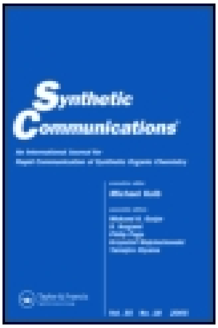

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Direct Synthesis of α,β-Unsaturated Nitriles in Solid/Liquid Heterogeneous Medium

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DIRECT SYNTHESIS OF α,β-UNSATURATED NITRILES IN SOLID/LIQUID HETEROGENEOUS MEDIUM

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ABSTRACT

α,β-unsaturated nitriles are obtained with high yields by condensation of diversely substituted aldehydes using nitriles in the presence of K_2CO_3. These basic active species avoids aldolisation generally observed in this type of reaction.

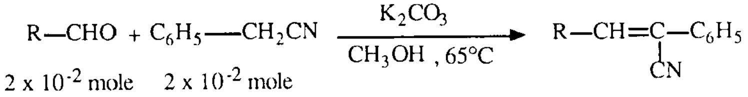
The economic interest for α,β-unsaturated nitriles explains why numerous works deal with their production (1-3). The condensation of a carbonyl function is, of various synthetic methods the most commonly used for it is efficient and easy to use. This procedure carried out in homogeneous (2,4-9) or liquid-liquid (10) or solid-liquid (11-14) heterogeneous medium is generally used for the conversion of aromatic carbonyl compounds into α,β-unsaturated nitriles. This technique being applied to aliphatic aldehydes reacts differently since aldolisation preponderates in the presence of basic species generally used under these operating conditions. α,β-unsaturated nitriles are generally obtained from aliphatic aldehydes by the Wittig-Horner reaction (15).

A direct and novel synthetic method using solid/liquid biphasic medium being applicable to the synthesis of α,β-unsaturated nitriles from both aromatic and aliphatic aldehydes is reported here (Table 1).

Modulation of acido-basic interactions resulting from K_2CO_3 (16-18) makes it possible to selectively tear the α carbon-bearing proton from the nitrile function with no interaction on aldehyde protons. This advantage leads to high yields of corresponding α,β-unsaturated nitriles by inhibiting aldolization.

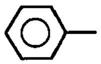
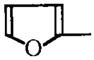
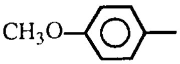
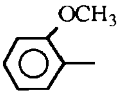
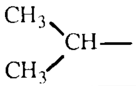
Concerning aromatic aldehydes, the lacking reactivity of carbonate ions towards the carbonyl function inhibits the Cannizzaro reaction resulting in lower yields also observed in the presence of KOH in solid-liquid biphasic medium (12-14).

TABLE I: α,β-unsaturated nitriles from aldehydes and phenyl acetonitrile



$$R{-}CHO + C_6H_5{-}CH_2CN \xrightarrow[CH_3OH\ ,\ 65°C]{K_2CO_3} R{-}CH{=}\underset{CN}{\underset{|}{C}}{-}C_6H_5$$

2×10^{-2} mole 2×10^{-2} mole

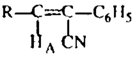
R	Time (hours)	Yield (%)
	0,15	95
	0,05	95
	0,5	90
	0,7	90
C_2H_5 –	1	70
C_3H_7–	3	70
	4	80

This easy procedure involving reactives in solution in the solvent and potassium carbonate in the solid state, offers an efficient accessibility for α,β-unsaturated nitriles from aldehydes with different reactivities such as aromatic and aliphatic aldehydes.

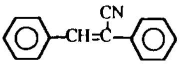
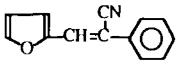
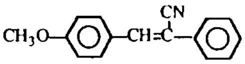
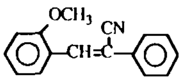
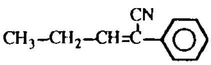
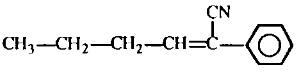
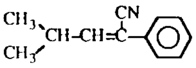
GENERAL PROCEDURE

The apparatus was a 100 ml flask, fitted with a mechanical stirrer, a thermometer and a reflux condenser. A mixture of phenylacetonitrile (0.02 mol), potassium hydroxide (3g), 20 ml of methanol as solvent and aldehyde (0.02 mol) was shaken at 65°C for the various times given in Table I. After completion of the reaction, the mixture was filtrated and the solvent evaporated under reduced pressure. The residue was easily purified by chromatography on a short and broad column of silica gel 60 Merck using hexane/ether (1:1) as eluent. Physico-chemical characteristics of the various α,β-unsaturated nitriles obtained are reported in Table II.

TABLEAU II : IR and RMN data



$R-C(H_A)=C(CN)-C_6H_5$

Products	Molecular formula	Elementary analysis found % calc %				ν C≡N cm⁻¹	δ (A) ppm
		C	H	N	O		
	$C_{15}H_{11}N$	87,75 (87,80)	5,39 (5,36)	6,86 (6,84)	- -	2210	-
	$C_{13}H_9ON$	80,10 (80,00)	4,60 (4,62)	7,14 (7,17)	8,16 (8,21)	2205	7,28*
	$C_{16}H_{13}ON$	81,75 (81,70)	5,50 (5,53)	5,95 (5,96)	6,80 (6,81)	2207	-
	$C_{13}H_{13}ON$	81,75 (81,70)	5,50 (5,53)	5,95 (5,96)	6,80 (6,81)	2208	-
	$C_{11}H_{11}N$	84,10 (84,07)	7,00 (7,01)	8,90 (8,92)	- -	2208	6,77**
	$C_{12}H_{13}N$	84,15 (84,21)	7,62 (7,60)	8,22 (8,19)	- -	2206	6,75**
	$C_{12}H_{13}N$	84,15 (84,21)	7,62 (7,60)	8,22 (8,19)	- -	2207	6,62***

* a singulet. ** a triplet. *** a doublet.

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