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GEL ENTRAPPED BASE CATALYSED (GEBC) HENRY REACTION : SYNTHESIS OF CONJUGATED NITROALKENES

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ABSTRACT : A new, simple and practical procedure for direct transformation of aldehydes or ketones and nitromethane into conjugated nitroalkenes by using novel gel entrapped base catalyst (GEBC) has been described.

Nitroalkenes were found to be important because of their biological activities such as insecticidal,[1,2] fungicidal,[2-5] bactericidal[6,7] rodentrepellent[8] and antitumor agents[9] and pharmocologically valuable substances.[6-9] They have proved to be valuable precursors to a wide variety of target molecules. The utility of nitroalkenes in organic synthesis is largely due to their ease of conversion into a variety of functionalities.[10, 11] Alternatively they are powerful dienophiles in Diels-Alder reactions and readily undergo addition reactions with many different nucleophiles.[11] A few nitroalkenes also occur in nature.[12]

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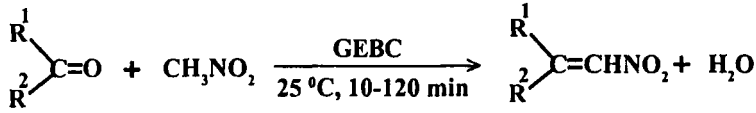
The most versatile and classical preparation of nitroalkenes involves the Henry condensation reaction followed by dehydration of the resultant β-nitro alcohols.[13] For this purpose several reagents have been used.[14-15] Recently nitroalkenes have been synthesized using Envirocat[16] EPZG[R] and microwaves[17] under drastic conditions. The significance of nitroalkenes and applications of heterogenous catalysts in organic synthesis, prompted us to investigate the Henry reaction.

We wish to report herein rapid synthesis of conjugated nitroalkenes using gel entrapped base catalyst (GEBC) under very mild condition. 20% Agar-agar aqua gel containg 10% KOH forms a solid hard agar-agar gel which serves as a GEBC to catalyse the Henry reaction. The GEBC does not absorb moisture and may be reused.



Scheme

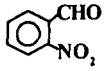
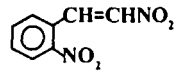
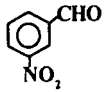
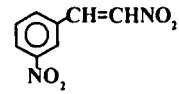
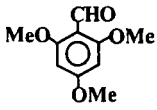
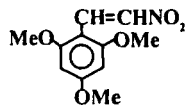
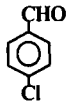
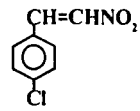
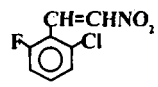
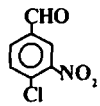
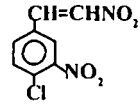
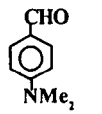
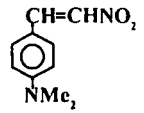
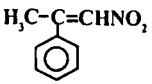
This method is useful for rapid synthesis of conjugated nitroalkenes under mild condition. Isolation of pure products in excellent yields by simple filtratioin and evaporation is important feature of this method.

Experimental : IR spectra were recorded on Bomem MB 104 FTIR spectrometer whereas ^{1}H NMR and ^{13}C NMR were recorded on 90 MHz instrument. GEBC was prepared using reported procedure.[18]

General Procedure for the Synthesis of Conjugated Nitroalkenes :

A mixture of aldehyde/ketone (5 mmol) and GEBC (1 g) in acetonitrile / ethanol (10 ml) was stirred at room temperature for specified time (Table). After

Table : Synthesis of conjugated nitroalkenes by using GEBC at 25 °C

Sr. No.	Aldehyde/Ketone	Product	Reaction time (min)	Yield[a,b](%)
1			10	96
2			10	94
3			120	83
4			120	70
5			30	83
6			10	84
7			30	61
8			15	40
9			15	56
10			120	70

a . Isolated yields of the products b. Products were characterised by IR, ^{1}H NMR and comparison with authentic samples.

completion of the reaction (TLC), GEBC was filtered off and washed with ether (3 x 10ml). Removal of the solvent under reduced pressure gave conjugated nitroalkene in almost pure form and excellent yield.

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