ABSTRACT: A series of substituted styryl 4-methyl-1-naphthyl ketones \((2E)-1-(4-methyl-1-naphthyl)-3-phenyl-2-propan-1-ones\) were synthesized eco-friendly under solvent free conditions using a green catalyst SiO\(_2\)-H\(_2\)SO\(_4\) in an oven. The catalyst silica is reusable and the yields of chalcones are more than 90\%. They are characterized by their physical constants, micro analysis, infrared (KBr, 4000-400 cm\(^{-1}\)) and NMR both \(^1\)H and \(^{13}\)C and Mass spectral data. From infrared spectra, the \(\nu\)-cis and \(\nu\)-trans vibrations of carbonyl group and deformation modes \(\text{CH}_2\) in-plane and out of plane, \(\text{CH}=\text{CH}\) out of plane and \(\text{C}=\text{C}\) out of plane of vinyl parts, from NMR spectra the aromatic proton, carbons and carbonyl carbon chemical shifts (ppm) are assigned. These spectral data are correlated with various Hammett substituent constants. From the results of statistical analysis the effect of substituents on CO, \(\alpha\) and \(\beta\) proton, carbons and deformation modes are explained.

Keywords: Solvent Free Synthesis, Silica-sulphuric Acid, Styryl Naphthyl Ketones, IR and NMR Spectra, Substituent Effects, Correlation Analysis

INTRODUCTION

Stereo specific and regioselective synthetic methods are important for synthesis of biologically active carbonyl compounds through solvent free organic reactions like Claisen-Schmidt, Knoevenagel, aldol, and Crossed-aldol, Bayer-Villiger, Michael addition, oxidative methods and complex reaction like cyanohydrin formation were employed for synthesis of carbonyl compounds due to the operational simplic-
ity, easier work-up, better yield and eco-friendly nature. Among these reactions aldol condensation is useful for the formation of carbon-carbon bond in many kinds of carbonyl compounds. Due to the importance of methylene structural unit, which is found in many naturally occurring compounds, antibiotics and the use of cyclic and acyclic ketones as precursor for the synthesis of pyrimidine, flavones and coumarone derivatives. The basic skeleton of chalcones are widely figured in natural products are known to have multipronged activity.

Many of the chalcones are used as agrochemicals, drugs \(^1\) and antimicrobial agents \(^2\) such as antifungal, antibacterial, antiviral, insect antifeedant and anti-AIDS. Condensation of ketones with aldehydes is special interest and crossed-aldol condensation is an effective pathway for those preparations. But traditional acid-base catalyzed reactions suffer from the reverse reaction \(^3\) and self-condensation of starting molecules. \(^4\)

Many reagents and metal complexes of Mn (II), Fe (II), Co (II), Ni (II), Cu (II) and Zn (II) ions with various ligands have been employed for aldol condensation. \(^5\) Metal salts of Cp2ZrH2 are used for condensation of cycloalkanones. \(^6\) KF-Al2O3 and bis (p-methoxy phenyl) tellurides have been used for crossed condensation under microwave irradiation. \(^7\) Anhydrous ReCl3 and TiCl4(SO2CF2) have also been applied for aldol condensation reactions under solvent free conditions. \(^8\) Kalluraya et al. \(^9\) reported to obtain 60-70% yield of sydnone chalcones under solvent free condition by aldol condensation reaction by grinding of ketones and aldehydes with sodium hydroxide. Hassan et al. \(^10\) synthesized 60-92% yields of various 2E-3-arylideneoct-2-en-1-one by crossed aldol condensation reaction in sodium hydroxide-water heterogeneous phase reaction medium. Silica-sulphonic acid is used as a versatile and stable solid acid catalyst for organic synthesis. The author wish to report an efficient and selective method for condensation of 4-methyl-1-naphthyl ketone with various substituted benzaldehydes under solvent free conditions using silica-sulphonic acid as a catalytic reagent in an oven to yields more than 90% of the respective E-2-propen-1-ones.

