SUPPORTING INFORMATION

A Nitro Hunsdiecker Reaction: From Unsaturated carboxylic acids to Nitrostyrenes and Nitro arenes

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CONTENT

General method & Procedure for nitrodecarboxylation.

Table (**S1-S3**).

GC retention times of products.

References, Spectroscopic & Analytical data of products.

General Methods:

All reactions were performed under an inert atmosphere of argon. Substituted α,β -unsaturated carboxylic acids were prepared from the corresponding aldehydes by malonic acid condensation reaction using standard protocol. AIBN (Sigma-Aldrich), N-hydroxyphthalimide (Lancaster), lithium nitrate (E-Merck) and silver nitrate (E-Merck) were used as received. MeCN was distilled over P_2O_5 prior to use. Concentrated HNO_3 was found to be 21.35 M by titrimetric analysis.

All the starting materials were >98% pure vide NMR. Pre-coated silica gel 60F₂₅₄ (Merck) was used for thin layer chromatography and silica gel 100-200 mesh, SRL was used for column chromatography.

Gas chromatographic analysis.

GC analysis was performed on a Chemito-8610 instrument fitted with flame ionization detector using Supelcowax-10 30 m/ 0.25 mm ID, capillary column. The analysis was carried out under isothermal condition using the following temperature settings: column temperature 230 °C, injector temperature 220 °C and detector temperature 250 °C. The yields of the products were estimated from the peak areas based on the internal standard technique.

General procedure for the synthesis of substituted nitrostyrenes.

Concentrated nitric acid (21.35 M, 0.3 mL, 6 mM) was added to a stirred solution of carboxylic acid (2 mM) in 5 mL of MeCN at room temperature, under argon atmosphere. To this reaction mixture catalytic amount of AIBN (7 mg, 2 mol%) was added and the mixture was stirred at 50°C. Upon completion (TLC monitoring) ice-cold water (5 mL) was added and the product was extracted with diethyl ether (4x10 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, concentrated and subjected to column chromatography over silicagel affording nitrostyrenes (**2**, **6**, **8**, **10**, **12**, **14**) in 30-80% yield and nitroarenes (**16**, **18**) in 78 and 40% yield respectively. All the products were confirmed by spectroscopic and GC comparison with authentic samples.

Table S1.

Nitrodecarboxylation of 4-methoxycinnamic acid 1, using nitric acid-cat. AIBN: Effect of nitric acid concentration. GC Yield (%) of 4-methoxy- β -nitrostyrene **2** and 4-methoxybenzaldehyde **2a** at different time interval.^a

HNO₃ Conc.	AIBN (mol%)	15 minute (Yield %)		30 minute (Yield %)		60 minute (Yield %)		120 minute (Yield %)		240 minute (Yield %)		360 minute (Yield %)	
		2	2a	2	2a	2	2a	2	2a	2	2a	2	2a
2eqv.	2%	12	4	20	7	25	10	39	16	45	20	40	22
3eqv.	2%	55	8	62	10	65	12	70	13	75	16	72	17
4eqv.	2%	59	8	66	10	64	12	62	13	61	15	55	17
6eqv.	2%	59	9	68	12	63	14	61	17	50	19	42	22
3eqv.[#]	-	47	7	56	10	60	12	65	13	73	15	66	17
3eqv.[*]	-	18	3	33	6	40	8	45	9	43	9	42	10

^a All the reactions are carried out under nitrogen atmosphere unless otherwise stated. [#] in absence of catalyst

^{*} in absence of catalyst under O₂ atmosphere

Table S2.

Nitrodecarboxylation of 4-methoxycinnamic acid 1, using 3 eqv. of nitric acid: Effect of additives. GC Yield (%) of 4-methoxy- β -nitrostyrene **2** and 4-methoxybenzaldehyde **2a** at different time interval.

