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Synthesis and Spectral Correlations of Some Novel Chalcones

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Abstract

A series of novel chalcones have been synthesized by SiO2-H2SO4 catalyzed microwave assisted oxidative coupling of ketones and aldehydes under solvent-free conditions. The yield of the chalcones has been found to be more than 90%. The purity of all chalcones has been checked using their physical constants and spectral data as published earlier in literature. The spectral frequencies of these chalcones have been correlated withHammett substituent constants, F and Rparameters. From the results of statistical analyses the effects of substituent on the group frequencies were discussed.The antimicrobial activities these chalcones have been studied using Bauer-Kirby method.

Keywords: *Styryl 2-methylphenyl ketones, SiO2-H2SO4, Crossed-Aldol condensation, Solvent free synthesis, Antimicrobial activities*

INTRODUCTION

Chalcones are α, β-unsaturated ketones consisting of two aromatic rings (ring A and B) having diverse array of substituents. Rings are interconnected by a highly electrophilic three carbon α, β-unsaturated carbonyl system that assumes linear or nearly planar structure [1,2]. They contain the ketoethylenic group (–CO–CH=CH-)[3]. fundamentally they are considered as derivatives of phenyl styryl ketone. Chalcones possess conjugated double bonds and a completely delocalized π-electron system on both benzene rings. Chalcones, which are the main precursors for the synthesis of flavonoids, are attracting increased attention because of numerous pharmacological applications.

They exhibit various biological activities [4, 5]. A significant variety of methods are existing in literature for the synthesis of chalcones. The most opportune way is the one, which involves the Claisen-Schimidt condensation of equimolar quantities of aryl methylketones with aryl aldehyde in presence of alcoholic alkali[6]. Several condensing agents used are alkali of different strength[7,8] hydrochloric acid[9,10], phosphorous oxychloride[11], piperidine[12], anhydrous aluminium chloride[13], boron trifluoride[14], aqueous solution of borax[15], amino acids[16], perchloric acid[17] etc.

Over the years various innovative methods have been devised to speed up the chemical reactions. In these environmentally conscious days, the development of technology is directed towards environmentally sound and eco friendly methods. The usage of microwave energy to accelerate the organic reactions is of increasing interest and offers several advantages over conventional heating techniques[18]. Numerous green catalysts such as fly-ash: sulphuric acid, silica-sulphuricacid[19,20] anhydrous zinc chloride[21], green chemistry catalysts-grinding the reactants with sodiumhydroxide[22], aqueous alkali in lower temperature[23], solid sulphonic acid from bamboo[24], barium hydroxide[25], anhydrous sodium bicarbonate[26], microwave assisted synthesis[27], Fly-ash:water[28], triphenyl phosphite[29], alkali earth metals[30], KF/Al2O3[31], sulfated titania [32] and silicotungstic acid[33]have been reported for the synthesis of many number of organic compounds.

Therefore the authors have taken efforts to synthesized some substituted styryl 2-methylphenyl ketones by SiO2-H2SO4 catalyzed microwave assisted oxidative coupling of 2-methylacetophenonewith various substituted benzaldehydes, studied the quantitative structure property relationship from the group frequencies.

EXPERIMENTAL

Materials and Methods

All chemicals used were purchased from Sigma-Aldrich and E-Merck chemical companies. Melting points of all chalcones were determined in open glass capillaries on SUNTEX melting point apparatus and are uncorrected.

Table 1: The yield and physical constants of styryl 2-methylphenyl ketones

Entry	X	M.F.	M.W.	Yield (%)	m.p. °C
1	H	$C_{16}H_{14}O$	222	95	54-55
2	4-Br	$C_{16}H_{13}BrO$	301	96	58-59
3	2-Cl	$C_{16}H_{13}ClO$	256	90	106-107
4	4-Cl	$C_{16}H_{13}ClO$	256	85	58-59
5	4-F	$C_{16}H_{13}FO$	240	90	60-61
6	4-CH_3	$C_{17}H_{16}O$	236	94	64-65
7	2-NO_2	$C_{16}H_{13}NO_3$	267	95	100-101
8	3-NO_2	$C_{16}H_{13}NO_3$	267	88	98-99
9	4-NO_2	$C_{16}H_{13}NO_3$	267	90	111-112

The UV spectra of all synthesized chalcones were recorded in ELICO-BL222 SPECTROMETER (λ_{max} nm) in spectral grade methanol. Infrared spectra (KBr, 4000-400cm^{-1}) were recorded on AVATAR-300 Fourier transform spectrophotometer. Bruker AV400 NMR spectrometer operating at 400 MHz has been utilized for recording ^{1}H NMR spectra and 100 MHz for ^{13}C spectra in $CDCl_3$ solvent using TMS as internal standard.

