Copper Sulphate is an Efficient Catalyst for Knoevengel Condensation Reaction under Microwave Irradiation

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Abstract

Copper Sulphate has been found to be an efficient and inexpensive catalyst for Knoevengel condensation by reaction between aromatic aldehydes 1 and active methylene compounds 2 to get benzylidene compounds 3 in better yield under solvent free condition.

Keywords: Knoevengel condensation reaction, aromatic aldehydes, active methylene complounds, copper sulphate, microwave irradiation

INTRODUCTION

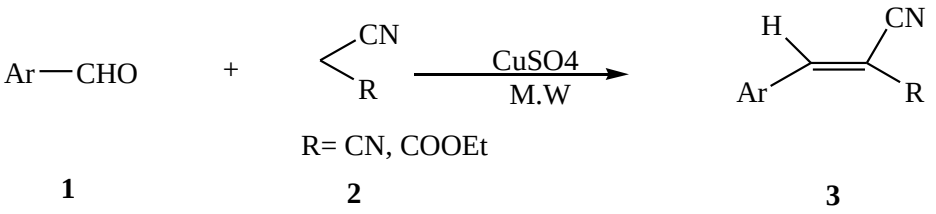
Knoevengel condensation reaction is one the most important Organic reaction in carbon- carbon bond formation. The Unsaturated products obtained have been used as intermediate in synthesis of Therapeutic drugs [1] and fine chemicals [2]. These reactions has been carried out between carbonyl compounds and active methylene compounds in the presence of wide range of catalyst such as $BiCl_3$ [3], Al_2O_3 [4], $TiCl_4$/Base [5], an ion exchange resins [6], Ionic liquids[7], organic bases such as piperidine [8], ethylene diamine[8].However, some of these methods have its own drawbacks by considering environmental waste and pollution. Therefore development of new method to get desirable product with better yield is desirable. Recently use of non conventional methods such as microwave [9,], ultrasonic irradiation [10] and grinding [11] has been increased enormously in organic synthesis. Among the microwave assisted reaction [12], using NH_4F [13] has been reported. In view of this and our interest on microwave assisted reaction we here report the simple and efficient copper sulphate catalysed microwave irradiation knoevengel condensation reaction.

EXPERIMENTAL WORK

Melting Points were determined by open capillary method and are uncorrected. The homogeneity of compounds was checked on silica gel TLC plates. IR spectra were recorded on a FT-IR spectrophotometer. ^{1}H NMR spectra on a BRUKER AVANCE II 400 NMR spectrometer with $CDCl_3$ as solvent and chemical shift (δ) are expressed in ppm using TMS as internal standard.

Material and Method

Simple Knoevengel condensation reaction requires aromatic aldehydes, active methylene compounds such as malanonitrile, cyno ethyl acetate and stoichiometric amount of copper sulphate catalyst. These reactions are carried out in microwave irradiation under solvent free conditions.



R= CN, COOEt

1 **2** **3**

Procedure

Euimolar quantities of aromatic aldehyde **1** (0.01 mole), active methylene compound **2** (0.01 mole) and $CuSO_4$.$5H_2O$ (0.01 mole) were taken in a 100 ml beaker and subjected to microwave irradiation at 450 W intermittently at 10 s interval of time. After completion of reaction was indicated by TLC, the reaction mixture was cooled to room temperature and poured on crushed ice. The solid thus obtained was filtered and purified by recrystallisation from ethanol to get product **3**. The prepared compounds **3** were characterised by spectral (IR and ^{1}H NMR) data.

Characterisation

IR and ^{1}H NMR spectral data for selected compounds

3a: IR (KBr): 3034 (C-H), 2225 (CN), 1574 (C=C) cm^{-1} ; ^{1}H NMR ($CDCl_3$): δ 2.42 (s, 3H ,CH_3), 7.40 (d, 2H, Ar-H), 7.87 (d, 2H, Ar-H), 8.42 (s,1H, =CH).

3b: IR (KBr): 3008 (C-H), 2224 (CN), 1591 (C=C) cm^{-1} ; ^{1}H NMR($CDCl_3$):δ 7.70 (m, 3H, Ar-H), 7.94 (d, 2H, Ar-H), 8.54 (s,1H, =CH).

3d: IR (KBr): 3036 (C-H), 2225 (CN), 1574 (C=C), 1093 (Ar-Cl) cm^{-1} ; ^{1}H NMR ($CDCl_3$): δ 3.95 (s,3H,CH3), 7.51 (d,2H,Ar-H), 7.53 (d,2H,Ar-H), 8.46 (s,1H,=CH).

