JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Water mediated Potassium carbonate catalyzed by Knoevenagel condensation

Kiran F. Shelke
.Department of Chemistry, Late Pushpadevi Patil Arts and Science College, Risod, Dist. Washim-444 506 (MS), India

Abstract

The gentle synthesis of 2,2-dimethyl-5- [(4-oxo-4*H*-chromen-3-yl) methylene]-1,3-dioxane-4,6-diones by Knoevenagel condensation of 4-oxo-4*H*-benzopyran-3-carbaldehydes with Meldrum's acid in water mediated at room temperature with potassium carbonate (K_2CO_3) present as a catalyst is reported. Notable benefits of this approach include a straightforward process, environmentally friendly conditions, and decent to exceptional product yields.

Keywords Knoevenagel reaction; potassium carbonate; aldehyde; Meldrum's acid.

Introduction

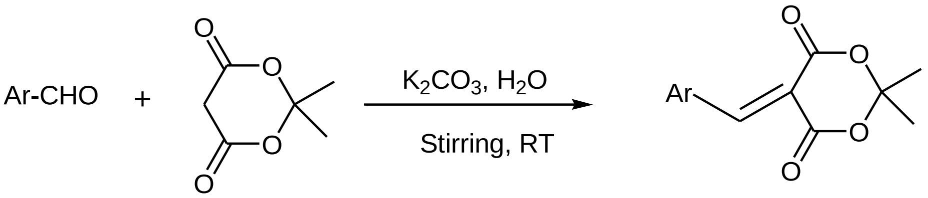
One of the most crucial techniques for creating substituted alkenes through the reaction of carbonyl compounds with active methylene compounds is the Knoevenagel condensation [1a]. Carbon-Carbon bonds formation reduction are important derivation in perfume, pharmaceutical, polymer applications [1b].

Due to growing public awareness of environmental risks, environmentally friendly solvents such as water and solvent-free processes have gained widespread use. Use of the green chemical technologies have many advantages such as low cost, reduced pollution, enhanced rate of reaction and simple work-up procedure. The amount of catalyst and the substitution of volatile organic solvents from the reaction medium are the two most crucial elements of green chemistry among its many other components [2].

Previously, the use of K_2CO_3 in the synthesis of many biologically important molecules like 5-aryl-2,6-dicyano-3-methylanilines [3a], Knoevenagel condensation [3b].

The active methylene molecule Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) hydrolyzes readily. [4]. Recently, there have been several methods reported in the literature for the Knoevenagel condensation of aldehydes with Meldrum's acid [5].

Synthetically useful molecules with a reactive carbonyl group are compounds containing a chromone moiety. Their biological actions provide them significant importance [6] and for their reactivity towards nucleophiles, which allow the synthesis of a wide variety of heterocycles. The substrate, 4-oxo-(4*H*)-1-benzopyran-3-carbaldehyde has three active sites such as, α, β-unsaturated carbonyl group, a carbon–carbon double bond and a formyl group. Of these, the formyl group has the highest reactivity towards active methylene compounds. The condensation reactions of 4-oxo-(4*H*)-1-benzopyran-3-carbaldehyde with active methylene compounds are well known [7]. It is well known that 2,2-dimethyl-5- [(4-oxo-4*H*-chromen-3-yl) methylene]-1, 3-dioxane-4, 6-diones are generally synthesized by condensation of 4-oxo-4*H*-benzopyran-3-carbaldehyde with Meldrum's acid in presence of alumina under microwave irradiation [8].



1(a-h) **2** **3(a-h)**

Scheme

Experiment

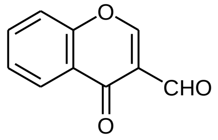
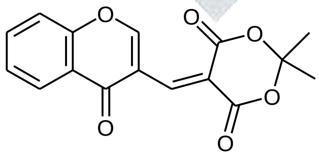
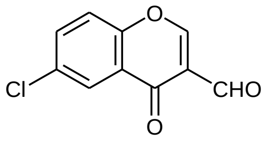
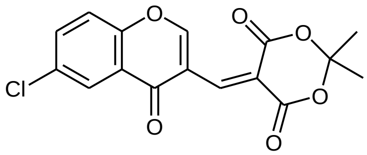
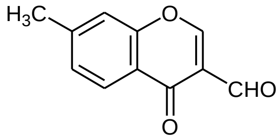
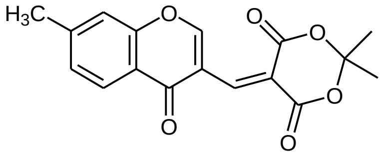
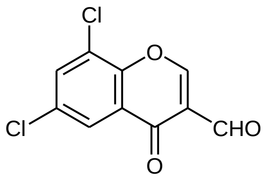
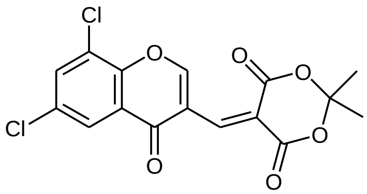
Materials

