

Synthesis, characterization and substituent effects in substituted styryl 4-chloro-1-naphthyl ketones

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Abstract : A series of substituted styryl 4-chloro-1-naphthyl ketones [(2*E*)-1-(4-chloro-1-naphthyl)-3-phenyl-2-propen-1-ones] were synthesized using microwave assisted condensation reaction. The yield of chalcones is more than 87%. They are characterized by their physical constants, microanalyses and spectral (IR, ^1H and ^{13}C NMR) data. These spectral data are correlated with various Hammett substituent constants. From the results of statistical analysis the effect of substituents on CO, α - and β -protons and carbons are explained.

Keywords : Ketones, substituent effect, statistical analysis.

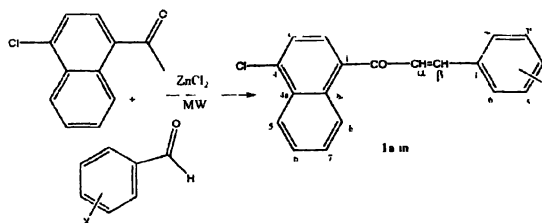
Microwave irradiation of substituted benzaldehydes and 4-chloro-1-naphthyl ketones in presence of anhydrous zinc chloride gave exclusively high yield of substituted styryl 4-chloro-1-naphthyl chalcones. Their basic chalcone skeletons are widely figured in natural products and are known to have multi pronged activity¹. Many of the chalcones are used as agrochemicals and drugs²⁻⁴. Recently much attention has paid on the synthesis of chalcones mainly from acetophenone analogs⁵ with various substituted benzaldehydes. Several catalysts such as basic alumina⁶, $\text{Al}_2\text{O}_3\text{-AlPO}_4$ ⁷, $\text{P}_2\text{O}_5\text{-piperidone}$ ⁸ ultrasonic rays using C-200⁹ and Lewis acids^{10,11} have been used for Knoevenagel condensation and bases¹²⁻¹⁵ or quaternary ammonium salts¹⁶ have also been employed. Further studies on the efficient synthesis of chalcones are of current interest because of their wide range of application. Thus the authors to report here for the first time a simple facile approach to synthesis high yield of substituted styryl 4-chloro-1-naphthyl chalcones.

Experimental

General procedure for synthesis of chalcones under microwave conditions :

A mixture of substituted benzaldehyde (0.01 mol) and 4-chloro-1-naphthyl ketones (0.01 mol) and anhydrous zinc chloride (0.001 mol) was taken in ACE tube and flushed with argon and tightly capped. The mixture is subjected to microwave heating for 5-8 min in a domestic microwave oven (LG Microwave Oven MG-395WA) and then it is allowed to reach room temperature. The

reaction mixture was treated with ethanol and the separated solid was filtered, washed with *n*-hexane and dried. The solid was recrystallised by benzene-hexane mixture¹⁷. The reaction is shown in Scheme 1.

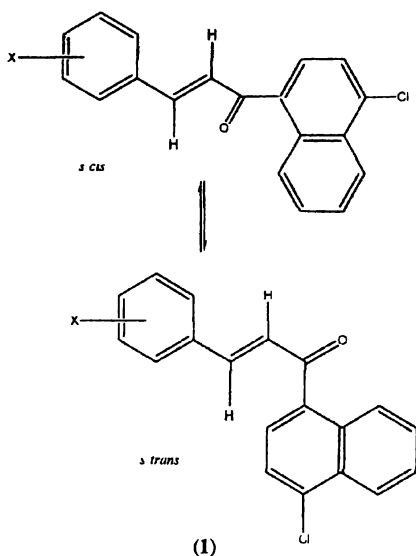


where X = H, *m*-NH₂, *p*-NH₂, *m*-Br, *m*-Cl, *p*-Cl, *p*-N(CH₃)₂,
p-OH, *p*-OCH₃, *p*-CH₃, *o*-NO₂, *m*-NO₂, *p*-NO₂

Scheme 1

Melting points were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000-400 cm⁻¹) were recorded on JASCO IR-700 spectrophotometer. The nuclear magnetic resonance spectra both (^1H - and ^{13}C -) of chalcones were recorded using UNITYPLUS-300 "KIBSIPS" 300 MHz spectrometer, operating at 200 MHz for ^1H NMR spectra and 75.45 MHz for ^{13}C NMR spectra. The micro analyses of the chalcones were performed in Perkin-Elmer 240C analyzer.

