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CONVENIENT SYNTHESIS OF α, α[1] - BIS (SUBSTITUTED FURFURYLIDENE) CYCLOALKANONES AND CHALCONES UNDER MICROWAVE IRRADIATION.

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Abstract: Condensation of furfural with cycloalkanones and substituted acetophenones catalyzed by solid NaOH results in α, α[1]-bis (substituted furfurylidene) cycloalkanones and chalcones in high yield under microwave irradiation for a duration of 2 minutes.

Microwave heating and its application in organic synthesis has been reviewed recently.[1] Rate enhancement in many reactions has been reported[2] in recent years. Microwave promoted Knoevenagel condensation catalyzed by piperidine[3] , Claisen condensation of rhodanine with aromatic aldehydes under basic supports[4] and Claisen condensation of benzaldehydes with cycloalkanones catalyzed by bis (p-ethoxyphenyl)telluroxide[5] and solid NaOH[6] have been reported in the literature. Herein we wish to report a very simple and convenient synthesis

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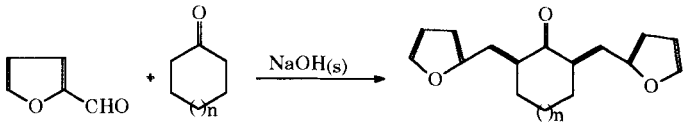
of α, α^1-bis (substituted furfurylidene)cycloalkanones and chalcones by condensation of furfural with cycloalkanones and acetophenones.

Claisen condensation of furfural with cycloalkanones has been reported in the literature.[7] Since under microwave irradiation condition reaction time gets reduced and yields get improved, in the present work, studies have been carried out for the Claisen condensation of furfural with cycloalkanones catalyzed by solid NaOH under microwave irradiation for 1-2 min. wherein very good yield of 2,8-bis(furfurylidene)cyclooctanone was obtained. (Scheme). Claisen condensation of furfural with p-substituted acetophenones results in excellent yield of chalcones within 2 minutes. (Scheme).

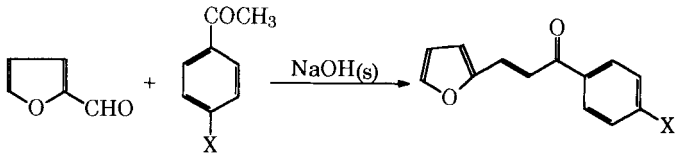
Knoevenagel condensation of furfural catalyzed by piperidine[3] , cadmium iodide[8], anhydrous $ZnCl_2$[9], $AlPO_4$ - Al_2O_3[10] in the absence of solvent has been reported. In the present study, Knoevenagel condensation of furfural with ethylcyanoacetate and cyanoacetamide catalyzed by solid NaOH under microwave irradiation has been carried out which results in the reduction of reaction time to 1 min. with excellent yields (Scheme). The results of the microwave irradiation condensation reactions are summarized in the Table.

From the table it is evident that employing microwave irradiation for Claisen condensation of furfural with cyclooctanone results in excellent yields of 2,8-bis(furfurylidene)cyclooctanone (80%) within 2 minutes.



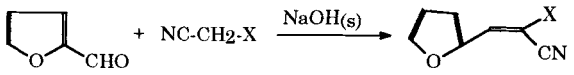
1 a - d

1a n = 0
1b n = 2
1c n = 2
1d n = 3



2 a - d

2a X = H
2b X = OCH_3
2c X = CH_3
2d X = Cl



3 a - b

3a X = $CONH_2$
3b X = $COOC_2H_5$

Scheme

Table 1. Condensation products of furfural with cycloalkanones and acetophenones under microwave irradiation.

Compound	Mole ratio Aldehyde : Ketone	Reaction time MW (Secs)	m.p (°C)[b] (lit)	Yield[a]
1a	2:1	60	164-65 (163 - 64)[7]	100
1b	2:1	90	143-44 (144 - 45)[7]	100
1c	2:1	120	111-12 (110 - 12)[7]	88
1d	2:1	120	Viscous liquid.	80
2a	1:1	120	35-36 (35.5 - 36.5)[11]	95
2b	1:1	120	78-79 (79 - 81)[12]	88
2c	1:1	120	71-72 (71 - 72)[13]	85
2d	1:1	120	77-78 (78.5 - 79)[14]	90
3a	1:1	60	151-52	85
3b	1:1	60	91-92 (93)[8]	90

a : Yield of the isolated pure product.
b: Mp were taken on a Raaga hot stage apparatus and uncorrected.

Typical Experimental Procedure:

To a solution of ketone (0.01 mole) and furfural (0.01 mole or 0.02 mole) in dry ethanol (20 ml) taken in an Erlenmeyer flask (100 ml), catalytic quantity of sodium hydroxide (2 pellets) was added and subjected to microwave irradiation at 30% power (at 210 watts) for 1-2 minutes and then cooled in an ice bath and the

product formed was filtered and washed with water till the washings were neutral. The authenticity of the products were established by their melting points, elemental analysis and spectral data.

Spectral data for 2,8-bis(furfurylidene)cyclooctanone **(1d)**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, J=4, 1H), 6.81 (s, 1H), 6.51 (m, 1H), 6.44 (d, J=4, 1H), 2.85 (t, 2H) and 1.76 - 1.52 (m, 4H); C^{13} NMR (75 MHz, $CDCl_3$): δ 202.10, 151.94, 143.90, 139.03, 120.16, 113.82, 111.77, 29.73, 27.42 and 27.18; IR (Neat) 3136, 2928, 2864, 1661, 1587, 1453, 1286 and 1152 cm^{-1}; m/z 282(M^+).

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