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Microwave Assisted Synthesis of Some Substituted 1,3-diaryl Propenones and 3,5-diaryl-6-carbethoxy Cyclohexenones and their antibacterial activity

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ABSTRACT

Microwave induced solvent free solid phase syntheses of substituted 1,3-diaryl propenones 1a-f using basic alumina and their subsequent rapid transformation to 3,5-diaryl-6-Carbethoxy cyclohexenones 2a-i with ethyl acetoacetate in the presence of basic alumina and piperidine under solvent free condition using domestic microwave oven has been described. These products have been screened for their antibacterial activities.

Key words: Microwave solvent free syntheses, 3,5 diaryl-6-Carbethoxy cyelohexenones, antibacterial activity.

INTRODUCTION

A wide range of methods are available for synthesis of organic compounds. Real need exists for new simple procedures that support many kinds of structural diversity and various substitution pattern in the target molecules. The wide applicability of microwave activation[1-5] in chemical reaction is due to cleaner products, higher yield, shorter reaction time, operational simplicity and minimization of side reaction. In recent years the microwave heating under solvent free reaction condition on an inorganic solid support is a promising alternative to conventional method as these reactions represent a clean, efficient, safe, economical and eco-friendly procedure. In view of the above and the chemistry of chalcones[6-12] and use of microwave in various organic synthesis1[3-15], we report herein environmentally benign solvent free procedures in the presence of inorganic solid support for the synthesis of 1, 3-diaryl propenones and their cyclohexenone derivatives under microwave irradiation.

EXPERIMENTAL

All melting points were determined in open capillaries on electrically heated metal blocks and are uncorrected IR spectra were recorded on a Perkin-elmer 16pc spectrophotometer and 'HNMR spectra in $CDCl_3$ and acetone d_6 on a burker DRX-300 spectrometer. The reactions were carried out

in unmodified microwave oven. 1,3-diaryl propenones required during the course of our present investigation were synthesized by condensing substituted acetophenones 1 and aromatic aldehydes -2-using basic alumina under solvent free microwave irradiation in a modified claisen-schmidt condensation reaction, microwave irradiation for 2-3 min of the substarts provided the condensation products in high yields where as the conventional method required longer periods and with low yields.

The structures of chalcones were supported by elemental analyses. IR spectra exhibited the conjugated carbonyl at 1630 cm^{-1} and 'H NMR showed trans-coupled doublets (J-15 Hz) at 7.63 (H_2) and 7.82 (Hp) for vinylic hydrogens.

The synthesis of 3,5-diaryl-6-carbethoxy cyclohexenones have been carried out by condensing chalcones with ethyl acetoacetate in the presence of basic alumina and piperidine under microwave irradiation without using any solvent in high yields as compared to conventional methods.

General procedure for the synthesis of 1,3-diaryl propenones

To a solution of substituted acetophenone and substituted aromatic aldehyde in ethanol taken in a 100 ml borosil flask was added basic alumina. The mixture was uniformly mixed with glass rod and air dried to remove the solvent. Adsorbed material was irradiated inside a microwave oven for 2-3 min. at medium power level. After the completion of reaction the reaction mixture was cooled at room temperature and the product was extracted with ethanol. Removal of the solvent and subsequent recrystallisation with ethanol resulted in analytical samples of the desired products.

General procedure for the synthesis of 3, 5 - diaryl-6-carbethoxy cyclohexenones

A mixture of ethyl acetoacetate and piperidine was dissolved in ethanol and taken in a 100 ml borosil flask. To this basic alumina was added and the reactants properly mixed with the help of glass rod. Adsorbed material was dried in air and irradiated inside the microwave oven at medium power level intermittently at 0.5 min. intervals. On completion of the reaction the mixture was cooled to room temperature and then product was extracted with ethanol. The product separated after concentrating the solvent, was filtered and recrystallised to afford the desired products.

Antibacterial activity

Synthesized compounds 1 and 2 were tested against $gram^{+ve}$ organisms *staphylococcus aureus*, *streptococcus fecalis* and $gram^{-ve}$ organisms *Escherichia coli*, proteus mirabilis, using DMF as solvent at 200 mg/ml concentration by paper disc-diffusion method, the zone of inhibition after 18 hr of incubation at 37°C was compared with that of standard drugs Amicacin and Tobramycin.