3e: IR (KBr): 2859 (C-H), 2226 (CN), 1573 (C=C), 1085 (Ar-Br) cm^{-1} ; ^{1}H NMR ($CDCl_3$):δ 7.68 (d, 2H, Ar-H), 7.78 (d, 2H, Ar-H), 8.56 (s, 1H, =CH).

3f: IR (KBr): 2992 (C-H), 2228 (CN), 1589 (C=C), 1710 (C=O), 1093 (Ar-Cl) cm^{-1}; ^{1}H NMR($CDCl_3$): δ 1.45 (t, 3H, OCH_2CH_3), 2.45 (s, 3H, CH_3), 4.40 (q, 2H, 1.36 (t, 3H, OCH_2CH_3), 4.58 (q, 2H, OCH_2CH_3)) 7.30 (d, 2H, Ar-H), 7.87 (d, 2H, Ar-H), 8.15 (s,1H, =CH).

3g: IR (KBr): 2986 (C-H), 2226 (CN), 1595 (C=C), 1725 (C=O), cm^{-1} ; ^{1}H NMR($CDCl_3$): δ 1.40 (t, 3H, OCH_2CH_3), 4.40 (q, 2H, OCH_2CH_3), 7.52 (m, 3H, Ar-H), 7.95 (d, 2H ,Ar-H), 8.20 (s,1H,=CH).

3i: IR (KBr): 2982 (C-H), 2230 (CN), 1590 (C=C), 1718 (C=O), 1093 (Ar-Cl) cm^{-1} ; ^{1}H NMR ($CDCl_3$): δ 1.36 (t, 3H, OCH_2CH_3), 4.58 (q, 2H, OCH_2CH_3), 7.46 (d, 2H, Ar-H), 7.93 (d, 2H, Ar-H), 8.12 (s, 1H, =CH).

3j: IR (KBr): 2958 (C-H), 2224 (CN), 1591(C=C), 1715 (C=O) 1088 (Ar-Br) cm^{-1} ; ^{1}H NMR($CDCl_3$):δ 1.46 (t, 3H, OCH_2CH_3), 4.40 (q, 2H, OCH_2CH_3), 7.72 (d, 2H, Ar-H), 7.80 (d, 2H, Ar-H), 8.01 (s,1H, =CH).

Observations

Table I- Microwave assisted Knoevengel condensation reaction catalysed by $CuSO_4$ under solvent free condition

Compd	Ar	R	Reaction time(sec.)	Yield	M.P. (^{o} C) obtained	M.P. (^{o} C) reported
3a	4-$CH_3C_6H_4$	CN	30	96	126	128-130
3b	C_6H_5	CN	25	95	88	87-88
3c	$4CH_3OC_6H_4$	CN	30	94	114	114-116
3d	4-Cl C_6H_4	CN	25	98	163	161-163

3e	4-Br C_6H_4	CN	30	92	154	154-156
3f	4-$CH_3C_6H_4$	COOEt	40	96	90	91-93
3g	C_6H_5	COOEt	40	95	46	46-48
3h	$4CH_3OC_6H_4$	COOEt	45	94	50	52-54
3i	4-Cl C_6H_4	COOEt	40	98	90	92-94
3j	4-Br C_6H_4	COOEt	45	92	88	86-88

RESULT AND DISCUSSION

Initially the model reaction was carried out between 0.01 mol 4-Methyl benzaldehyd and 0.01 mol of malononitrile in the presence 0.01 mol of $CuSO_4$ under Microwave irradiation of 10s interval of time. The reaction completed within 25 sec about 98% yield. Inspiring from this various aromatic aldehydes was treated with malononitrile and ethyl cyanoacetate (Table 1) to get excellent yield. All prepared compounds were structurally elucidated by using physical data and spectroscopic methods such as ^{1}HNMR, and IR specra and compared with authentic samples (Table1).The IR spectrum of products showed no stretching band of carbonyl group (aldehyde group) at 1680–1698 cm^{-1}. Absorption peak at 2200–2228cm^{-1} is attributed to the nitrile group, while its ^{1}H NMR spectrum shows a singlet for one proton at δ 8.42-8.45 ppm.

CONCLUSION

Knoevenagel condensation reactions between aromatic aldehydes and active methylene compounds catalysed by copper sulphate assisted by microwave irradiation under solvent free conditions are clean, ecofriendly, completed at within few seconds, work-up is simple with better yield.

ACKNOWLEDGEMENT

The authors are thankful to P.G. Department of Chemistry, Tuljaram Chaturchand College and Management of Anekant Education Society, Baramati for constant encouragement and providing necessary research facilities and to the Director, SAIF, Panjab University, Chandigarh, for providing spectral data.

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