**EXPERIMENTAL SECTION**

**Materials and Methods**

All chemicals and analytical grade solvents were purchased from E-Merk chemical company. Melting points of all chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr) were recorded on Perkin Elmer-Fourier transform spectrophotometer. The nuclear magnetic resonance spectra both 1H and 13C of chalcones were recorded using UNITPLUS-300 "KBSIPS" 300 MHz spectrometer. Electron impact (EI) (70 eV) and chemical ionization (CI) were recorded with a Finnigan MAT 95S spectrometer. Micro analyses of all chalcones were performed in Perkin Elmer 240C Analyzer.

**General procedure for crossed-aldol condensation of aromatic ketones with benzaldehydes**

4-Methyl-1-naphthyl ketone (2 mmol), m- and p-substituted benzaldehydes and silicic acid-sulphonic acid (1.5 g equal to 4 mmol of H+ ions) were mixed thoroughly, placed in a glass tube and capped (Scheme 1). The mixture was heated in an oven at 80°C for 2-3h. After complete conversion of the ketones as monitored by TLC, the mixture was cooled to room temperature. Dichloromethane (20-30 ml) was added and heated for 3-5 minutes. The reagent was removed by filtration. The filtrate was concentrated and the solid residue was recrystallized from ethanol to afford the glistening pale yellow colour pure products. After the product was isolated, the remaining catalyst was washed with ethyl acetate (20 ml) followed by drying in an oven at 50°C for half an hour and reused with fresh substrate for further reactions. Chalcones 1a and 1h are known and other compounds are unknown. The characterization data of all compounds are summarized.

(2E)-1-(4-Methyl-1-naphthyl)-3-phenyl-2-propen-1-one (1a) Yield: 97%; m.p.98-99(99°C); IR (KBr, cm\(^{-1}\)): δ = 1660 (CO s-trans), 1621 (CO s-trans); 1H NMR(CDC\(_3\), ppm): ν = 8.767(d, 1H, α), 8.247(d,

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(2E)-1-(4-Methyl-1-naphthyl)-3-(3-aminophenyl)-2-propen-1-one (1b) Yield: 95%; m.p. 70-71°C; IR (KBr, cm⁻¹): υ = 1652 (CO s-cis), 1626 (CO s-trans), 3569 (-NH). 1H NMR (CDCl₃, ppm): δ = 8.152(d, 1H, α), 8.194(d, 1H, β), 7.055-7.876(m, 10H, Ar-H), 4.320(s, 2H -NH₂), 2.687(s, 3H -CH₃). 13C NMR (CDCl₃, ppm): δ = 121.33(C), 142.62(C), 191.58(CO).

(2E)-1-(4-Methyl-1-naphthyl)-3-(4-aminophenyl)-2-propen-1-one (1e) Yield: 96%; m.p. 122-123°C; IR (KBr, cm⁻¹): υ = 1647 (CO s-cis), 1605 (CO s-trans), 3526(-NH). 1H NMR (CDCl₃, ppm): δ = 8.034(d, 1H α), 8.134(d, 1H β), 7.676-7.402 (m, 10H Ar-H), 4.871(s, 2H -NH₂), 2.599(CH₃). 13C NMR (CDCl₃, ppm): δ = 119.234(C), 140.606(C), 189.544(CO), 134.921(C), 128.992(C), 127.921(C), 135.059(C), 128.093(C), 127.940(C), 135.927(C), 125.814(C), 133.144(C), 129.124(C), 26.064(-CH₃), 125.270(C), 128.770(C), 117.410(C), 141.730(C). Anal. Calcd. for C₁₉H₁₄NO: C, 83.59; H, 5.96; N, 4.81. Found: C, 83.42; H, 5.90; N, 4.81. MS: m/z = 287[M⁺], 271, 169, 146, 141, 127, 118, 102, 93.