RESULTS AND DISCUSSION

The synthesized chalcones 1,3-diaryl propenones and 3,5-diaryl-6-cabemoxycycloh-exenones were subjected to elemental analysis carbon & hydrogen and molecular formulas were assigned. The colours of these product were noted. The M.P.^{0}C were determined.

These products were characterized by IR and NMR spectroscopy

3,4,5-trimethoxy-2-hydroxy 1,3-diaryl propenones-IR ; 3438. 3045, 2938, 2834, 1634, 1516, 1498, 1446, 1374, 1263, 1199, 1020, 825, 760, 664 cm^{-1}, H-NMR: δ 3.9 (S, 9H, 3x OCH_3), 6.8 - 7.1 (M, 6H, Ar-H) 7.3 (S, 1H, OH), 7.6 - 7.7 (d, 1H, = C-Ha), 7.8 - 7.9 (d. 1H=C-H_b), MS: M/Z (%) 311 (M+,4) 274(2), 210(2), 194 (3), 171(8), 179(10), 165(12), 141(20), 91 (20), 71 (20), 71 (30), 87 (35), 51 (38).

N, N - dimethyl - 4 - amino - 2 -hydroxy 1.3-diaryl propenones IR : 3434. 3050, 2907, 1616, 1522, 1432, 1375, 1312, 1202, 1156, 985, 812, 763, 711 cm^{-1} HNMR : δ 3.0 [S, 6H, -N $(CH_3)_2$], 6.6-6.7, 6.9-7.0 (m, 8H, Ar-H) 7.3 (S. 1H, OH) 7.5 - 7.6 (d,1H, = C-Ha), 7.7 - 7.8 (d, 1H, = C-H_b) MS : M/Z (%) 267 (M^+, 2), 238(2), 196(1), 183(1), 189(2), 165(2), 147(4), 125 (3), 111(45), 97 (20), 83(28), 69(42), 57(100), 53(18).

3-Chloro-2-hydroxy-1,3-diaryl propenones-IR -3440, 3050, 2917, 1629, 1529, 1565, 1489, 1426, 1356, 1326, 1209, 1157, 1088, 1033, 986,820, 716 cm^{-1}, MS M/Z (%) 510 (M^+, 100), 483(9), 746 (21), 439 (5), 384(55), 374(29), 346(6),

Table 1: Elemental Analysis & physical data of 1,3-diaryl propenones

S. No	Mol. formula of propenones	Colour	M.P. °C	Elemental analyses (cacld.values)				
				% of C	% of H	% of N	% of Br	% of Cl
1a	$C_{15}H_{12}O_2$	Yellow	89	80.10 (80.36)	2.26 (5.31)	-	-	-
1b	$C_{15}H_{14}O_3$	Orange	92	74.20 (74.38)	5.65 (7.78)	-	-	-
1c	$C_{15}H_{11}O_2Cl$	Pale Yellow	149	70.50 (70.58)	4.25 (4.31)	-	-	13.65 (13.72)
1d	$C_{18}H_{18}O_5$	Brown	142	57.20 (57.32)	5.70 (5.73)	-	-	-
1e	$C_{17}H_{17}NO_2$	Red	160	76.10 (76.40)	6.30 (6.36)	5.20 (5.24)	-	-
1f	$C_{15}H_{11}O_2$ C l	Yellow	180	69.60 (69.76)	4.20 (4.26)	-	-	13.50 (13.56)
1g	$C_{15}H_{10}Br_2$ O_2	Orange Yellow	190	47.20 (47.36)	2.60 (2.63)	-	41.40 (41.57)	-
1h	$C_{16}H_{12}O_3$ Br_2	Orange Yellow	195	46.60 (46.82)	2.80 (2.92)	-	38.40 (38.53)	-
1I	$C_{15}H_9Br_2$ O_2 Cl	Green yellow	205	41.70 (41.86)	2.05 (2.09)	-	36.70 (36.74)	8.08 (8.13)
1J	$C_{18}H_{16}O_5$ Br_2	Orrange Yellow	208	45.70 (45.95)	3.20 (3.30)	-	33.50 (33.11)	-
1k	$C_{19}H_{15}O_2$ N Br_2	Red yellow	210	48.10 (48.22)	3.40 (3.54)	3.20 (3.30)	37.20 (37.35)	-
1l	$C_{15}H_9O_2$ Br_2 Cl	Yellow	212	43.30 (43.47)	2.10 (2.17)	-	38.05 (38.16)	8.30 (8.45)