Additive	15 minute (Yield %)		30 minute (Yield %)		60 minute (Yield %)		120 minute (Yield %)		240 minute (Yield %)		360 minute (Yield %)	
	2	2a	2	2a	2	2a	2	2a	2	2a	2	2a
No Catalyst	47	7	56	10	60	12	65	13	73	15	66	17
AIBN (2%)	55	8	62	10	65	12	70	13	75	16	72	17
AgNO₃ (10%)	45	7	49	10	52	12	72	14	68	17	65	18
LiNO₃ (10%)	8	3	20	7	32	13	42	17	60	25	60	26
NHPI (10%)	35	6	44	10	50	12	43	13	42	15	40	18
^aNITRONE	34	10	45	14	48	18	49	19	57	25	58	25

^a = N- α -diphenylnitrone

Table S3: G.C. retention time (R_T in minute) of β -nitrostyrenes and nitroarenes

No.	Structure	R_T	No.	Structure	R_T
2		18.77	12		10.53
4		10.58	14		15.59
6		dec.	16		13.32
8		43.68	18		8.73
10		9.08			

β -Nitrostyrenes and Nitroarenes in Table 1:
References, Spectroscopic & Analytical data:

1. **4-methoxy- β -nitrostyrene 2:**
 Lancaster Catalog 2002-3: No. 6685 (page 1172).
2. **4-(2-nitro-propenyl)-anisole 4:**
 Denmark, S. E.; Kesler, B. S.; Moon, Y. C. *J. Org. Chem.* **1992**, 57, 4912.
 Ferreira, A.B.B.; Salisbury, K. *J. Chem. Soc., Perkin Trans. 2*, **1978**, 995.
 Ayoubi, S.A.; Texier-Boullet, F.; Hamelin, J. *Synthesis*, **1994**, 258.
3. **(E)-3,4-methylenedioxy- β -nitrostyrene 6:**
 Revial, G.; Lim, S.; Viossat, B.; Lemoine, P.; Tpmas, A.; Duprat, A. F.; Pfau, M.;
J.Org.Chem. **2000**, 65, 4593.
 Menicagli, R.; Samaritani, S.; *Tetrahedron* **1996**, 52, 1425.
 Marsden, R.; MacLean, D. B.; *Can. J. Chem.* **1984**, 62, 1392.
4. **3,4,5-trimethoxy- β -nitrostyrene 8:**
¹H NMR (CDCl₃) δ : 3.91 (s, 6H), 3.92 (s, 3H), 6.76 (s, 2H), 7.53 (d, 1H, J = 13.6 Hz),
 7.94 (d, 1H, J = 13.6 Hz). ¹³C δ : 56.28, 61.01, 106.51, 125.28, 136.37, 139.27, 141.83,
 153.69. Anal. Calcd. for C₁₁H₁₃NO₅: C, 55.23; H, 5.48; Found: C, 55.84; H, 5.29.
5. **β -Nitrostyrene 10:**
 Lancaster Catalog 2002-3: No. 14367 (page 1348).
6. **1-(2-nitrovinyl)-naphthalene 12:**
¹H NMR (CDCl₃) δ : 6.57 (d, 1H, J= 15.8 Hz), 7.20 (d, 1H, J= 8.0 Hz), 7.4-8.0 (m, 5H),
 8.22 (d, 1H, J= 7.6 Hz), 8.63 (d, 1H, J= 15.8 Hz). Anal. Calcd. for C₁₂H₉NO₂: C, 72.35;
 H, 4.55; Found: C, 72.66; H, 4.21.
7. **α -Nitro-trans-stilbene 14:**
 Blake, K. W.; Jaques, B. *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1660.
 Yamamura, K.; Watarai, S.; Kinugasa, T. *Tetrahedron Lett.* **1972**, 2829.
8. **1,2,3-trimethoxy-5-nitro-benzene 16:**
 Tepe, J. J.; Madalengoitia, J. S.; Slunt, K. M.; Werbovetz, K. W.; Spoors, P. G.;
 Macdonald, T. L. *J. Med. Chem.* **1996**, 39, 2188.
9. **4-nitroanisole 18:**
 Lancaster Catalog 2002-3: No. 3588 (page 1321).