Based on Hays and Timmons^{18,19} infrared carbonyl stretching frequencies of *s-cis* and *s-trans* conformers are assigned. The NMR chemical shifts (ppm) of ethylene α ,



where X = H, *m*-NH₂, *p*-NH₂, *m*-Br, *m*-Cl, *p*-Cl, *p*-N(CH₃)₂,
p-OH, *p*-OCH₃, *p*-CH₃, *o*-NO₂, *m*-NO₂, *p*-NO₂

β protons and carbons are assigned on the basis of literature values²⁰⁻²⁵. Physical constants, micro analysis and the spectral characterization data of all compounds are summarized (1a-m).

1a. (2*E*)-1-(4-chloro-1-naphthyl)-3-phenyl-2-propen-1-one : m.p. 122–123°C; IR (KBr, cm⁻¹) 1664 (CO *s-cis*), 1637 (CO *s-trans*), 1027 (CH=CH); ¹H NMR (CDCl₃) δ 8.293 (1H, d, H-α), 8.340 (1H, d, H-β), 7.380–8.257 (11H, m, Ar-H); ¹³C NMR (CDCl₃) δ 122.320 (C-α), 142.420 (C-β), 193.130 (CO), 134.651 (C-1), 129.204 (C-2), 128.680 (C-3), 142.698 (C-4), 128.439 (C-5), 128.031 (C-6), 134.651 (C-7), 121.204 (C-8), 129.204 (C-4a), 132.800 (C-8a), 137.600 (C-1'), 126.511 (C-2',6'), 128.430 (C-3',5'), 127.353 (C-4') (Found : C, 77.91; H, 4.43. Calcd. for C₁₉H₁₃ClO (292.75) : C, 77.95; H, 4.48%).

1b. (2*E*)-1-(4-chloro-1-naphthyl)-3-(3-aminophenyl)-2-propen-1-one : m.p. 97–98°C; IR (KBr, cm⁻¹) 1666 (CO *s-cis*), 1611 (CO *s-trans*), 1020 (CH=CH), 3578 (NH₂); ¹H NMR (CDCl₃) δ 8.162 (1H, d, H-α), 8.280 (1H, d, H-β), 6.813–7.9073 (10H, m, Ar-H), 4.580 (2H, s, NH₂); ¹³C NMR (CDCl₃) δ 121.620 (C-α), 142.580 (C-β), 192.820 (CO), 134.924 (C-1), 130.001 (C-2), 127.917 (C-3), 141.942 (C-4), 127.990 (C-5), 127.990 (C-6), 136.471 (C-7), 119.004 (C-8), 130.940 (C-4a), 131.997 (C-8a), 133.417 (C-1'), 117.018 (C-2'), 144.114 (C-3'), 117.018 (C-4'), 130.417 (C-5'), 117.018 (C-6') (Found : C, 73.93; H, 4.56; N, 4.49. Calcd. for C₁₉H₁₄ClNO

(307.77) : C, 74.15; H, 4.58; N, 4.55%).

1c. (2*E*)-1-(4-chloro-1-naphthyl)-3-(4-aminophenyl)-2-propen-1-one : m.p. 78–79°C; IR (KBr, cm⁻¹) 1658 (CO *s-cis*), 1613 (CO *s-trans*), 1007 (CH=CH), 3513 (NH₂); ¹H NMR (CDCl₃) δ 8.124 (1H, d, H-α), 8.250 (1H, d, H-β), 6.952–7.907 (10H, m, Ar-H), 4.520 (2H, s, NH₂); ¹³C NMR (CDCl₃) δ 121.101 (C-α), 146.620 (C-β), 189.700 (CO), 133.457 (C-1), 129.240 (C-2), 127.240 (C-3), 138.010 (C-4), 127.214 (C-5), 126.274 (C-6), 136.017 (C-7), 120.004 (C-8), 130.015 (C-4a), 131.815 (C-8a), 125.117 (C-1'), 127.117 (C-2',6'), 118.174 (C-3',5'), 134.170 (C-4') (Found : C, 74.13; H, 4.52; N, 4.54. Calcd. for C₁₉H₁₄ClNO (307.77) : C, 74.15; H, 4.58; N, 4.55%).