(2E)-1-(4-Methyl-1-naphthyl)-3-(3-bromophenyl)-2-propen-1-one (1d) Yield: 95%; m.p. 126-127°C; IR (KBr, cm⁻¹): υ = 1654 (CO s-cis), 1636 (CO s-trans). 1H NMR (CDCl₃, ppm): δ = 8.102(d, 1H α), 8.161(d, 1H β), 7.342-7.892(m, 10H Ar-H), 2.695(s, 3H -CH₃). 13C NMR (CDCl₃, ppm): δ = 122.40(C), 140.818(C), 192.39(CO), 134.100(C), 130.381(C), 121.630(C), 156.990(C), 127.257(C), 126.635(C), 133.363(C), 121.475(C), 132.990(C), 129.019(C), 25.652(-CH₃), 140.571(C), 129.553(C), 123.580(C), 131.528(C), 130.998(C), 124.475(C). Anal. Calcd. for C₁₉H₁₄BrO: C, 68.30; H, 4.25. Found: C, 68.30, H, 4.25. MS: m/z = 352, 350 [M⁺], 271, 211, 183, 181, 170, 168, 164, 153, 141, 89, 77, 65.

(2E)-1-(4-Methyl-1-naphthyl)-3-(3-chlorophenyl)-2-propen-1-one (1f) Yield: 92%; m.p. 97-98°C; IR (KBr, cm⁻¹): υ = 1657 (CO s-cis), 1629 (CO s-trans). 1H NMR (CDCl₃, ppm): δ = 8.315(d, 1H α), 8.327(d, 1H β), 7.520-7.843(m, 10H Ar-H), 2.864(s, 3H -CH₃). 13C NMR (CDCl₃, ppm): δ = 125.662(C), 141.886(CO), 133.492(C), 129.188(C), 126.632(C), 136.102(C), 128.414(C), 126.658(C), 133.492(C), 125.778(C), 131.492(C), 129.235(C), 24.247(CH₃), 158.551(C), 127.006(C), 133.492(C), 128.703(C), 129.188(C), 124.656(C). Anal. Calcd. for C₁₉H₁₄ClO: C, 78.30; H, 4.93. Found: C, 78.25; H, 4.86. MS: m/z = 308, 306[M⁺²], 271, 179, 167, 165, 139, 156, 113, 111, 91, 79, 77, 53, 51.

(2E)-1-(4-Methyl-1-naphthyl)-3-(4-chlorophenyl)-2-propen-1-one (1f) Yield: 93%; m.p. 80-81°C; IR (KBr, cm⁻¹): υ = 1655 (CO s-cis), 1631 (CO s-trans). 1H NMR (CDCl₃, ppm): δ = 8.174(d, 1H α), 8.297(d, 1H β), 7.127-8.000(m, 10H Ar-H), 2.543(-CH₃). 13C NMR (CDCl₃, ppm): δ = 122.966(C), 142.997(C), 191.927(CO), 133.140(C), 129.289(C), 126.63(C), 156.246(C), 128.890(C), 126.834(C), 133.020(C), 125.392(C), 130.331(C), 129.81(C), 25.648(-CH₃), 136.230(C), 127.855(C), 129.289(C), 135.276(C). Anal. Calcd. for C₁₉H₁₄ClO: C, 78.30; H, 4.93. Found: C, 78.28; H, 4.90. MS: m/z = 306, 304[M⁺²], 271, 179, 167, 158, 139, 113, 91, 79, 65, 26.

(2E)-1-(4-Methyl-1-naphthyl)-3-(4-dimethylaminophenyl)-2-propen-1-one (1g) Yield: 95%; m.p. 135-136°C; IR (KBr, cm⁻¹): υ = 1640 (CO s-cis), 1604 (CO s-trans). 1H NMR (CDCl₃, ppm): δ = 8.003(d, 1H α), 8.425(d, 1H β), 6.830-7.880(m, 10H Ar-H), 2.874(s, 3H -CH₃), 2.878(s, 6H -CH₂). 13C NMR (CDCl₃, ppm): δ = 121.659(C), 140.031(C), 1879.465(CO), 135.819(C), 129.889(C).
126.684(C₂), 136.957(C₂), 127.700(C₂), 126.684(C₂), 133.819(C₂), 124.289(C₂), 131.512(C₂), 130.641(C₂), 26.023(-CH₃), 126.684(C), 127.565(C), 114.659(C), 148.654(C), 41.043(-CH₃)). Anal. Calcd. for C₇H₆NO: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.72; H, 6.61; N, 4.39. MS: m/z = 315[M⁺], 271, 168, 146, 142, 128, 120, 91, 77, 65.