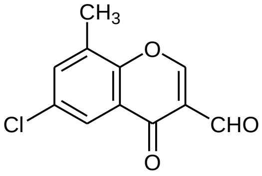
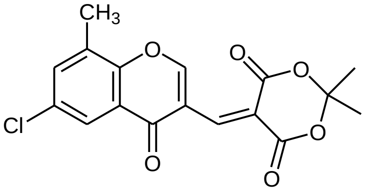
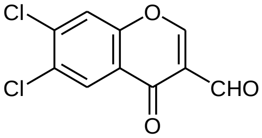
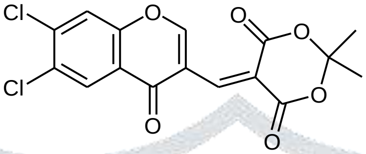
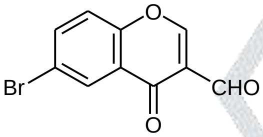
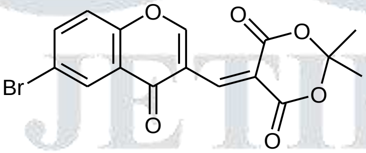
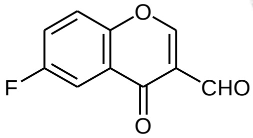
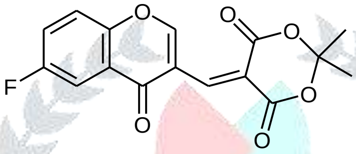
The uncorrected melting points of compounds were taken in an open capillary in a paraffin bath. The progress of the reactions was monitored by TLC (Thin Layer Chromatography). IR spectra were recorded on Perkin-Elmer FTIR spectrophotometer in KBr disc. ^{1}H NMR spectra were recorded on an 300 MHz FT-NMR spectrometer in $CDCl_3$ as a solvent and chemical shift values are recorded in units δ (ppm) relative to tetramethylsilane (Me_4Si) as an internal standard.

General procedure

A mixture of 4-oxo-*4H*-benzopyran-3-carbaldehyde (1 mmol), Meldrum's acid (1 mmol), K_2CO_3 (10 mol%) and water were taken in a single neck round bottom flask. The content of flask was stirred at room temperature for the appropriate time given in Table I. When TLC shows complete disappearance of starting material, the mixture was poured over ice-water to afford the corresponding product **3a-h** in excellent yield. The structures of the products were confirmed by IR, ^{1}H NMR and mass spectral data.

Table I. Knoevenagel condensation of 4-oxo-4*H*-benzopyran-3-carbaldehydes with Meldrum's acid in presence of K_2CO_3 at room temperature^a.

Entry	Ar	Product	Time (min)	Yield (%)^b	M.p.(°C) Found	M.p.(°C) Reported
3a			20	92	180-181	182[8]
3b			15	95	199-200	198[8]
3c			25	89	184-186	186[8]
3d			20	94	176-178	180[8]

3e			25	92	198-200	200[8]
3f			15	94	240-242	248[8]
3g			20	93	200-201	205[8]
3h			15	96	198-200	-

[a] All the products were characterized by IR,^{1}H NMR, and mass spectra; [b] Isolated yields based upon starting aldehyde.

Result and Discussion

In keeping with our research on Knoevenagel condensations and the creation of innovative synthetic techniques [9] herein, we would like to report a simple, efficient and green methodology for the synthesis of 2, 2-dimethyl-5- [(4-oxo-4*H*-chromen-3-yl) methylene]-1, 3-dioxane-4, 6-diones. The synthetic route has been shown in Scheme.

In search of the best experimental conditions, the reaction of 4-oxo-4*H*-benzopyran-3-carbaldehyde **1a** and Meldrum's acid **2** at room temperature has been considered as the model reaction. We screened different mole % of K_2CO_3 such as 5 mol%, 10 mol%, 15 mol% and 20 mol% is for the model reaction. Considering the reaction time and yield of product, 10 mol% was selected as the optimum mol% to promote the synthesis of **3a**.