1d. (2*E*)-1-(4-chloro-1-naphthyl)-3-(3-bromophenyl)-2-propen-1-one : m.p. 118–115 °C; IR (KBr, cm⁻¹) 1674 (CO *s-cis*), 1622 (CO *s-trans*), 1033 (CH=CH); ¹H NMR (CDCl₃) δ 8.373 (1H, d, H-α), 8.600 (1H, d, H-β), 7.361–7.999 (10H, m, Ar-H); ¹³C NMR (CDCl₃) δ 123.006 (C-α), 142.616 (C-β), 194.033 (CO), 131.881 (C-1), 129.416 (C-2), 128.809 (C-3), 142.616 (C-4), 129.416 (C-5), 128.640 (C-6), 138.809 (C-7), 120.243 (C-8), 131.851 (C-4a), 131.851 (C-8a), 142.616 (C-1'), 129.410 (C-2'), 123.006 (C-3'), 131.851 (C-4'), 129.416 (C-5'), 125.441 (C-6') (Found : C, 61.37; H, 3.21. Calcd. for C₁₉H₁₂BrClO (371.65) : C, 61.40; H, 3.25%).

1e. (2*E*)-1-(4-chloro-1-naphthyl)-3-(3-chlorophenyl)-2-propen-1-one : m.p. 67–68°C; IR (KBr, cm⁻¹) 1668 (CO *s-cis*), 1627 (CO *s-trans*), 1036 (CH=CH); ¹H NMR (CDCl₃) δ 8.362 (1H, d, H-α), 8.372 (1H, d, H-β), 7.348–7.908 (10H, m, Ar-H); ¹³C NMR (CDCl₃) δ 120.636 (C-α), 142.704 (C-β), 192.570 (CO), 135.240 (C-1), 128.953 (C-2), 128.703 (C-3), 140.765 (C-4), 128.952 (C-5), 128.438 (C-6), 135.233 (C-7), 120.405 (C-8), 129.310 (C-4a), 131.724 (C-8a), 126.785 (C-1'), 126.676 (C-2'), 135.233 (C-3'), 128.438 (C-4'), 128.953 (C-5'), 124.903 (C-6') (Found : C, 69.70; H, 3.69. Calcd. for C₁₉H₁₂Cl₂O (327.20) : C, 69.74; H, 3.70%).

1f. (2*E*)-1-(4-chloro-1-naphthyl)-3-(4-chlorophenyl)-2-propen-1-one : m.p. 115–116°C; IR (KBr, cm⁻¹) 1669 (CO *s-cis*), 1634 (CO *s-trans*), 1031 (CH=CH); ¹H NMR (CDCl₃) δ 8.040 (1H, d, H-α), 8.329 (1H, d, H-β), 7.479–7.855 (10H, m, Ar-H); ¹³C NMR (CDCl₃) δ 121.472 (C-α), 142.672 (C-β), 195.470 (CO), 134.950 (C-1), 128.740 (C-2), 128.623 (C-3), 134.800 (C-4), 128.564 (C-5), 127.019 (C-6), 136.760 (C-7), 123.590 (C-8), 129.400 (C-4a), 131.340 (C-8a), 136.540 (C-1'), 127.019 (C-2',6'), 129.720 (C-3',5'), 135.472 (C-4') (Found : C, 69.71; H, 3.66. Calcd. for C₁₉H₁₂Cl₂O (327.20) : C, 69.74; H, 3.70%).