(2E)-1-(4-Methyl-1-naphthyl)-3-(4-hydroxyphenyl)2-propen-1-one (1h) Yield: 91%; m.p. 111°C; IR (KBr, cm⁻¹): ν = 1649 (CO s-trans), 1615 (CO s-trans), 3473(OH). ¹H NMR (CDCl₃, ppm): δ = 8.200(d, 1H, α), 8.318(d, 1H, β), 6.989-7.778(m, 10H, Ar-H), 4.660(s, 1H, -OH), 2.507 (-CH₂). ¹³C NMR (CDCl₃, ppm): δ =118.997(C), 141.111(C), 190.356(CO), 133.407(C), 130.603(C), 126.428(C), 137.114(C), 127.700(C), 126.485(C), 132.909(C), 120.232(C), 131.937(C), 130.603(C), 24.601(-CH₂), 124.893(C), 127.051(C), 118.794(C), 157.778(C). Anal. Calcd. for C₂₁H₁₈NO: C, 83.31; H, 5.50. Found: C, 83.29; H, 5.48. MS: m/z = 328[M⁺], 271, 199, 141, 128, 108, 119, 107, 103, 91.

(2E)-1-(4-Methyl-1-naphthyl)-3-(4-methoxyphenyl)2-propen-1-one (1i) Yield: 94%; m.p. 106-107°C; IR (KBr, cm⁻¹): ν = 1641 (CO s-trans), 1618 (CO s-trans); ¹H NMR (CDCl₃, ppm): δ = 8.008 (d, 1H, α), 8.037(d, 1H, β), 7.022-7.894(m, 10H, Ar-H), 2.760(s, 3H, -CH₃), 8.625(s, 3H, OCH₃). ¹³C NMR (CDCl₃, ppm): δ = 119.554(C), 140.364(C), 190.573(CO), 135.024(C), 130.587(C), 125.401(C), 139.024(C), 127.095(C), 126.491(C), 132.901(C), 120.401(C), 131.879(C), 130.381(C), 24.758(-CH₂), 127.498(C), 127.090(C, β, 1H, 193.471(CO), 137.343(C), 24.963(CH₃). Anal. Calcd. for C₂₃H₂₃NO: C, 88.08; H, 6.34. Found: C, 88.03; H, 6.29. MS: m/z = 286[M⁺], 271, 168, 140, 128, 117, 103, 91, 77, 65.

(2E)-1-(4-Methyl-1-naphthyl)-3-(2-nitrophenyl)2-propen-1-one (1k) Yield: 94%; m.p. 87-88(88°C); IR (KBr, cm⁻¹): ν = 1664 (CO s-trans), 1658 (CO s-trans); ¹H NMR (CDCl₃, ppm): δ = 8.261(d, 1H, α), 8.329(d, 1H, β), 7.375-8.029(m, 10H, Ar-H), 2.301(s, 3H, -CH₃); ¹³C NMR (CDCl₃, ppm): δ = 142.909(C), 143.137(C), 193.498(CO), 134.185(C), 129.153(C), 126.397(C), 141.185(C), 128.192(C), 126.390(C), 130.173(C), 128.090(C), 131.185(C), 130.708(C), 24.247-CH₃), 125.273(C), 148.486(C), 114.415(C), 125.310(C), 123.170(C), 124.930(C). Anal. Calcd. for C₂₃H₂₃NO: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.62; H, 4.72; 4.38 MS: m/z = 317[M⁺], 168, 142, 126, 116, 103, 91.