Table 2: Elemental Analysis & physical data of 3,5-diaryl-6 Carbethoxy cyclohexenones

S. No	Mol. formula of propenones	Colour	M.P. °C	Elemental analyses (cacld.values)				
				% of C	% of H	% of N	% of Br	% of Cl
2a	$C_{21}H_{17}O_4$	Cream	155	75.50 (75.67)	5.00 (5.10)	-		
2b	$C_{22}H_{19}O_5$	Cream	165	72.40 (72.72)	5.10 (5.23)	-		
2c	$C_{21}H_{16}O_4C$	Orange	178	68.40 (68.66)	4.30 (4.35)	-		9.50 (13.72)
2d	$C_{23}H_{22}O_4Nl$	Cream	155	73.10 (73.40)	5.70 (5.85)	3.60 (3.72)		
2e	$C_{24}H_{23}O_7$	Cream	150	68.00 (68.08)	5.35 (5.43)	-		
2f	$C_{21}H_{16}O_4Cl$	Yellow	172	68.40 (68.66)	4.20 (4.35)	-		9.45 (9.53)

Figures in parenthesis are observed values.

321(5), 254(40), 218(16), 165 (76), 137(42), 114(10), 101 (50), 91 (30), 63(20).

2-hydroxy-3,5-diaryl-6-Carbethoxy cyclohexenones - IR-3500, 2900, 2880, 2840, 1730, 1030, 1590, 1570, 1460, 1370, 1310, 1300, 1240, 1200, 1170, 1150, 1120, 100, 1080, 1030, 900, 860, 870, 750 cm^{-1} H-NMR : δ 0.9-1.2 [t, 3H, O-CH_2 - CH_3), 2.6 (m, 2H, 4-CH_2) 3.0 - 3.1 (distorted t, 1H, C_5-H), 3.6 - 3.8 (d, 1H, C_6-H), 3.9 - 4.0 (q, - O-CH_2 - CH_3) 6.4 (S, 1H, C_2&H) 6.8 - 7.7 (m - 9H, Ar - H).

2-hydroxy-4-methoxy 3,5-diaryl-6-Carbethoxy cyclohexenones - IR-3340, 2920, 2860, 1720, 1620, 1580, 1500, 1450, 1376, 1320, 1220, 1140, 1020, 900, 880, 800, 710, 680, 600 cm^{-1} H-NMR : δ 1.0-1.2 [t, 3H, O-CH_2 - CH_3), 1.6 (m, 2H, C_2-H) 2.2 (m, 2H, 4-CH_2) 2.9 - 3.0 (distorted t, 1H, C_5-H), 3.5 - 3.6 (d, 1H, C_6-H), M..S. : M/Z - 366 (M^+, 55.2), 293 (100), 367 (14.9), 321 (9.4), 319 (11.9), 318 (20.7), 294 (21.9), 292 (20.3), 289 (9.5), 213 (13.1), 161 (26.2), 134 (12.1), 133 (14.1), 132 (24.5), 131 (30.5), 121 (51.5).

2-hydroxy-4-chlaro 3,5 - diaryl-6-Carbethoxy cyclohexenones - IR-3340, 2950, 2875, 1710, 1610, 1550, 1450, 1360, 1320, 1290, 1240, 1210, 1140, 1020, 980, 950, 830, 740, 710, 700, 670 cm^{-1} H-NMR : δ 1.0-1.2 [t, 3H, O-CH_2 - CH_3), 2.3 (m, 2H, C_4-H) 3.01 - 3.04 (distorted t, 1H, C_5-H), 3.7 - 3.8 (d, 1H, C_6-H), 4.0-4.2 (q, 2H, OCH_2H_3) 6.7-7.2 (m, 9H, Ar-H) M..S. : M/Z - (%) 371 (M, 85), 352 (4), 341 (3), 327 (6), 324 (25), 297 (100), 289 (25), 279 (7), 266 (6), 259 (15), 244 (12), 231 (7), 213 (27), 202 (6), 187 (10), 165 (26), 157 (4), 131 (45), 115 (4), 101 (13), 91 (8), 83 (8), 77 (14).