We have created a more modern path for the water mediated condensation of various 4-oxo-(4*H*)-1-benzopyran-3-carbaldehyde with Meldrum's acid in the presence of K_2CO_3 at room temperature. (Table I). All the reactions were carried out using mild reaction conditions at room temperature with constant stirring. Using this methodology, condensation reactions were completed in outstanding yields with reduced reaction

Conclusion

Finally, we created a straightforward, safe, effective, and environmentally friendly water mediated process for the synthesis of 2, 2-dimethyl-5- [(4-oxo-4*H*-chromen-3-yl) methylene]-1, 3-dioxane-4, 6-dione from the condensation of substituted 4-oxo-4*H*-benzopyran-3-carbaldehyde with Meldrum's acid in the presence of K_2CO_3 at room temperature. This methodology's noteworthy advantages include mild reaction conditions, straightforward procedures, cleaner reactions, short reaction times, and high product yields.

Spectral data ofrepresented compounds

(3b) IR (KBr, cm^{-1}): 3061, 2992, 1730, 1669, 1372, 1296, 797. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.9 (6H, s, 2×CH_3), 7.2-8.2 (3H, m, aromatic), 8.6 (1H, s, olefinic), 9.6 (1H, s, C_2-H of chromone moiety). EIMS (m/z, %): = 335 [M+1].

(3e) IR (KBr, cm^{-1}): 3060, 2996, 1718, 1649, 1396, 1283, 796. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.5 (3H, s, Ar–CH_3), 1.9 (6H, s, 2-CH_3), 7.2-7.5 (2H, s, aromatic), 8.6 (1H, s, olefinic), 9.5 (1H, s, C_2-H of chromone moiety). EIMS (m/z, %): = 349 [M+1].

Refernces

1. (a) G. Jones (2004). "The Knoevenagel Condensation". Organic Reactions. pp. 204–599; (b) Kantevari , S ; Bantu, R., Nagarapu, L; J. Mol. Catal. A : Chem. (2007); 269, 53-57.
2. M. A. Pasha, K, Manjula, V.P. Jayashankara, Synth. React. Inorg. Met. Org Nano–Met. Chem. (2006), 36, 321-323.
3. (a) B. Datta, M. A. PASHA, J. Chem. Sci. 125, 2, (2013), 291–294. (b) N. S. Pawar, M. V. Dipak, K. S. Maqsood Inter. J. Emerging Technologies Innovative Rese. (IJETIR) 3, 3, 2023, 90-93.
4. H. McNab, Chem. Soc. Rev. **7** (1978) 345
5. (a) S. Aimin, W. Xiaobing, S. L. Kit, Tetrahedron Lett. 44 (2003) 1755; (b) U. V. Desai, D. M. Pore, R. B. Mane, S. B. Solabannavao, P. P. Wadgaonkar, Synth. Commun. 34 (2004) 25
6. W. H. Gerwick, A. Lopez, G. D. Van Duyne, J. Clardy, W. Ortiz, A. Buez, Tetrahedron Lett. 270 (1979) 1986
7. (a) J. Prousek, Colt. Czech. Chem. Commun. 58 (1993) 3014; (b) G. V. S. Rama Sarma, V. M. Reddy, Ind. J. Hetero. Chem. 3 (1993), 111
8. S. S. Shindalkar, B. R. Madje, M. S. Shingare, Ind. J. Chem. Sec. B 45 (2006), 2571
9. (a) K. F. Shelke, B. R. Madje, S. A. Sadhaphal, N. V. Shitole, M. S. Shingare, Chem. Ind. J. 4 (2008) 277. (b) K. F. Shelke, S. B. Sapkal, M. S. Shingare, Chine. Chem. Lett. 20 (2009) 1453. (c) Kiran F. Shelke Research Journey, (2023), 106-109, ISSN: 2348-7143. (d) Kiran F. Shelke Inter J Scientific Res in Sci & Tech (2024), 12 (1), 369-372. (e) K. F. Shelke, J. V. Gholave J. Applicable Chem. (2019), 8 (5), 2213-2216. (f) J. V. Gholave, N. S. Gadhari, S. S. Patil, S. S. Upadyay, V. R. Patil, K. F. Shelke Analytical Chemistry Letter, (2020), 10 (5), 577-589.