(2E)-1-(6-Methyl-1-naphthyl)-3-(3-nitrophenyl)2-propen-1-one (1l) Yield: 95%; m.p. 133-134°C; IR (KBr, cm⁻¹): ν = 1667 (CO s-trans), 1654 (CO s-trans); ¹H NMR (CDCl₃, ppm): δ = 8.273(d, 1H, α), 8.344 (d, 1H, β), 7.335-8.025(m, 10H, Ar-H), 2.803(s, 3H, -CH₃); ¹³C NMR (CDCl₃, ppm): δ = 119.603(C), 145.643(C), 193.309(CO), 133.028(C), 130.578(C), 126.443(C), 140.925(C), 121.350(C), 126.443(C), 131.920(C), 124.288(C), 131.028(C), 130.180(C), 26.297(CH₃), 135.079(C), 111.178(C), 145.642(C), 115.083(C), 126.432(C), 121.028(C), Anal. Calcd. for C₂₃H₂₃NO: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.65; H, 4.70; 4.32. MS: m/z = 317[M⁺], 168, 142, 126, 116, 103, 91, 77, 65.

(2E)-1-(4-Methyl-1-naphthyl)-3-(4-nitrophenyl)2-propen-1-one (1m) Yield: 95%; m.p. 96-97°C; IR (KBr, cm⁻¹): ν = 1665 (CO s-trans), 1649 (CO s-trans); ¹H NMR (CDCl₃, ppm): δ = 8.299(d, 1H, α), 8.492(d, 1H, β), 7.379-8.092(m, 10H, Ar-H), 2.638(s, 3H, -CH₃); ¹³C NMR (CDCl₃, ppm): δ = 123.703(C), 145.182(C), 193.471(CO), 134.659(C), 130.524(C), 125.568(C), 140.944(C), 128.890(C), 126.520(C), 135.524(C), 120.495(C), 131.659(C₆H₅)}
RESULTS AND DISCUSSION

6-Methyl-2-naphthyl ketone is subjected to condensation with various m- and p-substituted benzaldehydes, containing either electron-releasing or electron withdrawing groups, in the presence of the SiO₂·H₂SO₄ reagent under solvent free condition (Scheme 1). The results are summarized in the experimental section. The reactions were completed 2-3h and high yields of chalcones were obtained. In this condition, no self-condensation of the starting materials was observed. Attempts to the condensation of this ketone with α-substituted hydroxy, methoxy benzaldehydes were not successful.

The promoting effect of silica sulfuric acid in these reactions was shown good performance by obtaining good percentage of yields up to five consecutive condensations of ketone and benzaldehydes.

The product was isolated and the remaining catalyst was washed and reloaded with fresh substrates for further runs. No decrease in the yield was observed up to five runs, demonstrating that silica-sulfuric acid can be reused in crossed-aldol condensation reaction without environmental discharge. After five runs the yield was decreases from 0.5 to 1%.

Correlation analysis

A large number of spectral data relating to substituted styryl naphthyl chalcones accumulated in the previous investigations were correlated in the present work using a variety of LFER models, conventionally used for the study of structure-reactivity and structure-property relationships. It was assumed that it should be possible to find an adequate approach to study the transmission of substituent effects in the multi-substituted chalcones, considering that their aromaticity has been established. It was always initially attempted to use a simple Hammett Equations as presented in eq. 1.a., but it was frequently more appropriate to use other approaches, like the Hammett-Taft (Extended Hammett Equation) DSP model, eq. 1.b., and Swain-Lupton eq. 1.c., which are usually given in the literature in their general form.²⁸

\[ \sigma = \rho \sigma_a - \sigma_p \]  
\[ \sigma = \rho \sigma_a + \rho \sigma_p + \sigma_s \]  
\[ \sigma = f \sigma + r \sigma \]  

In these models, the author applied Eq. 1. a. and c. only for evaluation of electronic effects in this aromatic system and s is the measured spectral
characteristics, $\sigma_{\text{w}}$, $\sigma$, $\sigma_\text{m}$, F and R are substituent constants, $p$, $r$, $f$ and $r$ are the corresponding calculated proportionality constants, which in a broad sense reflect the sensitivity of the spectral characteristics to substituent effects and $s$ is the intercept. On certain occasions, when other model failed, combined multiparameter equations were applied, the method known to be used before and with the same precision as obtained here.