1g. (2*E*)-1-(4-chloro-1-naphthyl)-3-(4-dimethylamino-phenyl)-2-propen-1-one : m.p. 123–124°C; IR (KBr, cm^{-1}) 1654 (CO *s-cis*), 1606 (CO *s-trans*), 999 (CH=CH); ^1H NMR (CDCl_3) δ 8.009 (1H, d, H- α), 8.014 (1H, d, H- β), 6.184–8.004 (10H, m, Ar-H), 3.19 (6H, s, $(\text{CH}_3)_2$); ^{13}C NMR (CDCl_3) δ 120.620 (C- α), 141.702 (C- β), 189.339 (CO), 42.220 (CH_3), 137.470 (C-1), 126.410 (C-2), 127.001 (C-3), 130.017 (C-4), 126.994 (C-5), 126.984 (C-6), 127.009 (C-7), 128.947 (C-8), 129.019 (C-4a), 129.091 (C-8a), 125.474 (C-1'), 126.417 (C-2',6'), 115.470 (C-3',5'), 156.401 (C-4') (Found : C, 75.01; H, 5.33; N, 4.14. Calcd. for $\text{C}_{21}\text{H}_{18}\text{ClNO}$ (335.82) : C, 75.11; H, 5.40; N, 4.17%).

1h. (2*E*)-1-(4-chloro-1-naphthyl)-3-(4-hydroxyphenyl)-2-propen-1-one : m.p. 82–83°C; IR (KBr, cm^{-1}) 1661 (CO *s-cis*), 1618 (CO *s-trans*), 1011 (CH=CH), 3535 (OH); ^1H NMR (CDCl_3) δ 8.043 (1H, d, H- α), 8.217 (1H, d, H- β), 7.551–7.993 (10H, m, Ar-H), 4.630 (1H, s, OH); ^{13}C NMR (CDCl_3) δ 120.396 (C- α), 142.257 (C- β), 190.222 (CO), 141.231 (C-1), 129.057 (C-2), 127.075 (C-3), 130.213 (C-4), 128.325 (C-5), 126.541 (C-6), 126.541 (C-7), 120.517 (C-8), 130.213 (C-4a), 131.365 (C-8a), 130.213 (C-1'), 120.213 (C-2',6'), 120.366 (C-3',5'), 155.323 (C-4') (Found : C, 73.87; H, 4.22. Calcd. for $\text{C}_{19}\text{H}_{13}\text{ClO}_2$ (308.75) : C, 73.91; H, 4.24%).

1i. (2*E*)-1-(4-chloro-1-naphthyl)-3-(4-methoxyphenyl)-2-propen-1-one : m.p. 140–141°C; IR (KBr, cm^{-1}) 1664 (CO *s-cis*), 1651 (CO *s-trans*), 1015 (CH=CH); ^1H NMR (CDCl_3) δ 8.102 (1H, d, H- α), 8.431 (1H, d, H- β), 7.554–7.990 (10H, m, Ar-H), 4.070 (3H, s, OCH_3); ^{13}C NMR (CDCl_3) δ 122.651 (C- α), 142.311 (C- β), 191.475 (CO), 54.730 (OCH_3), 135.813 (C-1), 130.557 (C-2), 129.613 (C-3), 133.024 (C-4), 129.693 (C-5), 126.491 (C-6), 126.927 (C-7), 125.403 (C-8), 134.879 (C-4a), 130.381 (C-8a), 130.581 (C-1'), 129.547 (C-2',6'), 117.308 (C-3',5'), 156.324 (C-4') (Found : C, 74.38; H, 4.58. Calcd. for $\text{C}_{20}\text{H}_{15}\text{ClO}_2$ (322.78) : C, 74.42; H, 4.68%).