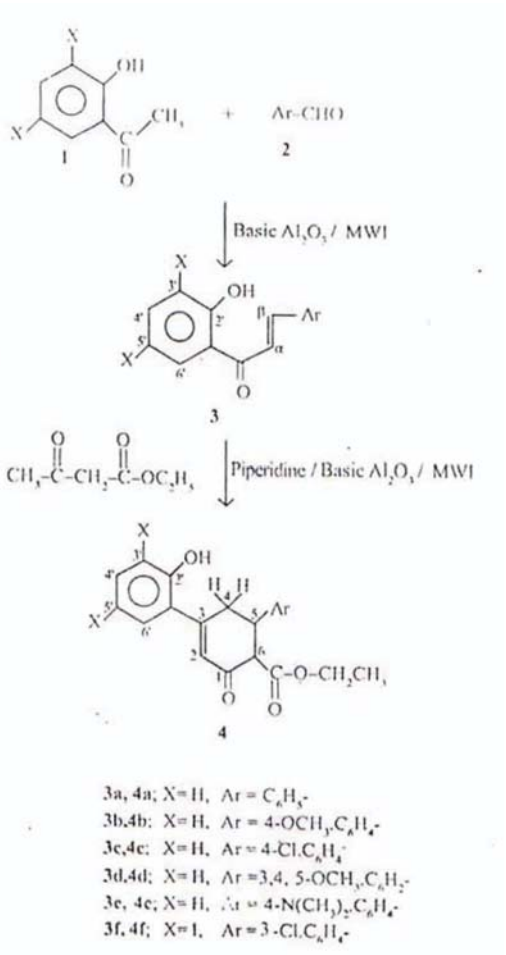
2-hydroxy 3,4,5-trimethoxy 3,5-diaryl-6-Carbethoxy cyclohexenones - IR-3319, 2940, 2840, 1736, 1640, 1544, 1504, 1451, 1352, 1319, 1269, 1239, 1123, 1037, 1007, 855, 755, 662 cm^{-1}, M..S. : M/Z - (%) 426 (M^+, 100), 410 (2), 397 (1), 380 (52), 365 (6), 353 (82), 338 (12), 322 (7), 311 (7), 293 (6), 280 (5), 266 (15), 251 (10), 234 (4), 213 (15), 194 (8), 181 (38), 168 (16), 153 (8), 131 (17), 115 (6), 91 (6), 77 (8).

2-hydroxy-N,N-dimethyl 3,5-diaryl-6-Carbethoxy cyclohexenones - IR-3310, 2977, 2794, 1740, 1596, 1522, 1447, 1353, 1309, 1238, 1206, 1164, 1114, 1039, 944, 885, 814, 763, 679 cm^{-1}, H-NMR : d1.06-1.01 [t, 3H, O-CH_2 - CH_3), 2.90-2.92 (m, 2H, C_4-H) 3.0 - 3.1[t, 6H, $N(CH_3)_2$), 3.2 - 3.3 (distorted t, 1H, C_5-H), 3.4 - 3.5 (d, 1H, C_6-H), 3.9-4.0 (q, 2H, OCH_2H_3) M..S. : M/Z - (%) 379 (M^+, 100), 333 (55), 306 (57), 289 (9), 277 (10), 269 (9), 256 (5), 246 (2), 219 (50), 202 (6), 183 (8), 174 (14), 158 (7), 147 (24), 134 (32), 121 (23), 103 (7), 91 (13), 77 (19).

2-hydroxy-4-chloro 3,5 - diaryl-6-carbethoxy cyclohexenone IR - 8448, 2948, 2885, 1733, 1640, 1588, 1488, 1448, 1381, 1295, 1248, 1200, 1165, 1037, 954, 824, 668 cm^{-1}.

Antibacterial activity

The screening data indicated that compound 1b-showed excellent activity where



compounds 1c and 3d showed moderate activity against *S. aureus* compounds 3b and 3c displayed significant activity against *E. coli*. None of the compounds was found to exhibit any significant activity against *S. fecalis* and *P. mirabilis.*

Amongst the 3, 5-diaryl-6-carbethoxycyclohexenones 4b and 4c showed good activity against S. aureus, S. fecalis and E. Coli. Weak to moderate activity has also been displayed by 4a, 4c and 4d against S. fecalis. Compounds 4 showed no significant activity against P. mirabilis.

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