Quantitative structure property relationships involves the prediction of ground state molecular equilibriums of organic substrates such as s-cis and s-trans isomers of alkenes, alkyenes, benzyl-chlorides, styrenes and $\alpha$, $\beta$-unsaturated ketones from spectral data. Their use in structure parameter correlations has now becomes popular for studying transition state study of reaction mechanisms and normal coordinate analysis. Dhami and Stofflers have extensively studied the $^1\text{H}$ 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 shielding, first observed by Lauterber. Savin and coworkers obtained the NMR spectra of unsaturated ketones of the type R$_2$C=CH-CH=CH-COCMe, and sought Hammett correlations for the ethylenic protons. Solcanova and coworkers have measured $^1\text{H}$ and $^13\text{C}$ NMR spectra of substituted phenyl styrenes and substituted styryl phenyls and obtained good Hammett correlations for the olefinic protons and carbons. Now a day's scientists have paid more interest to correlate the group frequencies of spectral data with Hammett substituent constants to explain the substituent effect of organic compounds. Recently Sung and Nadar investigated the multi substituent effects by spectral data of biphenyl and 9H-Fluorenyl chalcones. With in the above view there is no information available in the literature in the past with substituted styryl 4-methyl-1-naphthyl ketones. Hence the author has synthesized thirteen chalcones of the above type using silicic-sulphuric acid supported crossed - aldol condensation reaction between 4-methyl-1-naphthyl ketone and various $m$- and $p$-substituted benzaldehydes and the substituent effects of above compounds are investigated from infrared and NMR spectra were made.

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 (I). The infrared spectra were all recorded on the KBr disc in order to avoid the shoulder formation on carbonyl doublets. The s-cis conformers exhibit higher frequencies than the s-trans conformers due to the bulkier naphthalene group causes greater strain and they 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 were produce fair degree of correlation with Hammett sigma constants in the s-cis conformers of all chalcones. The correlations in the s-cis conformers is fair enough with $\sigma$ ($r = 0.996, I = 1652.2, \rho = 8.74, s = 0.18, n = 13$) constants in these compounds implies that through 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 see that in these compounds the s-cis conformers, the $\sigma$ and $\sigma_\text{m}$ parameters do not satisfactorily predict the reactivity individually. This is due to the cross conjugation of methyl substituent in fourth position of naphthyl ring as shown in (II).

It is interesting to note that in the s-trans conformers of all chalcones produce satisfactory correlation with $\sigma$ ($r = 0.995, I = 1648.0, \rho = 6.34, s = 0.13, n = 13$) and good correlation with $\sigma^+$ ($r = 0.999, I = 1652.6, \rho = 4.43, s = 0.02, n = 13$) constants. The $\sigma_\text{m}$ and $\sigma_\text{m}$ constants are failed to produce correlation. This shows that conjugation between the C=O and the -CH=CH- parts of the system was not determines the substituent effects.

In view of the inability of some of the $\sigma$ constants to produce individually satisfactory correlations, it was thought worthwhile to seek multiple correlations involving collectively either $\sigma$, and $\sigma_\text{m}$ constants or Swain-Lupton's F and R parameters.
The correlation equations generated are in equations (2-4).

\[ v_{c=0}(s-cis) \text{(cm}^{-1}) = 1652.2(\pm 5.147) \\
+ 8.683\sigma_i (\pm 1.581) + 8.2173\sigma_a (\pm 0.878) \] \hspace{1cm} (2)

