

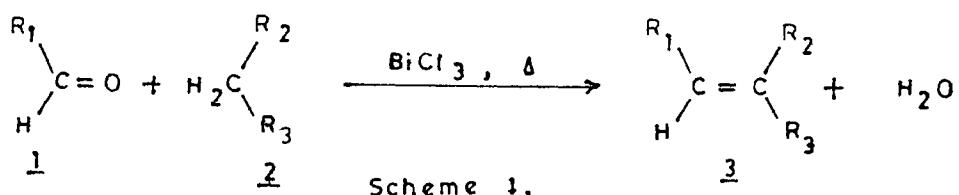
Bismuth(III)chloride as a New Catalyst for Knoevenagel Condensation  
in the Absence of Solvent

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The Knoevenagel condensation of various aldehydes was carried out under heterogenous catalysts conditions using bismuth(III)chloride in absence of solvent. The method gives high yields of Knoevenagel products.

Knoevenagel condensation is one of the important reactions of organic chemistry<sup>1)</sup> and its synthetic utility has special place of significance in organic synthesis. The reaction<sup>2)</sup> is usually catalysed by organic bases like primary, secondary, tertiary amines, ammonia and ammonium salts.<sup>1,3)</sup> In recent years efforts have been made in search of new catalysts of this reaction and subsequently use of silica gel functionalised with amine groups,<sup>4)</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>5)</sup> AlPO<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub>,<sup>6)</sup> TiCl<sub>4</sub>/base,<sup>7)</sup> and dopped xonontlite<sup>8)</sup> have been reported. Here we wish to disclose the use of a new catalyst, bismuth trichloride for Knoevenagel condensation in heterogenous phase and in the absence of solvents. It can perform the reaction to produce the olefinic products in good purity and high yields. The results obtained with different aliphatic, aromatic and heterocyclic aldehydes and different active methylene compounds, according to Scheme 1 are recorded in Table 1.



The aromatic  $\alpha,\beta$ -unsaturated aldehydes gave the corresponding olefinic Knoevenagel products and there was no evidence for the formation of Michael type addition products. Thus for example, the reaction of cinnamaldehyde with malononitrile led to 1,1-dicyano-4-phenyl-1,3-butadiene in 72% conversion after 20 min of reaction (entry 3b). When the same reaction was repeated in refluxing benzene it required longer period (approximately 15 h) and gave poor yields of 3b.

A typical procedure is as follows: To a mixture of the carbonyl compound 1a (1.06 g, 10 mmol) and active methylene compound 2a (0.66 g, 10 mmol) was added bismuth trichloride<sup>9)</sup> (0.32 g 1 mmol) at room temperature. After stirring for 5 min, the resulting mixture was heated at 80 °C for 15 min just to initiate the reaction. The reaction was then cooled to room temperature until solidifies. The solid material was treated with a solution of 1% aqueous alcohol. It was filtered, dried and chromatographed using benzene-hexane (9:1) to obtain 3a (1.14 g, 75%) in good purity.

In conclusion, the present investigation offers a convenient method for the stereospecific preparation of E olefins, wherein work-up is easier reaction condition is simple, and afford pure products in high yields.

Table 1. Knoevenagel products.<sup>10)</sup>

Entry	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Reaction time/min	Yield of <u>3</u> %	Mp/°C of <u>3</u>
a	Ph	CN	CN	20	75	82
b	Ph-CH=CH-(E)	CN	CN	20	72	127
c		CN	CN	25	78	72
d	Ph	COOEt	CN	30	75	50
e	Ph-CH=CH-(E)	COOEt	CN	20	75	116
f	Ph	COOH	CN	30	73	179
g	Ph-CH=CH-(E)	COOH	CN	15	72	210
h	Ph	CONH <sub>2</sub>	CN	25	70	121
i	Ph-CH=CH-(E)	CONH <sub>2</sub>	CN	25	71	142
j	Ph	COOEt	COOEt	30	75	oil
k	Ph	MeCO	COOEt	30	70	oil
l	Me	CN	CN	25	71	77
m	Me	CN	COOEt	25	65	oil
n	Et	CN	COOEt	30	70	oil

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- 10) The products were identified by comparison of mp/bp and spectral data with standard samples.

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