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Synthesis of 5-Arylidene-2, 4-thiazolidinediones by Knoevenagel Condensation Using Tannic Acid as Catalyst

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ABSTRACT

The synthetic work has been carried out by simple Knoevenagel condensation reaction between various substituted aromatic aldehydes and active methylene compound (Thiazolidine-2,4-dione) using tannic acid as an efficient catalyst in ethanol solvent under reflux condition.

Keywords: Tannic Acid; Thiazolidine-2,4-diones; 5-Arylidene-2,4-Thiazolidinediones, Knoevenagel condensation

I. INTRODUCTION

Tannic acid catalyzed Knoevenagel condensation of aromatic aldehydes and active methylene compounds (Thiazolidine-2,4-diones) has been performed. Knoevenagel condensation is multi-components reactions resulting in the formation of new C–C bonds. The reaction is applicable for the synthesis of substituted alkenes, α, β-unsaturated nitriles, esters, acids, dyes and polymers..[1-4]

The condensation of 2,4-thiazolidinediones with aldehydes has been a subject of considerable interest. The products 5-arylidene-2,4-thiazolidinediones are important structural elements in medicinal chemistry and are found to possess significant hypoglycemic,[5] anti-inflammatory,[6] antitumor,[7] antifungal, [8] antidiabetic, [9] and antimicrobial [10]activities.

There are several methods reported in the literature for the synthesis of benzylidenethiazolidine-2, 4-dione derivatives such as, baker's yeast,[11] piperidine in ethanol under reflux conditions [12], piperidinium acetate in DMF under microwave irradiation, [13] grinding with ammonium acetate in the absence of solvents, [14] sodium acetate in acetic acid under microwave irradiation [15] , KAl(SO4)2·12H2O in H2O at 90 C, [16] polyethylene glycol-300 at 100–120°C, [17] L-proline,[18] thiourea,[19] sodium acetate in acetic acid under reflux conditions [20] hydrochloric acid,[21] glycine/solvent free condition under microwave irradiation, [22] (DABCO) in aqueous media, [23] ethylenediamine diacetate, [24] catalyst free/water as green solvent under

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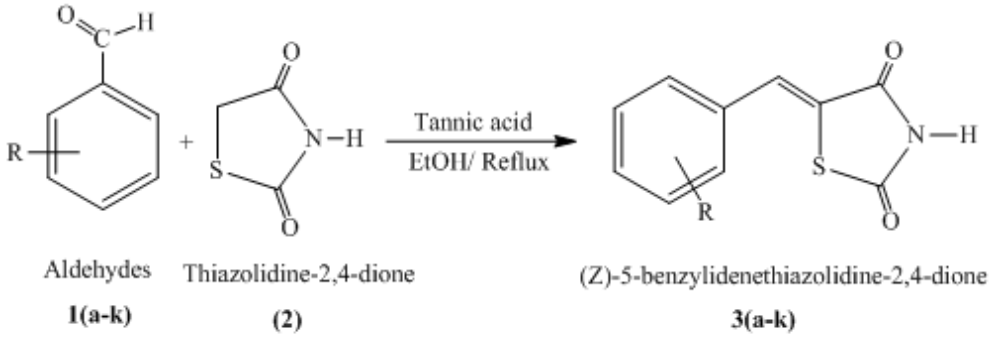
microwave irradiation, [25] L-tyrosine/water [26] acidic ionic liquid,[27] calcium hydroxide, [28] tungstic acid, [29].

However, most of the reported methodologies still have certain limitations such as expensive catalysts, toxicity of solvents, restrictions for large scale applications, critical product isolation procedures, difficulty in recovery of high boiling solvents, excessive amounts of catalysts. Thus, the development of a simple and efficient method for the synthesis of 5-arylidene-2,4-thiazolidinediones derivatives would be highly desirable.



Scheme 1. Synthesis of substituted Benzylidenethiazolidine-2,4-dione derivatives.

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II. RESULTS AND DISCUSSION

During optimization of reaction conditions and solvent, it is obtained that reaction is not taking place at room temperature and not even at 50ºC while at 100ºC in ethanol reaction is faster and completed in less time as compared to other solvents such as water, DMF, DMSO, and mixture of ethanol : water.

Table1: Optimization of different solvents for the synthesis of 3c model product.

Entry	Solvent	Time (Hrs)	Yield (%)
1	EtOH	11	70
2	EtOH:H2O	30	60
3	Water	22	55
4	DMF	20	62
5	DMSO	19	62
6	Solvent less	25	64

Table 2: Tannic acid catalyzed synthesis of 5-arylidiene-2,4-thiazolidinediones derivatives in ethanol

Entry	Product	Aldehyde	Time (Hours)	Yield(%)	M.P (ºC)	M.P Lit. (ºC)
1	3a	C_6H_5-	32	76	237	240-241[26]
2	3b	2-(Cl)C_6H_4-	30	72	208	210-212[29]
3	3c	4-(Cl)C_6H_4-	27	70	110	109[23]
4	3d	3-(NO2)C6H4-	31	74	184	186-188[26]

5	3e	4-(NO2)C6H4-	33	70	180	182-183[26]
6	3f	3-(OH)C_6H_4-	28	68	116	118-120[23]
7	3g	4-(OH)C_6H_4-	20	59	114	111-113[23
8	3h	4-(OCH3)C6H4-	21	61	236	235-237[26]
9	3i	Furan-2-CHO	22	69	238	240-242[29]
10	3j	Thiophene-2-CHO	21	68	223	-
11	3k	Pyridine-3-CHO	25	71	216	-

III. EXPERIMENTAL

All the chemicals used were obtained from commercial suppliers and used without further purification. Progress of the reaction was monitored by thin layer chromatography in ethyl acetate and n-hexane (3:7) mobile phase. Melting points were recorded on open capillary method and were uncorrected.

3.1. General procedure for the synthesis of Benzylidenethiazolidine-2,4-dione derivatives:

A mixture of substituted aromatic aldehydes (1mmol), active methylene compound (Thiazolidine-2,4-dione) (1mmol) and ethanol (10 ml) was stirred at reflux temperature in the presence of tannic acid catalyst for a given specific time. The progress of reaction was monitored by TLC. After completion of reaction the reaction mixture was cooled to room temperature and ice cold water is added to it. The solid product was filtered, washed with cold water and recrystallized from ethanol to obtain pure Benzylidenethiazolidine2,4-dione derivatives.

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