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RESEARCH ARTICLE

CECL₃.7 H₂O CATALYZED FRIEDLANDER SYNTHESIS OF QUINOLINES UNDER SOLVENT-FREE CONDITIONS

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Abstract

The Friedlander condensation of 2-aminobenzaldehyde 1 with various carbonyl compounds containing α -methylene group 2 in the presence of catalytic amount of reusable catalyst CeCl₃. 7H₂O in solvent-free grinding conditions at RT furnished the corresponding quinolines 3 (Scheme I). The development of new methods with greater efficacy, straightforward procedures and better yields still is desirable.

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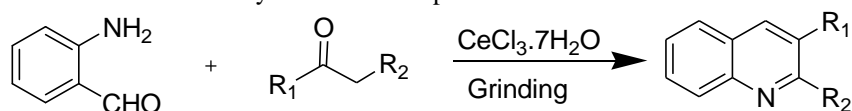
Introduction:-

The reaction proceeds efficiently in high yields at ambient temperature within a few minutes. Various 1,3-dicarbonyl compounds including alkyl acetoacetates, acetylacetone, benzoylacetone, ω -benzoylacetophenone, acetoacetamides and benzoylacetanilides give the corresponding substituted quinolines without any side products. In general the reaction is very clean, rapid and efficient and involves a simple work-up procedure. Unlike previous methods, the present protocol does not require high temperature to produce quinoline derivatives.

Friedlander synthesis is an acid or base catalyzed condensation followed by a cyclodehydration between an aromatic 2-aminoaldehyde or ketone with the carbonyl compound containing a reactive α -methylene group. 2-Aminobenzaldehyde condense readily with active methylene compounds in the presence of base1 and acid2 catalysts to give quinolines. However, some of these methods suffer from disadvantages such as long reaction times, lower yields and requirement of severe conditions. Therefore, the development of new methods with greater efficacy, straightforward procedures and better yields still is desirable.

Interest in solvent-free reactions has increased in recent years, though reactions in solution are much more common. This is due to the fact that, in many cases, ground state organic reactions occur more effectively and selectively than the solution reactions. Furthermore, the solvent-free reaction has many advantages such as reduced pollution, low costs and simplicity in process and handling.

In view of this, herein we report the CeCl₃. 7H₂O catalyzed Friedlander condensation under solvent-free grinding conditions at RT. The synthetic route is presented in Scheme I.



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3	R ₁	R ₂	3	R ₁	R ₂
a	CF ₃	COOC ₂ H ₅	j	CH ₃	4-CH ₃ OC ₆ H ₄ NHCO
b	CH ₃	COOC ₂ H ₅	k	CH ₃	2-ClC ₆ H ₄ NHCO
c	OH	COOC ₂ H ₅	l	CH ₃	4-ClC ₆ H ₄ NHCO
d	C ₆ H ₅	COOC ₂ H ₅	m	C ₆ H ₅	C ₆ H ₅ NHCO
e	CH ₃	COCH ₃	n	C ₆ H ₅	4-CH ₃ C ₆ H ₄ NHCO
f	CH ₃	COC ₆ H ₅	o	C ₆ H ₅	4-CH ₃ OC ₆ H ₄ NHCO
g	C ₆ H ₅	COC ₆ H ₅	p	C ₆ H ₅	2-ClC ₆ H ₄ NHCO
h	CH ₃	C ₆ H ₅ NHCO	q	C ₆ H ₅	4-ClC ₆ H ₄ NHCO
i	CH ₃	4-CH ₃ C ₆ H ₄ NHCO			

Scheme I

Experimental Section

A mixture of 2-aminobenzaldehyde 1 (0.01 mole), active methylene compound 2 (0.01 mole) and CeCl₃·7H₂O (0.01 mole) was ground by pestle and mortar at room temperature for the period indicated in Table II. On completion of the reaction as monitored by TLC, the reaction mixture was treated with cold water. The solid separated was filtered, washed with water and recrystallized from appropriate solvent to furnish 3 (Table II). The aqueous layer containing the catalyst could be evaporated under reduced pressure to give a white solid. The catalyst was recovered and reused in subsequent reactions, three times without losing any significant activity. The newly synthesized compounds were further confirmed by IR and ¹H NMR analysis data.

Results And Discussion:-

Spectral and analytical physical data were described below tables I & II.

Table I:- IR and ¹H NMR spectral data of quinolines 3.