1j. (2*E*)-1-(4-chloro-1-naphthyl)-3-(4-methylphenyl)-2-propen-1-one : m.p. 137–138°C; IR (KBr, cm^{-1}) 1663 (CO *s-cis*), 1633 (CO *s-trans*), 1021 (CH=CH); ^1H NMR (CDCl_3) δ 8.323 (1H, d, H- α), 8.421 (1H, d, H- β), 7.296–7.987 (10H, m, Ar-H), 2.460 (3H, s, CH_3); ^{13}C NMR (CDCl_3) δ 122.244 (C- α), 142.160 (C- β), 195.198 (CO), 24.780 (CH_3), 134.269 (C-1), 129.780 (C-2), 128.844 (C-3), 146.557 (C-4), 128.390 (C-5), 126.655 (C-6), 135.958 (C-7), 120.844 (C-8), 129.830 (C-4a), 131.693 (C-8a), 135.284 (C-1'), 126.024 (C-2',6'), 129.544 (C-3',5'), 136.505 (C-4') (Found : C, 78.26; H, 4.89. Calcd.

for $\text{C}_{20}\text{H}_{15}\text{ClO}$ (306.78) : C, 78.30; H, 4.93%).

1k. (2*E*)-1-(4-chloro-1-naphthyl)-3-(2-nitrophenyl)-2-propen-1-one : m.p. 111–112°C; IR (KBr, cm^{-1}) 1678 (CO *s-cis*), 1644 (CO *s-trans*), 1019 (CH=CH); ^1H NMR (CDCl_3) δ 8.553 (1H, d, H- α), 8.572 (1H, d, H- β), 6.452–8.110 (10H, m, Ar-H); ^{13}C NMR (CDCl_3) δ 124.473 (C- α), 143.120 (C- β), 194.310 (CO), 136.204 (C-1), 129.591 (C-2), 128.717 (C-3), 140.829 (C-4), 128.603 (C-5), 127.035 (C-6), 136.035 (C-7), 122.970 (C-8), 129.204 (C-4a), 132.461 (C-8a), 126.035 (C-1'), 148.630 (C-2'), 116.219 (C-3'), 128.970 (C-4'), 123.122 (C-5'), 124.219 (C-6') (Found : C, 67.52; H, 3.50; N, 4.02. Calcd. for $\text{C}_{19}\text{H}_{12}\text{ClNO}_3$ (337.75) : C, 67.56; H, 3.59; N, 4.15%).

1l. (2*E*)-1-(4-chloro-1-naphthyl)-3-(3-nitrophenyl)-2-propen-1-one : m.p. 126–127°C; IR (KBr, cm^{-1}) 1676 (CO *s-cis*), 1642 (CO *s-trans*), 1008 (CH=CH); ^1H NMR (CDCl_3) δ 8.368 (1H, d, H- α), 8.538 (1H, d, H- β), 7.344–8.232 (10H, m, Ar-H); ^{13}C NMR (CDCl_3) δ 123.351 (C- α), 142.771 (C- β), 193.643 (CO), 134.696 (C-1), 129.404 (C-2), 128.730 (C-3), 138.173 (C-4), 128.497 (C-5), 126.974 (C-6), 136.258 (C-7), 122.691 (C-8), 130.093 (C-4a), 131.693 (C-8a), 136.730 (C-1'), 122.691 (C-2'), 148.751 (C-3'), 123.351 (C-4'), 130.092 (C-5'), 131.693 (C-6') (Found : C, 67.48; H, 3.49; N, 4.02. Calcd. for $\text{C}_{19}\text{H}_{12}\text{ClNO}_3$ (337.75) : C, 67.56; H, 3.58; N, 4.15%).

1m. (2*E*)-1-(4-chloro-1-naphthyl)-3-(3-nitrophenyl)-2-propen-1-one : m.p. 101–102°C; IR (KBr, cm^{-1}) 1677 (CO *s-cis*), 1649 (CO *s-trans*), 1004 (CH=CH); ^1H NMR (CDCl_3) δ 8.393 (1H, d, H- α), 8.425 (1H, d, H- β), 7.412–8.210 (10H, m, Ar-H); ^{13}C NMR (CDCl_3) δ 123.445 (C- α), 143.270 (C- β), 197.634 (CO), 135.404 (C-1), 129.658 (C-2), 128.804 (C-3), 140.596 (C-4), 128.543 (C-5), 127.204 (C-6), 135.404 (C-7), 120.804 (C-8), 135.404 (C-4a), 132.447 (C-8a), 127.335 (C-1'), 124.96 (C-2',6'), 114.960 (C-3',5'), 142.584 (C-4') (Found : C, 67.49; H, 3.53; N, 4.09. Calcd. for $\text{C}_{19}\text{H}_{12}\text{ClNO}_3$ (337.75) : C, 67.56; H, 3.58; N, 4.15%).