Preparation of SiO_2-H_2SO_4 catalyst

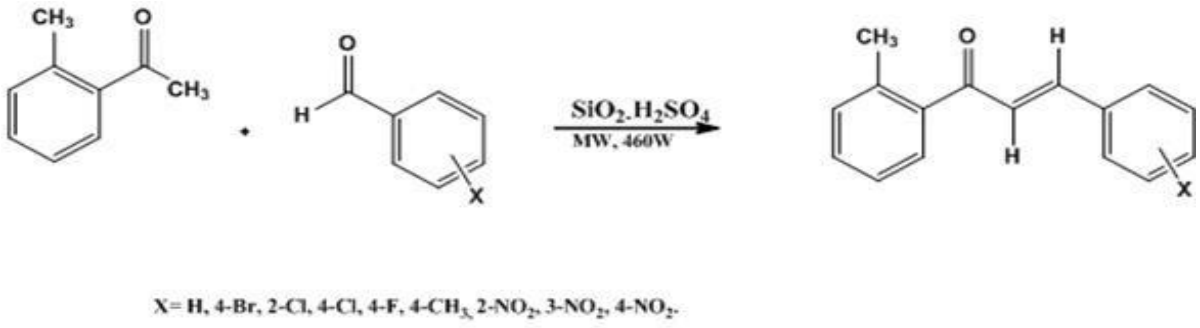
The Silica: H_2SO_4 catalyst has been prepared by the procedure published in literature[34]. In a 50 mL Borosil beaker, 1g of Silica and 0.8 mL (0.5mol) of sulphuric acid have been taken and mixed thoroughly with glass rod. This mixture has been heated on a hot air oven at 85°C for 1h, cooled to room temperature, stored in a borosil bottle and tightly capped.

General procedure for synthesis of substituted styryl 2-methyl phenyl ketones

An appropriate mixture of aryl 2-methyl--ketone (2 mmol) and substituted benzaldehydes (2 mmol) and SiO_2-H_2SO_4 (0.5 g) taken in 50 mL corning glass tube and tightly capped. The reaction mixture was subjected to microwave irradiation for 8-10 minutes in a microwave oven Scheme-1 (LG Grill, Intellowave, Microwave Oven, 160-800W) and then cooled to room temperature. Added 10mL of dichloromethane, the organic layer has been separated which on evaporation yields the solid product. The solid, on

recrystallization with benzene-hexane

Mixture gives glittering pale yellow solid.



X= H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2.

Scheme-1 Synthesis of substituted styryl 2-methylphenylketones

RESULTSANDDISCUSSION

In the present study the authors have studied the effects of substituents on the spectral data such as ultraviolet absorption maxima (λmax, nm), infrared spectral carbonyl and deformation modes (ν, cm-1), the chemical shifts (δ, ppm) of α, β protons & carbons and carbonylcarbons of synthesized 2-methyl chalcones with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis for predicting the reactivity on the group frequencies

UV spectral study

The measured ultraviolet absorption maxima (λmax, nm) of all 2-methyl chalcones were tabulated in Table - 2. These values are correlated [35 -39], with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis. While seeking Hammett correlation, involving UV Absorption maximum values, the form of the Hammett equation employed is as given in equation.

$\lambda max = \rho\sigma + \lambda 0$ …(1)

The results of statistical analysis are presented in Table - 3. From the Table - 3, the correlation of absorption maxima (λmax, nm) with Hammett constants σ, σI & σRand R parameter are found to be satisfactory. The remaining Hammett constant σ+ and F parameter were failing in correlation. The failure of some correlations with σ+ and F parameter are due to the fact that the polar and filed effects of the substituents are insufficient for predicting the reactivity on the absorption through conjugation. This is attributed to the resonance conjugative structure shown in Fig -1. All the correlations have shown negative ρ value

and it evidences the operation of reverse In single parameter correlation, the Hammett substituent constants not obeyed in the regression. While seeking these parameters in multi-regression, with F and substituent effect in all chalcones.

R Swain-Lupton's [40] constants, they gave satisfactory correlations. The multi correlation equations are given in 2 and 3.