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

\[ v_{C=0}(s-cis) \text{(cm}^{-1}) = 1663.8(\pm 3.777) \\
- 8.272F (\pm 7.484) + 23.129R (\pm 4.739) \] \hspace{1cm} (3)

\[ (R = 0.997, n = 13, P > 90\%) \]

\[ v_{c=0}(s-trans) \text{(cm}^{-1}) = 1626.9(\pm 6.175) \\
+ 31.584F(\pm 10.255) + 26.380R(\pm 6.499) \] \hspace{1cm} (4)

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

From the equations (2-4) it is inferred that in most of the cases the correlation is significant with either \( \sigma_i \) or \( \sigma_a \), or with \( F \) and \( R \) parameters together. The \( s-trans \) isomer failed to produce the correlation with \( \sigma_i \), or \( \sigma_a \) constants. This may treated exceptional and by large it is to be realized that the collective participation of either \( \sigma_i \) or \( \sigma_a \) parameters is more dependent than that of any single parameter role to predict the substituent effects.

**Substituent effects on infrared deformation modes**

Substituent effects on infrared deformation modes of vinyl ketones are first studied by Thirunarayanan et al. They prepared several substituted styryl 9H-fluorenyl ketones and studied the effects of substituents on \( \text{CH}, \text{CH}=\text{CH} \) and \( >\text{C} = \text{C}< \) deformation modes of vinyl portion with various Hammett \( \sigma \) constants and Swain-Lupton constants using linear regression analysis. In their investigation, they observed satisfactory correlation with \( \rho \) constants. Inductive and Resonance effects are failed to produce the correlation individually due to methylene resonance. But collectively \( \sigma_i, \sigma_a \), and Field effects are predicts the reactivity on the same deformation modes satisfactorily.

The author have follow the same trend for predict the substituent effects on deformation modes of vinyl part in substituted styryl 4-methyl-1-naphthyl ketones. The assigned infrared deformation modes of \( -\text{CH} \) out of plane, in-plane, \( -\text{CH}=\text{CH} \) out of plane and \( >\text{C} = \text{C}< \) out of plane stretches (cm\(^{-1}\)) of vinyl part of these ketones are presented in Table 1. These modes are separately analyzed using simple and multiple linear regression analysis through Hammett equation with various \( \sigma \) constants. All the correlation data are pertaining to single parameter correlation and they gave positive \( \rho \) values in all cases. These modes produce good, satisfactory and fair degree of correlation with \( \sigma_i \) and \( \sigma_a \) constants.

\[ v_{CHop}(\rho; r = 0.995, I = 754.72, \rho = 3.02, s = 1.5, n = 13); \]
\[ (\sigma_i; r = 0.992, I = 755.54, \rho = 5.60, s = 1.8, n = 13)); \]
\[ v_{CHop}(\rho; r = 0.999, I = 1153.91, \rho = 2.90, s = 0.15, n = 13); \]
\[ (\sigma_i; r = 0.997, I = 1.15968, \rho = 3.83, s = 0.83, n = 13); \]
\[ (\sigma_a; r = 0.980, I = 1139.81, \rho = 2.98, s = 1.57, n = 13)); \]
\[ v_{CHop}(\rho; r = 0.989, I = 1038.11, \rho = 6.90, s = 1.3, n = 13); \]
\[ (\sigma_i; r = 0.959, I = 1041.75, \rho = 7.39, s = 2.01, n = 13)); \]
\[ v_{CHop}(\rho; r = 0.999, I = 563.62, \rho = 7.82, s = 0.15, n = 13); \]
\[ (\sigma_i; r = 0.980, I = 571.25, \rho = 5.14, s = 1.05, n = 13)); \]

Individually the Hammett \( \sigma_i \), and \( \sigma_a \) constants are failed to produce correlation because the vinyl part is affected by the conjugative structure in (I) by the para-substituents. But collectively the inductive, resonance and Field effects are correlated with the deformation modes and they produce the correlation equations (5-10).

\[ v_{CH}(\text{cm}^{-1}) = 725.250(\pm 0.832) + 85.685(\pm 2.091) (5) \]
\[ (R = 0.983, n = 13, P > 95\%) \]
$v_{\text{CN}}$ (cm$^{-1}$) = 745.880(±1.015) + 54.49F (±1.783) + 38.752R(±1.053) (6)