Substituent effects :

Correlation study involves the prediction of ground state molecular equilibrations^{26,27} of organic substrates such as *s-cis* and *s-trans* isomers of alkenes, alkynes, benzoyl chlorides, styrenes and α,β -unsaturated ketones from spectral data. Their use in structure parameter correlations has now become popular for studying transition state study of reaction mechanisms²⁸ and normal coordinate analysis^{29–32}. Dhimi and Stothers³³ have extensively studied the ^1H NMR spectra of a large number of acetophenones and styrenes with a view to establish the validity of the additivity of substituent effects in aromatic

shieldings, first observed by Laturber³⁴. Savin *et al.*³⁵ obtained the NMR spectra of unsaturated ketones of the type $\text{RC}_6\text{H}_4\text{-CH=CH-COCMe}_3$ and sought Hammett correlations for the ethylenic protons. Solcaniova *et al.*^{36,37} have measured ^1H and ^{13}C NMR spectra of substituted phenyl styrenes and substituted styryl phenyls and obtained good Hammett correlations for the olefinic protons and carbons. Sethuram *et al.*³⁸ correlated the group frequencies of spectral data with Hammett substituent constants to explain the substituent effect of organic compounds. Recently Dae Dong Sung and Ananthakrishna Nadar³⁹ investigated elaborately the multisubstituent effects by spectral data of biphenyl and 9H-fluorenyl chalcones. To the best of our knowledge there is no information in the literature for correlation of spectral data of substituted styryl 4-chloro-1-naphthyl ketones with Hammett constants. Hence the authors have synthesized thirteen chalcones of the above type using microwave irradiation technique, and the substituent effects of above compounds are investigated from infrared and NMR spectral data.

Substituent effects from infrared spectra :

The carbonyl stretching frequencies (cm^{-1}) of *s-cis* and *s-trans* isomers of present study are shown in Table 1 and the corresponding conformers are shown in (1). The infrared spectra were all recorded on the KBr disc in order to avoid the shoulder formation^{40,41} on carbonyl doublets. The *s-cis* conformers exhibit higher frequencies than the *s-trans* conformers due to the bulkier naph-

thalene group causes greater strain and hence enhance the higher absorption of carbonyl group of *s-cis* isomer than the *s-trans* isomer. These frequencies are separately analyzed through various Hammett sigma constants.

The single parameter correlations produce fair degree of correlation with Hammett sigma constants in the *s-cis* conformers of all the chalcones. The correlations in the *s-cis* conformers are fair enough with σ ($r = 0.999$, $I = 1666.22$, $s = 2.44$, $n = 13$); σ^+ ($r = 0.985$, $I = 1668.61$, $s = 2.62$, $n = 13$) and σ_1 ($r = 0.900$, $I = 1659.13$, $s = 8.19$, $n = 13$) constants in these compounds because conjugation is less important due to non-coplanarity arising out of non bonded repulsion between naphthalene and styryl parts in the systems. Further it is important to note in these compounds that in the *s-cis* conformers, the σ_R parameters do not satisfactorily predict the reactivity individually. In the *s-trans* conformers, σ_R constants only predict the satisfactory correlation with the values, σ_R ($r = 0.989$, $I = 1636.55$, $s = 2.19$, $n = 13$) and the other constants are failed to produce the correlation. This shows that conjugation between the C=O and the -CH=CH- parts of the system was not the determining factor for the substituent effects.

In view of the inability of some of the σ constants to produce individually satisfactory correlations, it was thought worthwhile to seek multiple correlations involving either σ_1 and σ_R constants or Swain-Lupton's F and R parameters. The correlation equations generated are given in eqs. (1-3).