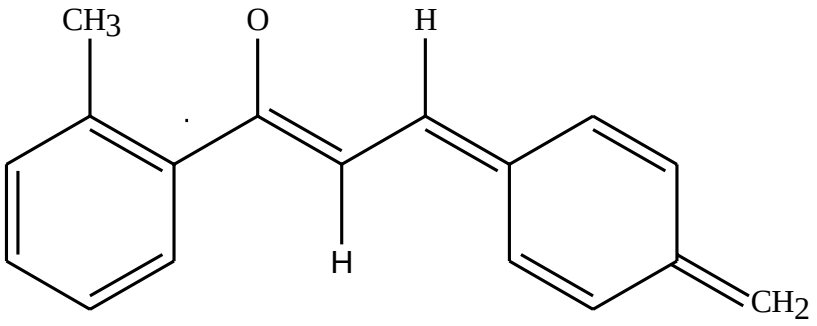


Fig 1: The resonance conjugated-structure

Table 2: The ultraviolet absorption maxima (λmax, nm) infrared absorptions (ν, cm^{-1}) and NMR chemical shifts (δ, ppm) of substituted styryl 2-methyl phenyl ketones

Entry	subt.	λmax(nm)	IR ν(cm^{-1})						^{1}H NMR δ(ppm)		^{13}C NMR δ(ppm)		
			CO cis	CO trans	CHip	CHop	CH=CHop	C=Cop	H_α	H_β	C_α	C_β	CO
1	H	306.5	1664.57	1593.2	1166.93	758.02	1049.28	557.43	7.55	7.67	122.32	144.66	190.76
2	4-Br	317.5	1670.35	1597.06	1066.64	761.88	1008.77	489.92	7.27	7.81	119.71	142.08	179.08
3	2-Cl	331	1618.28	1523.76	1091.71	754.17	1091.71	526.51	7.28	7.79	123.34	140.42	177.98
4	4-Cl	305.5	1668.43	1597.06	1089.78	761.88	1008.77	495.71	7.24	7.76	123.48	142.91	190
5	4-F	308.5	1664.57	1595.13	1118.71	754.17	1001.06	543.93	7.33	7.57	123.49	142.83	189.68
6	4-CH3	311.5	1658.78	1591.27	1120.64	775.38	1004.9	503.42	7.25	7.76	123.45	142.85	190.26
7	2-NO2	259	1668.43	1602.85	1138	742.59	1004.63	582.5	7.52	8.15	123.48	142.91	188.26
8	3-NO2	276.5	1668.43	1604.77	1093.64	731.02	997.2	570.93	7.47	8.26	123.46	142.76	190.24
9	4-NO2	309	1666.5	1591.27	1109.07	742.59	995.27	540.07	7.46	8.05	122.61	143.33	187.98

Table 3: Results of statistical analysis of ultraviolet absorption maxima ($\lambda_{max,}$ nm) infrared absorptions (v, cm1) and NMR chemical shifts (δ, ppm) of substituted styryl 2-methylphenyl ketones with Hammett σ, σ^+, σ_I, σ_R and F and R parameters.

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
λmax (nm)	σ	0.906	315.007	- 38.45	17.808	7	H,4-Br,2-Cl,4-Cl,4-F,4- CH_3, 4-NO_2.
	σ^+	0.821	310.46	- 24.18	20.82	9	H,4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4- NO_2.
	σ_I	0.903	315.88	-30.6	21.57	7	H,4-Br,2-Cl,4-Cl,4-F, 4-CH_3, 4-NO_2.
	σ_R	0.906	297.81	- 62.27	18.34	7	H,4-Br,2-Cl,4-Cl,4-F,4- CH_3, 4-NO_2.
	F	0.832	315.75	- 29.24	21.63	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	R	0.905	296.96	- 50.87	19.24	7	H,4-Br,2-Cl,4-Cl,4-F,4- CH_3, 4-NO_2.
CO*s-cis*	σ	0.854	1657.4	11.06	16.94	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	σ^+	0.802	1660.59	1.06	17.47	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	σ_I	0.909	1658.46	5.76	17.4	8	H,4-Br,4-Cl,4-F,4-CH_3,2-NO_2, 3-NO_2, 4-NO_2.
	σ_R	0.733	1662.97	25.61	16.45	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	F	0.815	1656.85	9.19	17.27	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	R	0.9	1662.7	15.53	17.01	8	H,4-Br, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
CO*s-trans*	σ	0.9	1583.57	15.46	25.73	8	H,4-Br,4-Cl,4-F,4-CH_3,2-

