

A Facile and Regioselective Synthesis of 1-Anilino-2-nitro-1-phenylethylenes (2-Nitro-1-phenylenamines)

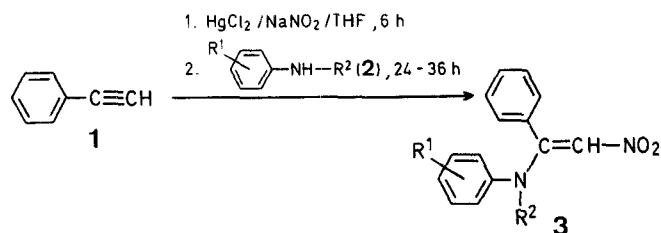
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Nitroaliphatic compounds have in recent years attracted much interest as intermediates in organic synthesis^{1,2,3}. Nitroenamines are particularly valuable reaction components and some methods for the preparation of certain types of nitroenamines have been described^{4,5}. However, there is still need of further or more general procedures.

The ability of mercury(II) salts to promote the addition of nucleophiles to $C\equiv C$ triple bonds is well documented. In this context, we have recently reported the aminomercuration of 1-alkynes via an oxidative and/or catalytic process⁶. We now describe a facile and regioselective synthesis of 1-anilino-2-nitro-1-phenylethylenes (**3**) by the reaction of phenylacetylene (**1**) with mercury(II) chloride, sodium nitrite, and a primary or secondary aromatic amine (**2**) in the ratio 1:1:2:5.

The reaction with primary amines (**2**, $R^2=H$) leads exclusively to the (*Z*)-isomer because of an intramolecular hydrogen bond⁴ while in the case of secondary amines a ~3:7 mixture of the (*Z*)- and (*E*)-isomers is obtained.



1-Anilino-2-nitro-1-phenylethylenes (**3**); General Procedure:

Phenylacetylene (**1**; 2.2 ml, 20 mmol) is added to a suspension of mercury(II) chloride (5.43 g, 20 mmol) and anhydrous sodium nitrite (2.76 g, 40 mmol) in dry tetrahydrofuran (50 ml) and the mixture stirred at room temperature for 6 h. The yellow suspension is then filtered, the aromatic amine (**2**; 100 mmol) added to the liquid phase, and the mixture allowed to react for 24–36 h (see Table). The resultant mixture is filtered and the filtrate evaporated in vacuo to half its original volume. For compounds **3f**, **g**, **h**, the concentrated solution is washed with aqueous 3 normal potassium hydroxide (20 ml), extracted with ether (2 × 25 ml), and dried with sodium sulfate; the solvents are evaporated and compounds **3f**, **g**, **h** are purified by recrystallization from hot ethanol. For compounds **3a–e**, the concentrated solution is shaken with 3 normal sulfuric acid (15 ml) and extracted with ether (2 × 25 ml) (the ether layer is discharged); the aqueous layer is made alkaline with aqueous 3 normal potassium hydroxide (20 ml) and extracted with ether (2 × 25 ml); the ether extract is dried with sodium sulfate and evaporated and the residual products **3a–e** are purified by recrystallization from hot ethanol.

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Table. 1-Anilino-2-nitro-1-phenylethylenes (**3**) prepared

3	R ¹	R ²	Reaction time, temperature	Yield ^a [%]	m.p. [°C] ^b (ethanol)	Molecular formula or Lit. m.p. [°C]	¹ H-N.M.R. (CDCl ₃ /TMS _{int}) δ [ppm]	¹³ C-N.M.R. (CDCl ₃ /TMS _{int}) δ [ppm]	
								C-1	C-2
a	H	H	24 h, r.t.	34	125–127°	126–128° ⁷	6.40 (s, 1 H); 6.5–7.5 (m, 10 H); 11.3 (br. s, 1 H)	153.4 (s)	113.9 (d)
b	2-CH ₃	H	24 h, r.t.	37	158–159°	158–159° ⁷	2.40 (s, 3 H); 6.5–7.5 (m, 9 H); 6.70 (s, 1 H); 11.4 (br. s, 1 H)	156.5 (s)	113.7 (d)
c	3-CH ₃	H	24 h, r.t.	38	122–124°	125° ⁸	2.20 (s, 3 H); 6.4–7.5 (m, 9 H); 6.50 (s, 1 H); 11.2 (br. s, 1 H) ^f	155.3 (s)	114.8 (d)
d	4-CH ₃	H	24 h, r.t.	31	112–114°	113–115° ⁷	2.30 (s, 3 H); 6.4–7.5 (m, 9 H); 6.70 (s, 1 H); 11.4 (br. s, 1 H)	155.7 (s)	113.7 (d)
e	2-OCH ₃	H	24 h, r.t.	44	116–118°	C ₁₅ H ₁₄ N ₂ O ₃ ^c (270.3)	3.90 (s, 3 H); 6.3–7.5 (m, 9 H); 6.50 (s, 1 H); 11.2 (br. s, 1 H)	155.1 (s)	111.0 (d)
f	H	CH ₃	36 h, r.t.	48	102–103°	101–103° ^{9,d}	3.20 ^g , 3.40 (2 s, 3 H); 6.50 ^g , 6.60 (2 s, 1 H); 6.9–7.5 (m, 10 H)	144.4 (s) ^g 160.4 (s)	116.3 (d) ^g 122.8 (d)
g	H	C ₂ H ₅	36 h, 60 °C	46	120–122°	72–73° ^{9,d}	1.1 (m, 3 H); 3.5 (m, 2 H); 6.50 ^g (s, 1 H); 6.7–7.5 (m, 10 H) ^h	142.0 (s) ^g 159.9 (s)	115.8 (d) ^g 123.5 (d)
h	H	—CH ₂ —C ₆ H ₅	36 h, 60 °C	37	117–118°	C ₃₁ H ₁₈ N ₂ O ₂ ^c (330.4)	4.70 ^g , 4.90 (2 s, 2 H); 6.70 ^g (s, 1 H); 6.8–7.5 (m, 15 H) ^h	143.8 (s) ^g 160.3 (s)	117.6 (d) ^g 121.9 (d)

^a Based on HgCl₂.

^b Uncorrected.

^c calc. C 66.65 H 5.22 N 10.36
found 66.59 5.26 10.31

^d (*Z*/*E*)-ratio not reported⁹.

^e calc.

C 76.34 H 5.49 N 8.47
found 76.28 5.42 8.55

^f In CCl₄.

^g This value corresponds to the (*E*)-isomer.

^h This multiplet includes a singlet corresponding to the (*Z*)-isomer.

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