A New and Convenient Method for the Synthesis of α,β-Unsaturated Aldehydes

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A new and convenient synthetic method for α,β-unsaturated aldehydes from the corresponding nitro compounds is described.

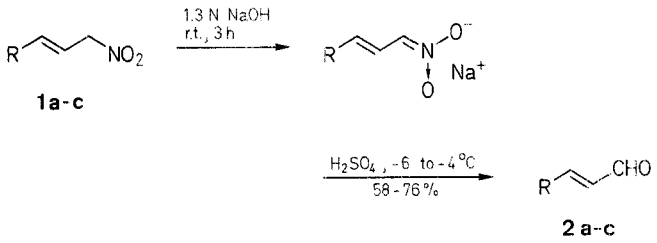
Several methods are available for the synthesis of α,β-unsaturated aldehydes. The most important methods were reviewed by Brettle in 1979.[1] In recent years, various new synthetic methods have been described.[2-30] However, most of the described methods have some limitations mainly due to the use of too drastic reaction conditions.

In the present work we describe a new and convenient synthetic method to obtain α,β-unsaturated aldehydes **2** by way of the salt formation and acid hydrolysis of the corresponding nitrocompounds **1**. This is a new extension of the Nef reaction[31] to form α,β-unsaturated aldehydes.

Table. α,β-Unsaturated Aldehydes **2** Prepared

Substrate[a]	Product	Yield (%)	b.p. (°C)/torr		2,4-Dinitrophenylhydrazone		IR (KBr) ν (cm^{-1})[b]
			found	reported[33]	m.p. (°C)		
					found	reported[33]	
1a	**2a**	76	50–52/760	52/760	163–165	165	3320, 3090, 3010, 1650, 1640, 1410, 970, 915[c]
1b	**2b**	68	103/760	102.2/760	196	196–197	3280, 3020, 1650, 1615, 1370, 1300, 960[c]
1c	**2c**	58	80–82/30	56–59/9.5	296–299[d]	300[d]	3290, 3040, 1655, 1635, 1310, 960[d,e]

[a] Prepared according to Ref. 32.
[b] Only main bands are reported.
[c] Identical with an authentic spectrum.[34]
[d] Di-(2,4-dinitrophenylhydrazone).
[e] Identical with an authentic spectrum.[35]



1	R	2	R
a	H	a	H
b	CH_3	b	CH_3
c	CH_2NO_2	c	CHO

The above method has the advantage of mild reaction condition, simple work up procedure and high yield, and thus compares favorably with known methods. Our results are summarized in the Table.

Acrolein (2a); Typical Procedure:
3-Nitro-1-propene (**1a**; 8.7 g, 0.1 mol) is dissolved in 1.3 normal aqueous sodium hydroxide solution (100 ml) and the mixture is vigorously stirred with a mechanical stirrer at room temperature for 3 h. The organic layer is separated by extracting with ether (3 × 20 ml) and the yellow aqueous solution is added dropwise to a stirred ice cold 6 normal sulfuric acid solution (100 ml). The stirring is continued at −6 to −4 °C for 1 h. The mixture is then distilled to give acrolein (**2a**); yield: 4.3 g (76%), which is collected in a dark bottle containing hydroquinone (about 0.3 g) to act as stabilizer for **2a** (Table).

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