							NO_2,3-NO_2,4-NO_2.
	σ^+	0.901	1588.77	-0.91	26.42	8	H,4-Br,4-Cl,4-F,4-CH_3,2-NO_2, 3-NO_2, 4-NO_2.
	σ_I	0.905	1586.4	4.86	26.39	8	H,4-Br,4-Cl,4-F,4-CH_3,2-NO_2, 3-NO_2, 4-NO_2.
	σ_R	0.722	1591.7	40.21	24.76	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	F	0.901	1583.36	11.55	26.21	8	H,4-Br,4-Cl,4-F,4-CH_3,2-NO_2, 3-NO_2, 4-NO_2.
	R	0.822	1591.26	24.27	25.68	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
CH_{ip}	σ	0.752	1113.94	- 10.61	31.58	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	σ^+	0.726	1116.75	-19.5	30.73	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	σ_I	0.742	1132.61	- 59.53	28.27	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	σ_R	0.872	1113.03	30.77	31.05	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	F	0.703	1128.58	- 40.62	29.54	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	R	0.821	1113.64	26.85	31.09	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
CH_{op}	σ	0.987	763.57	- 31.63	6.77	9	H,4-Br, 2-Cl, 4-Cl, 4-F,4-CH_3,2-NO_2,3-NO_2,4-NO_2..
	σ^+	0.983	762.22	- 27.43	7.65	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	σ_I	0.807	769.57	- 37.53	9.14	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.

	σ_R	0.805	750.86	- 33.23	11.8	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	F	0.802	768.7	- 34.23	9.84	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	R	0.808	750.14	- 29.54	11.83	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
CH=CH_{op}	σ	0.702	1027.5	- 30.04	32.09	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	σ^+	0.807	1020.25	-7.24	34.01	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	σ_I	0.902	1032.56	- 34.15	32.74	7	H,4-Br,4-Cl,4-F,2-NO_2, 3-NO_2, 4-NO_2.
	σ_R	0.802	1014.84	- 38.87	32.97	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	F	0.903	1037.51	- 44.11	31.61	7	H,4-Br,4-Cl,4-F,4-CH_3,2-NO_2, 3-NO_2, 4-NO_2.
	R	0.701	1015.95	- 17.48	33.86	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
C=C_{op}	σ	0.805	518.06	51.68	29.18	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	σ^+	0.704	522.2	38.71	31.3	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	σ_I	0.803	517.65	39.35	33.63	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	σ_R	0.804	540.55	75.85	30.86	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	F	0.803	515.7	42.37	33.2	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.
	R	0.804	542.07	66.23	31.09	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-CH_3,2-NO_2,3-NO_2,4-NO_2.

Chemical shifts	Constants	r	I	ρ	s	n	Correlated derivatives
δHα(ppm)	σ	0.9	7.31	0.18	0.11	8	4-Br,2-Cl,4-Cl,4-F,4- CH3,2-NO2,3-NO2,4- NO2.
	σ+	0.809	7.32	0.14	0.11	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σI	0.801	7.34	0.06	0.13	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σR	0.806	7.4	0.39	0.09	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	F	0.801	7.34	0.05	0.13	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	R	0.806	7.41	0.34	0.09	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
δHβ(ppm)	σ	0.989	7.69	0.56	0.11	7	H,4-Br,2-Cl,4-Cl,4-F,2- NO2, 4-NO2.
	σ+	0.883	7.16	0.48	0.13	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σI	0.857	7.65	0.49	0.2	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σR	0.808	7.94	0.89	0.14	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4-
							NO2.

	F	0.805	7.7	0.37	0.22	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	R	0.881	7.95	0.78	0.14	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
δCO(ppm)	σ	0.702	187.02	0.37	5.32	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σ+	0.741	188.22	-3.43	5.12	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σI	0.795	188.82	-3.94	5.19	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σR	0.851	187.61	5.89	5.14	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	F	0.802	187.92	-1.77	5.29	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	R	0.721	187.61	4.12	5.12	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
δCα(ppm)	σ	0.808	122.72	0.29	1.32	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σ+	0.804	122.91	-0.29	1.32	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4-
							NO2.

