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Aliquat 366: An Efficient Catalyst For Knoevenagel Condensation Under Solvent- Free Condition

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Abstract:

Aliquat 366 phase transfer catalyst has been utilized as a novel and efficient catalyst for the Knoevenagel condensation of aldehydes with active methylene compounds such as ethyl cyanoacetate, cyanoacetamide and malononitrile to afford substituted olefins. The reaction proceeds smoothly under mild and solvent-free conditions at room temperature and the products are obtained in excellent yields.

Keywords: Aliquat 366, Knoevenagel condensation, Grinding.

Introduction:

In recent years, solid-state organic reactions have caused great interests, which have many advantages such as high efficiency and selectivity, easy separation and purification, mild reaction conditions, and benefit to industry as well as environment. Organic synthesis in the absence of solvent is a powerful tool for the generation of structurally diverse molecules, due to their special selectivity, the ease of set-up and work-up, arousing great interest [1-3]. Moreover, solvent- free reactions sometimes are faster, taking just a few minutes rather than hours to complete, because the reactants are close contact with each other. This aspect, coupled with the lower overall costs of running a reaction without solvent and no specially needed equipment, could become a decisive factor.

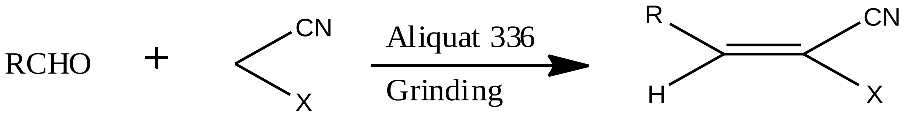
Knoevenagel condensation reactions have been extensively studied as an important carbon-carbon bond forming reaction. This condensation, various catalyst are used such as Te(IV)Cl_4 [3], Ammonium acetate [4], $ZnCl_2$ [5], KSF-montmorillonite [6], KF-Al_2O_3 [7], Ethylenediammonium diacetate [8], CaO [9], Mg-Al-*t*-Bu-Hydrotalcite [10], Phosphene [11], ionic liquid [bmim][BF_4] [12], PEG400 and anhydrous K_2CO_3 [13]. In recent years, chemists paid more and more attention to the clean synthesis of alkenes by condensation reactions.

Therefore, the introduction of efficient and new methods based on green methodology is still indemand.In continuation of our ongoing research to develop newer, environmentally benign methods Aliquat 336 is used as efficient catalyst for the Knoevenagel condensation of aldehydes with active methylene compounds such as ethyl cyanoacetate, cyanoacetamide and malononitrile to afford substituted olefins. Aliquat 336 is a water insoluble quaternary ammonium salt made by the methylation of tri octyl/decyl amine, which is capable of forming oil soluble salts of anionic species at neutral or slightly alkaline pH. Aliquat 336 is a versatile and affordable cation source for an entirely new family of hydrophobic ionic liquids [14]. It can form salts with anions over a wider pH range than primary, secondary or tertiary amines. For this reason Aliquat 336 finds application in environments from acid to slightly alkaline pH. It is used as a phase transfer catalyst [15].

Results and Discussion:

To investigate the role of catalyst and effect of grinding, first the reaction of p-chlorobenzaldehyde, ethylcyanoacetate and catalytic amount of aliquat 336 are ground together in mortar and pestle at room temperature, the reaction start immediately usually with gentle heat production, the reaction mixture turned in to brownish viscous liquid then to thick brownish mass and finally to free flowing powder. Surprisingly, reaction mixture turned into the desired product with in a short period.

