DIRECT SYNTHESIS OF α,β-UNSATURATED NITRILES OR IMINOCOUMARIN FROM PHENOL ALDEHYDES

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RÉSUMÉ : Les aldéhydes phénoliques sont transformés en une seule étape - par condensation avec un nitrile en milieu basique-en nitrile α, β - insaturés correspondant. L'instabilité du composé obtenu à partir de l'aldéhyde salicylique est à l'origine de son évolution vers la formation d'iminocoumarine.

ABSTRACT : Phenol aldehydes are transformed in a single step -by condensation with a nitrile in basic conditions- into corresponding α, β-unsaturated nitriles. The instability of the compound obtained from salicylaldehyde leads to the formation of iminocoumarin.

Due to their insecticide (1), microbicide (2), or pesticide (3) properties, α, β-Unsaturated nitriles are used in several industries. Some nitriles are incorporated into the formulation of perfumes (4,5) because of their olfactive properties.

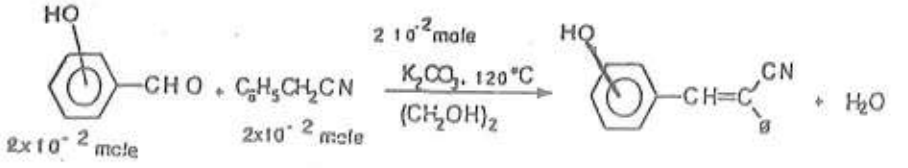
Since the obtention of this kind of compounds from phenol aldehydes involves a delicate process (6), we applied the operating protocol which proved to be very effective for the synthesis of various α, β-unsaturated nitriles (7).

The first results achieved during our preliminary trials compelled us to conduct a systematic study of the different parameters affecting the course of the reaction (8).
From this study, we concluded that a high thermic input allowed the transformation of phenol aldehydes into corresponding α, β-unsaturated nitriles with satisfactory yields

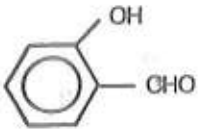
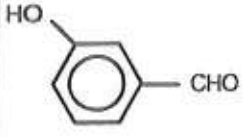
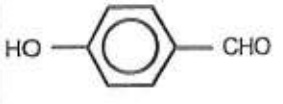
An analysis of the results reported in Table I shows that the yield of nitrile obtained from 3-hydroxybenzaldehyde rises from 10 % when the reaction is performed at 80°C to 70% when the reaction medium is heated to 120°C. This specific behavior is due to the presence of the phenol function and was also observed during the synthesis of vinylphenols using the reaction of Wittig (9).

It is also interesting to note that the position of the hydroxyl function in the aromatic cycle plays a fundamental role on the evolution of the reaction. In position 3, the hydroxyl function exhibits less electrodonating effect, allowing the reaction to evolve more favorably (70 % yield) than when it is in position 4 (50 % yield). The salicylaldehyde for which the hydroxyl function is in position 2, leads to the formation of the expected α, β-unsaturated nitrile. However, because of its structure, the α, β-unsaturated nitrile is unstable and thus evolves by intramolecular rearrangement to form iminocoumarin

Table I : α, β-unsaturated nitriles from phenoliques aldehydes and phenylacetonitrile



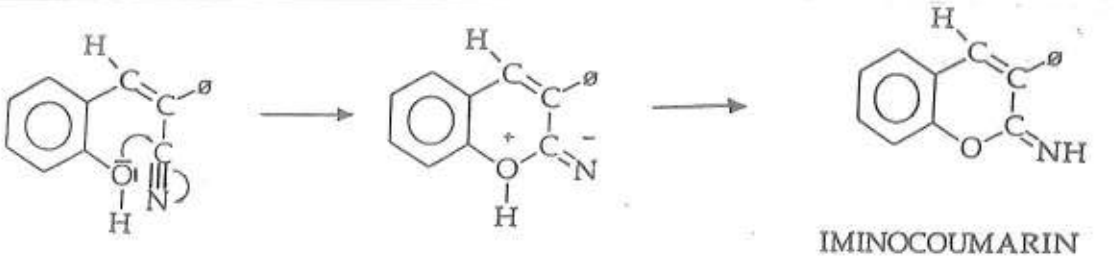
1, 2, 3 a 1a, 2a, 3a

Aldehyde	Température (°C)	Yield (%)
 1	120	(85)*
 2	80	10
	120	70
 3	120	50

* the instability of the α, β-unsaturated nitrile leads to the formation of iminocoumarin obtained with an 85 % yield.

Table II : RMN ^{13}C and IR data

Products	Molecular formula	Elementary analysis found (cal %)				$\nu C\equiv N$ (cm^{-1})	$\nu C=NH$ (cm^{-1})	δ-CH=C (ppm)	δ-C≡N (ppm)
		C	H	O	N				
1a	$C_{15}H_{11}ON$	81,47 (81,45)	4,95 (4,98)	7,28 (7.24)	6,30 (6,33)	-	1670	139,9	-
2a	$C_{15}H_{11}ON$	81,40 (81,45)	4,99 (4,98)	7,26 (7.24)	6,35 (6,33)	2220	-	142,1	115,1
3a	$C_{15}H_{11}ON$	81,50 (81,45)	4,96 (4,98)	7,22 (7.24)	6,32 (6,33)	2220	-	129,8	119,1



IMINOCOUMARIN

The absence of α, β-unsaturated nitrile at the end of the reaction shows that, for steric reasons, the intermediary α, β-unsaturated nitrile was present as a Z configuration. This geometric shape is the only one allowing the subsequent transformation of the α, β-unsaturated nitrile into iminocoumarin.

A similar evolution was observed by FOUCAUD (10) during synthesis of 4-H-chromene obtained by condensation of malonitrile with salicylaldehyde in basic conditions.

This procedure leading to the formation of iminocoumarin is all the more interesting that it is economical and easy to implement. Moreover, its hydrolysis allows the formation of coumarin, which is a compound with biological interest (11).

EXPERIMENTAL

- IR spectra were run in a $CHCl_3$ in a PERKIN-ELMER 177 spectrometer.

- Carbon ^{13} NMR Spectra were determined at ambient temperature with a BRUKER-WP 60 Spectrometer using $CDCl_3$ containing TMS as an internal standard.

- Elementary analysis were realized in the Elemental Analysis Center of Paul Sabatier University of Toulouse, France.

SYNTHESES OF α, β-UNSATURATED NITRILES

The reaction is performed in a 250 ml reactor equipped with a cooler, a mechanical stirrer and a thermometer.

We introduce into the reactor : 0,02 mole of phenylacetonitrile, 0,02 mole potassium carbonate and 50 ml ethylene glycol.

The mixture is stirred for 20 mn at the temperature indicated in table I. 0.02 mole of phenolaldehyde is added and the mixture is stirred for 3.5 hours.

At the end of the reaction, the reaction medium is cooled and decanted in a beaker containing 200 g of ice. A 1 N hydrochloric acid solution is added until neutral pH is obtained.

The product of the reaction is extracted with ether (3 x 50 ml). The organic phase is dried with anydrous Na_2SO_4 and evaporated. The residue is purified by silica gel

chromatography (hexane ether 3 : 1 as eluent), and gives the corresponding α, β-unsaturated nitrile. In the case of salicylaldehyde, the expected α, β-unsaturated nitrile transforms into iminocoumarin. The subsequent hydrolysis in an acid medium gives coumarin. The physicochemical characteristics of the various products obtained are reported in table II.

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