	σI	0.801	122.7	0.26	1.32	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σR	0.848	122.81	-0.03	1.33	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	F	0.84	122.57	0.54	1.32	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	R	0.82	122.83	0.13	1.33	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
δCβ(ppm)	σ	0.8	142.75	- 0.003	1.19	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σ+	0.813	142.93	-0.58	1.16	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σI	0.736	142.36	-1.43	1.12	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	σR	0.875	142.91	1.94	1.1	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	F	0.721	143.24	-1.1	1.14	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4- NO2.
	R	0.726	142.92	1.47	1.13	9	H,4-Br,2-Cl,4-Cl,4-F,4- CH3, 2-NO2, 3-NO2, 4-

λ_{max}CO (nm) = 308.017 (±12.923)– 22.995 (±7.334) σ_I– 57.611 (±19.331)σ_R

λ_{max}CO (nm)=310.268(±12.549) – 30.192 (±10.332) F – 51.600 (±17.100) R

The carbonyl stretching frequencies (cm1) of s-cis and s-trans of isomers…(2) (R = 0.967, tabulated in Table-2 and the corresponding conformers are shown in Fig 2. …(3) (R = 0.967,

3. 2. IR spectral study

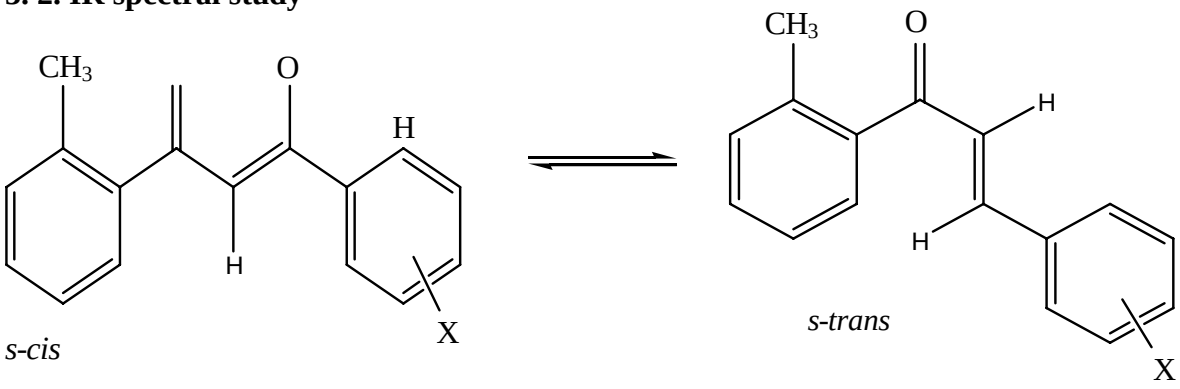


Fig 2: The s-cis and s-trans conformers of 2-methyl chalcones

The stretching frequencies for carbonyl absorption are assigned based on the assignments made by Hays and Timmons [39] for *s-c is* and *s-trans* conformers at 1690 and 1670 cm^{-1}, respectively. The assigned infrared CO *s-cis* and *s-trans* conformers have been correlated with Hammett substituent constants and Swain-Lupton constants [40]. In this correlation the structure parameter Hammett equation employed is as shown in the following equation:

$\nu = \rho\sigma + \upsilon_0$…(4)

Where υ is the carbonyl frequencies of substituted system and υ_0 is the corresponding quantity of unsubstitued system; σ is a Hammett substituent constant, which in principle is characteristics of the substituent and ρ is a reaction constant which is depend upon the nature of the reaction.

The results of statistical analysis [35 - 39] were shown in **Table 3**, From **Table 3**, the inductive and resonance components only correlated satisfactorily with CO *s- cis* conformer's stretches. The remaining Hammett substituent constants and F parameters were failing in correlation. However, the $CO_{s\text{-}trans}$ frequencies have shown satisfactory correlations with Hammett σ, σ^+&σ_I constants and F parameter have also shown satisfactory correlations. The resonance components only fail in correlations. This is due to the

reasons stated in earlier and is associated with the resonance conjugative structure shown in **Fig 1**.

the correlation of CH_{ip} modes with Hammett constants and F and R parameters were fail in correlations. But the Hammett σ and σ^+ constants are correlated satisfactorily with CH_{op} modes of all chalcones. The remaining Hammett substituent constants, F and R parameters gave poor correlation This failure in correlation is due to the incapability of polar and inductive effects of the substituent's and associated with the resonance conjugative structure as shown in **Fig 1**.