Compd	R ₁	R ₂	IR (KBr) v _{max} in cm ⁻¹	¹ H NMR (200 MHz, DMSO-d ₆) (δ, ppm)
3a	CF ₃	COOC ₂ H ₅	1734 (C=O) 1605 (C=N)	1.50 (t, 3H, CH ₂ CH ₃), 4.50 (q, 2H, CH ₂ CH ₃), 8.76 (s, 1H, C ₄ -H), 8.40 (m, 1H, C ₅ -H), 7.70 (m, 1H, C ₆ -H), 9.35 (m, 1H, C ₇ -H).
3b	CH ₃	COOC ₂ H ₅	1720 (C=O) 1608 (C=N)	1.50 (t, 3H, CH ₂ CH ₃), 2.72 (s, 3H, CH ₃), 4.42 (q, 2H, CH ₂ CH ₃), 8.31 (s, 1H, C ₄ -H), 8.68 (m, 1H, C ₅ -H), 7.62 (m, 1H, C ₆ -H), 9.12 (m, 1H, C ₇ -H).
3d	C ₆ H ₅	COOC ₂ H ₅	1705 (C=O) 1605 (C=N)	1.45 (t, 3H, CH ₂ CH ₃), 4.43 (q, 2H, CH ₂ CH ₃), 8.40 (m, 2H, C ₄ -H, C ₅ -H), 8.00 (m, 1H, C ₆ -H), 9.15 (m, 1H, C ₇ -H), 7.35-7.82 (m, 5H, Ar-H).
3e	CH ₃	COCH ₃	1685 (C=O) 1610 (C=N)	2.40 (s, 3H, COCH ₃), 2.82 (s, 3H, CH ₃), 8.40 (m, 2H, C ₄ -H, C ₅ -H), 7.72 (m, 1H, C ₆ -H), 9.10 (m, 1H, C ₇ -H).
3f	CH ₃	COC ₆ H ₅	1656 (C=O) 1600 (C=N)	2.73 (s, 3H, CH ₃), 8.45 (m, 2H, C ₄ -H, C ₅ -H), 7.93 (m, 1H, C ₆ -H), 9.00 (m, 1H, C ₇ -H), 6.98-7.52 (m, 5H, Ar-H).
3g	C ₆ H ₅	COC ₆ H ₅	1654 (C=O) 1602 (C=N)	7.92 (s, 1H, C ₄ -H), 8.35 (m, 1H, C ₅ -H), 9.12 (m, 1H, C ₇ -H), 6.83-7.62 (m, 11H, C ₆ -H, 10Ar-H).
3h	CH ₃	C ₆ H ₅ NHCO	3248 (N-H) 1679 (C=O) 1602 (C=N)	2.92 (s, 3H, CH ₃), 8.32 (m, 2H, C ₄ -H, C ₅ -H), 9.10 (m, 1H, C ₇ -H), 7.03-7.82 (m, 6H, C ₆ -H, 5Ar-H), 10.38 (s, 1H, NH).
3m	C ₆ H ₅	C ₆ H ₅ NHCO	3200 (N-H) 1655 (C=O)	8.10 (s, 1H, C ₄ -H), 8.65 (m, 1H, C ₅ -H), 7.86 (m, 1H, C ₆ -H), 9.16 (m, 1H, C ₇ -H).

		1600 (C=N)	6.97-7.78 (m, 10H, Ar-H), 10.25 (s, 1H,
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Table II:- Yield %, Reaction period and Physical data of quinolines **3**.

Compd	R ₁	R ₂	Reaction	Yield	m.p. °C		Mol. Formula
			Period	(%)	Found	Reported	
			(min)				
3a	CF ₃	COOC ₂ H ₅	5.5	92	125	125	C ₁₂ H ₉ F ₃ NO ₂
3b	CH ₃	COOC ₂ H ₅	5.0	94	85	85-86	C ₁₂ H ₁₂ NO ₂
3c	OH	COOC ₂ H ₅	5.0	90	206	205-207	C ₁₁ H ₁₀ NO ₃
3d	C ₆ H ₅	COOC ₂ H ₅	5.5	92	104	104	C ₁₇ H ₁₄ NO ₂
3e	CH ₃	COCH ₃	5.0	94	147	146-147	C ₁₁ H ₁₀ NO
3f	CH ₃	COC ₆ H ₅	5.0	92	143	143	C ₁₆ H ₁₂ NO
3g	C ₆ H ₅	COC ₆ H ₅	5.5	90	160	160	C ₂₁ H ₁₄ NO
3h	CH ₃	C ₆ H ₅ NHCO	5.0	92	215	215	C ₁₆ H ₁₃ N ₂ O
3i	CH ₃	4-CH ₃ C ₆ H ₄ NHCO	7.0	94	170	170	C ₁₇ H ₁₅ N ₂ O
3j	CH ₃	4-CH ₃ OC ₆ H ₄ NHCO	8.0	89	149	150	C ₁₇ H ₁₅ N ₂ O ₂
3k	CH ₃	2-ClC ₆ H ₄ NHCO	7.0	92	150	150	C ₁₆ H ₁₂ ClN ₂ O
3l	CH ₃	4-ClC ₆ H ₄ NHCO	6.5	96	206	205	C ₁₆ H ₁₂ ClN ₂ O
3m	C ₆ H ₅	C ₆ H ₅ NHCO	7.0	90	279	285	C ₂₁ H ₁₅ N ₂ O
3n	C ₆ H ₅	4-CH ₃ C ₆ H ₄ NHCO	6.5	92	277	278	C ₂₂ H ₁₇ N ₂ O
3o	C ₆ H ₅	4-CH ₃ OC ₆ H ₄ NHCO	7.0	90	218	218	C ₂₂ H ₁₇ N ₂ O ₂
3p	C ₆ H ₅	2-ClC ₆ H ₄ NHCO	8.0	92	276	277	C ₂₁ H ₁₄ ClN ₂ O
3q	C ₆ H ₅	4-ClC ₆ H ₄ NHCO	6.5	95	200	201	C ₂₁ H ₁₄ ClN ₂ O

Conclusion;-

We have demonstrated a simple and efficient procedure for the synthesis of quinolines by employing CeCl₃.7H₂O as a reusable catalyst. The salient features of this method include operational simplicity, improved reaction rates, high yields of products and avoidance of the use of hazardous acids or bases.

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