Table 1. IR carbonyl stretching band (cm^{-1}) and NMR chemical shifts (ppm) of olefinic protons and carbons of substituted styryl 4-chloro-1-naphthyl ketones

Compd.	IR ν (cm^{-1})		^1H NMR δ (ppm)		^{13}C NMR δ (ppm)	
	CO (<i>s-cis</i>)	CO (<i>s-trans</i>)	H_α	H_β	C_α	C_β
1a	1664	1637	8.293	8.340	122.320	142.420
1b	1666	1611	8.162	8.280	121.620	142.580
1c	1658	1613	8.124	8.250	121.101	146.623
1d	1674	1622	8.373	8.600	123.006	142.616
1e	1668	1627	8.362	8.372	123.662	141.886
1f	1669	1634	8.040	8.329	122.966	142.997
1g	1654	1606	8.009	8.014	121.659	140.031
1h	1661	1618	8.043	8.217	118.997	141.111
1i	1664	1651	8.102	8.431	119.554	140.364
1j	1663	1633	8.323	8.421	120.262	139.852
1k	1678	1644	8.553	8.572	124.909	143.137
1l	1676	1642	8.368	8.538	119.603	145.643
1m	1677	1649	8.393	8.425	123.703	145.182

$$\nu\text{C=O (cm}^{-1}\text{)} (s\text{-cis}) = 1660.62 (\pm 2.086) + 22.759\sigma_I (\pm 4.686) + 4.448\sigma_R (\pm 3.863) \quad (1)$$

$$(R = 0.998, n = 13, P > 90\%)$$

$$\nu\text{C=O (cm}^{-1}\text{)} (s\text{-cis}) = 1665.18 (\pm 2.076) + 16.075F (\pm 4.106) + 9.250\sigma_R (\pm 2.600) \quad (2)$$

$$(R = 0.990, n = 13, P > 90\%)$$

$$\nu\text{C=O (cm}^{-1}\text{)} (s\text{-trans}) = 1634.44 (\pm 2.286) + 5.656\sigma_I (\pm 0.514) + 4.598\sigma_R (\pm 0.649) \quad (3)$$

$$(R = 0.998, n = 13, P > 90\%)$$

From the eqs. (1–3) it is inferred that in most of the cases the correlation is significant with either σ_I or σ_R or with F and R parameters together. The *s-trans* isomer failed to produce the correlation with σ_I or σ_R constants. This may be treated as exceptional and by large it is to be realized that the collective participation of either σ_I or σ_R parameters is more dependent than that of any single parameter's role to predict the substituent effects.

Substituent effects from NMR spectra :

^1H NMR spectra :

The ^1H NMR spectral signals of ethylenic protons in all chalcones are assigned and presented in Table 1. The chemical shifts of H_α protons are at higher field than those of H_β protons in all chalcones. The ethylenic proton signals appears as an AB pattern and the β protons doublet in most cases is well separated from the signals of the aromatic protons. The chemical shifts of α , β protons are given in Table 1. In the recorded chemical shift values of α , β protons, it is observed that H_α protons appear at higher field than that of H_β protons which makes the subject very interesting. This may possibly due to the polarization of $\text{C}=\text{C}$ double bond in the system being predominantly caused by the carbonyl group so as to make electron density greater at the α position than that of β position.

All the attempted correlations involving substituent parameters gave only positive ρ values. This shows normal substituent effects is operated in all the chalcones. The chemical shifts observed for H_α and the H_β protons in the present investigation are correlated satisfactorily with Hammett sigma constants. The chemical shifts of H_α produced a significant correlation with σ ($r = 0.999$, $I = 8.230$, $s = 0.203$, $n = 13$); σ^+ ($r = 0.996$, $I = 8.282$, $s = 0.207$, $n = 13$) and satisfactory with σ_R ($r = 0.927$, $I = 8.295$, $s = 0.287$, $n = 13$) constants only and the σ_I constant failed. In H_β protons cases correlation with σ values produced good and satisfactory correlations [σ ($r = 0.991$, $I = 8.347$, $s = 0.105$, $n = 13$); σ^+

($r = 0.999$, $I = 8.393$, $s = 0.098$, $n = 13$)]. The satisfactory correlation with σ_I and σ_R parameters is satisfactorily implies that such σ values are capable of predicting chemical shifts individually. [σ_I ($r = 0.998$, $I = 8.247$, $s = 0.130$, $n = 13$); σ_R ($r = 0.907$, $I = 8.420$, $s = 0.148$, $n = 13$)].