The Hammett constant σ_I and F parameter gave satisfactory correlation with $CH{=}CH_{op}$ modes. The polar and resonance components of the substituents are failed in correlation. All the Hammett constants and F and R parameters were failed in correlations with C=C*op* modes. This is due to the reasons stated earlier and associated with the resonance conjugative structure as shown in **Fig - 1**.

Some of the single parameter correlations with Hammett substituent constants were not obeyed in the regression. While seeking these parameters in multi-regression, with F and R Swain-Lupton's constants [40], they gave satisfactory correlations with the infrared red group frequencies. The multi correlation equations are given in (5 – 16).

$\nu CO_{s\text{-}cis}^{(cm\text{-}1)}$=1661.891(±12.375)+2.442 (±0.140)σ_I+25.118 (±8.271)σ_R ……..…(5)
(R = 0.933,n=9, P>95%)

$\nu CO_{s\text{-}cis}^{(cm\text{-}1)}$=1658.525(±12.328) +9.485(±2.162) F+15.759(±4.330)R…..(6)
(R = 0.927,n=9,P>95%)

$\nu CO_{s\text{-}trans}^{(cm\text{-}1)}$=1591.904(±18.635)– 0.453 (±0.101)σ_I+ 40.306 (±13.223)σ_R.....(7)
(R = 0.934, n=9, P>95%)

$\nu CO_{s\text{-}trans}^{(cm\text{-}1)}$=1585.974 (±18.682) + 12.006 (±3.002) F + 24.561 (±8.051)R...(8)

$\nu CH_{ip}^{(cm\text{-}1)}$=1138.394(±20.017) 57.126 (±18.420)σ_I+42.346(±13.531)σ_R……(9)
(R = 0.955,n=9,P>95%)

$\nu CH_{ip}^{(cm\text{-}1)}$=1131.334(±21.138)– 40.153(±12.105)F+25.896(±7.204)R...(10)
(R = 0.942,n=9,P>90%)

$\nu CH_{op}^{(cm\text{-}1)}$=765.982(±5.209)–34.052 (±11.011) σ_I– 26.338 (±9.931)σ_R……(11)
(R = 0.987,n=9,P>95%)

$\nu CH_{op}^{(cm\text{-}1)}$=765.472(±4.407)–34.795 (±11.832) F – 30.373 (±10.431)R……(12)

$\nu CH{=}CH_{op}^{(cm\text{-}1)}$=1028.085(±24.001)–29.822(±9.491)σ_I–32.838(±10.496)$\sigma_{R...}$(13)
(R = 0.935,n=9,P>95%)

$\nu CH{=}CHo_{p}^{(cm1)}$=1035.542(±22.952)–44.459(±14.912)F18.553(±6.431)R…(14)
(R = 0.940,n=9,P>95%)

$\nu C{=}Co_{p}^{(cm\text{-}1)}$=527.178 (±22.343)+ 30.139 (±10.604)σ_I+ 69.754 (±23.131)σ_R……(15)
(R = 0.954,n=9,P>95%)

$\nu C{=}Co_{p}^{(cm\text{-}1)}$=522.854(±20.817)+ 43.615 (±6.391) F + 67.280 (±22.671)R……(16)

NMRSpectral study

^{1}HNMR spectra

From the ^{1}H NMR spectra of chalcones the chemical shifts (δ, ppm) H_α and $H_\beta$are assigned and tabulated in **Table - 2**. These chemical shifts were correlated with Hammett substituent constants, F and R parameters. The statistical analysis [35 - 39] of these chemical shifts is presented in Table 3. From Table 3, the H_α and H_β chemical shifts (δ, ppm) are correlated satisfactory with Hammett σ constant. The inductive, resonance and Field effects of the substituents were fail in correlations. The failure in correlation for both chemical shifts arethe reasons stated earlier and associated with the resonance conjugated structure shown in **Fig - 1**.

Some of the single parameter correlations with Hammett substituent constants were not obeyed in the regression. While seeking these parameters in multi-regression, with F and R Swain-Lupton's [40] constants, they gave satisfactory correlations with the chemical shifts of (δ, ppm) H_α and H_β. The multi correlation equations are given in (17-20).

