin-Elmer 297 spectrometer, compounds **3a** and **3c** were measured in KBr.^e Recorded at 90 MHz using a Varian EM 390 spectrometer.^f Purified by chromatography over silica gel (0.063–0.200 μ) with ethyl acetate/hexane (20/80) as eluent.

It is well known that all nitroalkenes polymerize with more or less rapidity, however our procedure works well on a gram scale and good results are obtained with substrates which are acid or base sensitive. We thus consider our procedure to be a further convenient utilization of chromatographic alumina¹⁵ in the synthesis of polyfunctional and reactive intermediates.

1-(2-Furyl)-2-nitroalk-1-enes (**3a-g**); General Procedure:

The nitro compound **1** (0.05 mol) and freshly distilled aldehyde **2** (0.05 mol) are charged in a 250 ml, two-necked flask equipped with a

mechanical stirrer. The solution is cooled in a cold water bath and stirred for 3 min. Chromatographic alumina (Carlo Erba RS, activity I according to Brockmann; 12 g) is added and stirring is continued at room temperature (for compounds **3a** and **3g** the temperature is kept at 40°C) for the appropriate time (see Table); the reaction progress is monitored by G.L.C. analysis with a Carlo Erba Fractovap 4160; column: OV 1, duran glass, 25 m \times 0.3 mm; film thickness 0.4–0.45 μ m; injector temperature: 300°C; detector flame ionization: 300°C; carrier nitrogen at 3 ml/min; column temperature: 65°C; programme: 3 min at 65°C, then from 65° to 250°C at 15°C/min and held). After that the alumina is washed with dichloromethane (3 \times 60 ml) and the filtered extract is evaporated at reduced pressure to give crude nitroalkenes **3** which are purified by distillation or by chromatography (Table).

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