The multiple correlations involving either σ_I and σ_R or F and R values for these ketones are presented. It is observed that in most cases the multiple correlations are successful. Some of the single parameter correlations are given in expressions (4–7).

$$\delta\text{H}_\alpha (\text{ppm}) = 8.281 (\pm 0.093) + 0.288\sigma_I (\pm 0.021) + 0.173\sigma_R (\pm 0.018) \quad (4)$$

$$(R = 0.999, n = 13, P > 97\%)$$

$$\delta\text{H}_\alpha (\text{ppm}) = 8.354 (\pm 0.094) + 0.582F (\pm 0.085) + 0.348R (\pm 0.015) \quad (5)$$

$$(R = 0.999, n = 13, P > 98\%)$$

$$\delta\text{H}_\beta (\text{ppm}) = 8.387 (\pm 0.064) + 0.223\sigma_I (\pm 0.014) + 0.282\sigma_R (\pm 0.012) \quad (6)$$

$$(R = 0.909, n = 13, P > 90\%)$$

$$\delta\text{H}_\beta (\text{ppm}) = 8.424 (\pm 0.078) + 0.155F (\pm 0.100) + 0.283R (\pm 0.099) \quad (7)$$

$$(R = 0.998, n = 13, P > 96\%)$$

^{13}C NMR spectra :

From ^{13}C NMR spectra the observed carbon chemical shifts of C_α and the C_β carbons are presented in Table 1. These chemical shifts are correlated with various Hammett substituent constants. The results of statistical analysis of substituent effects on both the carbons produced good, satisfactory and fair degree of correlation of chemical shifts with Hammett sigma constants [C_α : σ ($r = 0.999$, $I = 122.085$, $s = 0.654$, $n = 13$); σ^+ ($r = 0.985$, $I = 122.441$, $s = 0.695$, $n = 13$); σ_I ($r = 0.906$, $I = 124.275$, $s = 0.833$); σ_R ($r = 0.980$, $I = 122.681$, $s = 0.799$) and [C_β : σ ($r = 0.999$, $I = 143.950$, $s = 1.327$, $n = 13$); σ^+ ($r = 0.997$, $I = 142.891$, $s = 1.336$, $n = 13$); σ_I ($r = 0.990$, $I = 142.847$, $s = 1.457$); σ_R ($r = 0.940$, $I = 142.811$, $s = 1.540$)]. The degree of transmission of electronic effects is found to be more or less equal with C_α and C_β carbons. Uniformly σ_I and σ_R parameters or F and R values are adequately explained the substituent effects well in all chalcones as evidenced from the correlation eqs. (8–11) :

$$\delta\text{C}_\alpha (\text{ppm}) = 122.006 (\pm 0.408) + 1.802\sigma_I (\pm 0.091) + 2.301\sigma_R (\pm 0.780) \quad (8)$$

$$\begin{aligned} (R = 0.999, n = 13, P > 98\%) \\ \delta C_{\alpha}(\text{ppm}) = 123.07 (\pm 0.511) - \\ 0.870F (\pm 0.124) + 3.168R (\pm 1.617) \end{aligned} \quad (9)$$

$$\begin{aligned} (R = 0.997, n = 13, P > 95\%) \\ \delta C_{\beta}(\text{ppm}) = 142.484 (\pm 0.780) + \\ 0.884\sigma_I (\pm 0.075) + 1.154\sigma_R (\pm 0.113) \end{aligned} \quad (10)$$

$$\begin{aligned} (R = 0.997, n = 13, P > 90\%) \\ \delta C_{\beta}(\text{ppm}) = 146.72 (\pm 1.002) + \\ 1.405F (\pm 1.091) + 5.722R (\pm 0.041) \end{aligned} \quad (11)$$

$$(R = 0.998, n = 13, P > 90\%)$$

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