δH_α(ppm)=7.399(±0.072)+ 0.014(±0.011) σ_I+0.395(±0.173)σ_R…….(17)
(R = 0.969,n=9,P>95%)

(16) (R = 0.9

δH_α(ppm)=7.385(±0.706)+ 0.064(±0.133) F+0.351(±0.152)R…….……(18)
(R= 0.969,n=9,P>90%)

δH_β(ppm)=7.767(±0.060)+0.390(±0.117)σ_I +0.817(±0.145)σ_R……..…(19)
(R = 0.945,n=9,P>96%)

$\delta H_{\beta}^{(ppm)}$=7.785(±0.063)+0.391(±0.120) F+0.791 (±0.136) R……(20)
(R = 0.993,n=9,P>96%)

^{13}CNMR spectra

The carbonyl carbon, Cα and Cβ chemical shifts (δ, ppm) of 2-methylphenyl chalcones were assigned and tabulated in **Table 2**. These chemical shifts are correlated [35 - 39] with Hammett

substituent constants, F and R parameters. The results of statistical analysis are shown in **Table 3**. From **Table 3**, all the ^{13}C NMR chemical shifts of C_α, C_β and carbonyl carbons were failed in correlations with all the Hammett constants and F and R parameters this is due to the reasons stated in earlier and associated with the resonance conjugative structure shown in **Fig 1.**

The multi regression analysis of carbonyl carbon, Cα and Cβ chemical shifts (δ, ppm) of 2- methyl chalcones were satisfactorily correlated with σ_I, σR and Swain-Lupton's [40]F and R parameters.

$\delta C_\alpha(ppm)=122.592(\pm0.968)+0.542(\pm0.18)$ F +0.144 (±0.095)R ……(24)
(R= 0.920,n=9,P>92%)

$\delta C_\beta(ppm)=143.673(\pm0.746)–1.730(\pm0.442)\ \sigma_I–2.290(\pm0.786)\sigma_R$ ……(25)
(R = 0.955,n=9,P>95%)

$\delta C_\beta(ppm)=143.394(\pm0.795)–1.078(\pm0.509)$ F +1.453(±0.421)R ……(26)
(R = 0.941,n=9,P>95%)

CONCLUSION

We have synthesized a series of 2-methyl chalcones by solvent free solid SiO2-H2SO4 acid catalyzed crossed aldol condensation between 2-Methylcetophene-one and benzaldehydes. The yield sof the styryl 2-methylphenylketones were more than 85%. The effect of substituent on the group frequencies of the synthesized chalcones were studied using Hammett correlation and F & R parameters.

The multi-regression equation are given in(21-26)

$\delta CO(ppm)=189.760(\pm3.731)-4.846\ (\pm1.208)\sigma_I+ 6.874(\pm2.927)\sigma_R$…(21)
(R = 0.936,n=9,P>95%)

$\delta CO(ppm)=188.355(\pm3.809)-1.694(\pm0.224)$ F+4.080 (±1.238)R……(22)
(R = 0.922,n=9,P>95%)

$\delta C_\alpha(ppm)=122.691(\pm0.998)+0.273(\pm1.01)\ \sigma_I–0.090\ (\pm0.030)\sigma_R$……...(23)
(R = 0.905,n=9,P>91%)

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condensation between 2-Methylcetophene-one and benzaldehydes. The yield sof the styryl 2-methylphenylketones were more than 85%. The effect of substituent on the group frequencies of the synthesized

chalcones were studied using Hammett correlation and F & R parameters.