On the other hand, indication of softening for some seconds followed by immediate hardening were visually observed only in syntheses with P-chlorobenzaldehyde with malanonitrile (**entry 3r**). Subsequently, the scope of the Knoevenagel condensation of other aldehydes with various active methylene compounds catalyzed by Aliquat 336 scheme-1 in grinding was investigated. We found that the Knoevenagel condensation of aldehydes with malanonitrile occurred easily in the presence of grinding to form corresponding products.. Both electron-rich and electron-deficient aldehydes worked well to give the corresponding arylidene derivatives in excellent yields (3a-s) in **Table-1**. The results are summarized in table 1. Miscibility of Aliquat 336 with water makes the workup process quite easy as the catalyst can be easily removed from product simply by washing the product with water.



X= -$COOC_2H$
-$CONH_2$
-CN

Scheme-1: Knoevenagel condensation using Aliquat 336 catalyst

Table 1: Aliquat 336 catalyzed Knoevenagel condensation under solvent-free condition

Entry[a]	-R	-X	Time	Yield[b] (%)	Melting point (^oC)
3a	C_6H_5	$COOC_2H_5$	3 min.	92	52
3b	4-ClC_6H_4	$COOC_2H_5$	2 min.	96	163
3b	4-ClC_6H_4	$COOC_2H_5$	10 min	89	163
3c	2-$CH_3OC_6H_4$	$COOC_2H_5$	5 min.	92	69
3d	4-$H_3COC_6H_4$	$COOC_2H_5$	3 min.	93	99
3e	4-OHC_6H_4	$COOC_2H_5$	5 min.	90	171
3f	4-$NO_2C_6H_4$	$COOC_2H_5$	4 min.	95	171
3g	C_6H_5-CH=CH-	$COOC_2H_5$	3 min.	92	114
3h	Vanillin	$COOC_2H_5$	5 min.	94	112
3i	2-furyl	$COOC_2H_5$	3 min.	96	84
3j	C_6H_5	$CONH_2$	2 min.	92	120
3k	4-ClC_6H_4	$CONH_2$	2 min.	93	210
3l	3-$CH_3OC_6H_4$	$CONH_2$	3 min.	95	204
3m	4-$CH_3OC_6H_4$	$CONH_2$	3 min.	94	215
3n	Vanillin	$CONH_2$	3 min.	93	206
3o	4-$NO_2C_6H_4$	CN	3 min.	95	84
3p	4-$CH_3OC_6H_4$	CN	2 min.	94	80
3q	3-$CH_3OC_6H_4$	CN	1 min.	94	92
3r	4-ClC_6H_4	CN	2 min.	93	165
3s	2-furyl	CN	2 min.	95	64

[a] All the products are characterized by MP, IR and ^{1}H NMR
[b] isolated yields after recrystallized

Experimental section:

Melting points were determined in opencapillary tubes and are uncorrected. The purity of compounds was checked by Merck silica gel TLC plates, and the spots were detected by UV light absorption. The IR spectra were recorded in matrix of KBr with Perkin-Elimer spectrometer. ^{1}H NMR spectra were recorded on Varian NMR Spectrometer, Model Mercury Plus (400MHz) and the chemical shifts (δ) are given in ppm relative to signal for TMS as an internal standard. All the products were identified by comparison of analytical data (melting point, IR and ^{1}H NMR.) with those reported of authentic samples.

General procedure:

An equimolar quantity of the aldehydes (1 mmol), and active methylene compounds (1 mmol) mixed thoroughly and then 0.1 mmol of Aliquat 336 was added. The reaction mixture was ground in the mortar and pastel for 30 sec.to 5 min. at appropriate time mentioned in table 1. The reaction was monitored by TLC, on completion of reaction; the reaction mixture was treated with cold water. The product was filtered, dried, and the crude compounds were recrystallized from a mixture of ethanol and water to get the desired compound in pure form (3a-s).

Conclusion:

This new method is superior to the reported methods [5,9,10] with respect to the reaction time and simplicity of the procedure. The attractive features of this procedure are the mild and solvent-free reaction conditions, high conversions, cleaner reaction profiles and operational simplicity, all of which make it a useful and attractive strategy for the preparation of arylidene derivatives.

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