REFERENCES

1. Awasthi S.K., Mishra N., Kumar B., Sharma M., Bhattacharya A., Mishra L.C., Bhasin V.K., Potent antimalarial (2009).
2. LimS.S., Kim H.S., LeeD.U., Bulletin of the Korean Chemical Society 28 (2007) 2495-2497.
3. Ilango K, Valentina P, Saluja G, Biological and Chemical Sciences1 (2010) 354-359.
4. KuB.M., RyuH.W., LeeY.K.,Ryu J., Jeong J.Y., Choi J., Park K.H., Kang S.S., Biochem Biophys Res Commun 402 (2010) 525.
5. Dimmock J.R., Elias D. W., Beazely M.A., Kandepa N.M., Curr Med Chem 6 (1999) 1125
6. Kazauki, K., Htayama K., Yokomor S., Soki T., Chem. Abstr., 85(1976) 5913.
7. Rupe H, Wasserzug D., Chem. Ber., 34(1901) 3527
8. Szell T., Chem. Ber., 92 (1959) 1672
9. Lyle R. B., Paradis L. P., J. American Chem. Soc., 77(1955) 6667.
10. Hermes S. A., Chem. Abstr 70(1969) 96422h
11. Rawal A. A., Shah N. M., Indian J. Chem., 21(1962) 234
12. Cheng P. L., Fournari P., Tirouflet J., Bull. Soc. Chim. France, (1963)102248;Chem. Abstr.,60, 1683 (1964)
13. Kurodo C., Matsukuma T., Sci. Papers Inst. Phys. Chem. Res. (Tokyo), 18 (1932) 51.
14. Breslow, D. S. Houser C. R., J. American Chem. Soc., 62(1940) 2385.
15. Jadav G.V., Kulkarni V.G.,Curr. Sci. (1944).
16. ReichelL.,Naturwissenschallen,32(1944) 215; Chem. Abstr., 10(1946) 2441
17. Vlasov V. M., Izu. Sib. Otd, Akad. Nauk. S. Ser. Khim. Nauk.,2 (1971)96; Chem. Abstr., 76 (1972) 140411d.
18. Caddick S., Tetrahedron, 51(1995) 10403
19. Thirunarayanan, G., & Vananga--mudi,G.(2006). Arkivoc.12, 58
20. Salehi, P., Dabiri, M., Zolfigol, M. A., & Fard M.A.B.(2004).J. Braz. Chem. Soc.15 (5), 773.

21. Thirunarayanan, G., & Anantha krishna Nadar, P.(2006).
22. J. Indian Chem.Soc.83, 1107.
23. Palleros,D. R.(2004). J. Chem. Edu.81(9), 1345.
24. Basaif, S.A., Sobahi, T.R., Khalil, A.K., & Hassan, M.A.(2005).
25. Bull. Korean Chem. Soc. 26(11), 1677.
26. Xu,Q.,Yang, Z.,Yin, D, & Zhang,F.(2008).Catal. Commun.9(1), 1579.
27. Blackwell, H.E. (2006).Curr. Opin. Chem. Biol. 10 (3), 203
28. Zhang, Z., Dong, Y.W.,& Wang,G.W.(2003).Chem.Lett.32(10), 96
29. Thirunarayanan, G.(2010). Iup. JJThirunarayanan,G. "Proceedings of the 46th Annual convention of Chemists and International Johnson, B. F. G., Lewis, J., Stephenson, G.R., & Vichi, E.J. S.(1978). J. Chem. Soc. Dalton Trans. 369
30. Fernandes, N. S., Carvalho Filho, M.A. S., Mendes, R.A., Meliosand, C. B., & Ionashiro, M. (2010). J. Thermal Anal.Cal.76, 193.
31. Xiuying, Y., & An-shun,P.(2004). J.Linyi Teachers Coll. 23, O621.3.
32. Krishna Kumar, B., Velmuga R., & Swaminathan, M.(2011). Catal. Commun. 12(5), 375.
33. Conference on recent research trends in chemical sciences" 2009, No. ORG OP5, pp.C13.
34. Rajput, J.K., Kaur,G.(2012).
35. Tetrahedron Letters.53.646
36. Ranganathan, K, Arulkumaran, R., Kamalakkannan, D., Sundararajan, R., Sakthinathan, S. P., Vijaya Kumar, S., Suresh, R., Vanangamudi, G., Thirumurthy,K., Mayavel,P., & Thirunarayanan, G.(2012).Int. J.Pharm.Med. Bio.Sc. 1(1),62.
37. Janaki P., Sekar K. G., Thirunarayanan G.,) 68- Org. Chem: An Indian J. 9(2), (201380.
38. Thirunarayanan G., Vanangamudi G., Subramanian M., Organic Chem: An Indian J.9(1),(2013)1-
39. Vanangamudi G., Subramanian S., Jayanthi P., Arul kumaran R., Kamalakkannan D., Thirunarayanan G., Arab. J.Chem., 2010, DOI: 10.1016/j.arabjc.2010.07.019.
40. Thirunarayanan G., Anantha Krishna Nadar P., J. Indian Chem. Soc.83 (11),(2006)1107-1112.
41. Thirunarayanan G., Thirumurthy K., Vanangamudi G., Subramanian M., Arul

kumaran R., Kamalakkannan D., Sundararajan R., Sakthinathan S. P.,Vijayakumar S., Ranganathan K., Suresh R., Elixir Org. Chem. 45 (2012) 7898-7905.

42. Swain C.G., Lupton Jr .E.C.,J. Am.Chem.Soc.90(16),(1968) 4328-4337.