$(R = 0.921, n = 13, P > 90\%)$

$v_{\text{C\#H}}$ (cm$^{-1}$) = 1058.432 (±2.052) + 17.623F(±0.527) + 14.533R(±0.331) (7)

$(R = 0.942, n = 13, P > 90\%)$

$v_{\text{C\#C}}$ (cm$^{-1}$) = 1143.513(±5.395) + 46.613$\sigma_1$(±2.137) + 11.645$\sigma_5$ (±1.033) (8)

$(R = 0.900, n = 13, P > 90\%)$

$v_{\text{CH}-}$ (cm$^{-1}$) = 1153.890(±4.618) + 29.595F (±0.193) + 23.808R (±0.356) (9)

$(R = 0.953, n = 13, P > 90\%)$

$v_{\text{CCOH}}$ (cm$^{-1}$) = 562.800(±5.833) + 41.057F (±1.216) + 30.818R (±1.778) (10)

$(R = 0.946, n = 13, P > 90\%)$

Substituent effects from NMR spectra

$^1$H NMR Spectra

The $^1$H NMR spectral signals of ethylic protons in all chalcones investigated are assigned. The chemical shifts of $^1$H protons are at higher field than those of $^1$H protons in all chalcones. The ethylic proton signals give an AB pattern and the $^1$H protons doublet in most cases is well separated from the signals of the aromatic protons. The chemical shifts of $^1$H and $^1$H protons are given in Table 2. The observation that $^1$H protons appear at higher field than that of $^1$H protons makes the subject very interesting. This may possibly due to the polarization of C=C double bond in the system being predominantly caused by the carbonyl group so as to make electron density greater at $\alpha$ position than that of $\beta$ position.

All the attempted correlations involving substituent parameters gave only positive $\rho$ values. This shows normal substituent effects is operates in all the chalcones. The Chemical shifts observed for $^1$H and the $^1$H protons in the present investigation are correlated satisfactorily with Hammett sigma constants. The chemical shifts of $^1$H protons were produce a significant correlation with $\sigma^+$ $(r = 0.996, I = 8.131$, $\rho = 0.054, 0.32, n = 13)$ constants only and the other constants are failed. This is due to the domination of cross conjugation between carbonyl group and methyl group in naphthyl ring in (II). In $^1$H proton cases the correlation with $\sigma$ and $\sigma^+$ values is slightly better $(r = 0.99, I = 8.244, \rho = 0.080, s = 0.25, n = 13)$; $\sigma^=(r = 0.992, I = 8.299, \rho = 0.08, s = 0.34, n = 13)$. That the correlation with $\sigma$, and $\sigma^+$ parameters is good implies that this values are capable for predicting the substituent effects through chemical shifts individually $(\sigma, r = 0.999, I = 8.266, \rho = 0.77, s = 0.26, n = 13); \sigma^+ (r = 0.997, I = 8.230, \rho = 0.77, s = 0.85, n = 13)$.

The multiple correlations involving either $\sigma$ and $\sigma^+$ or $F$ and $R$ values for these ketones are presented. It is indeed satisfactorily that in most cases the multiple correlations are successful. Some of the single parameter correlations are given in expressions (11-14).

$$\delta_{\text{H}_\alpha}^{\text{(ppm)}} = 8.061(±0.037) + 0.279\sigma_1(±0.084) + 0.036\sigma_5(±0.071)$$

$(R = 0.999, n = 13, P > 90\%)$ (11)

$$\delta_{\text{H}_\beta}^{\text{(ppm)}} = 8.103(±0.004) + 0.221F (±0.089) + 0.092R(±0.056)$$

$(R = 0.996, n = 13, P > 90\%)$ (12)

$$\delta_{\text{H}_\gamma}^{\text{(ppm)}} = 8.274(±0.092) + 0.122\sigma_5(±0.099) + 0.150\sigma_6(±0.327)$$

$(R = 0.99, n = 13, P > 90\%)$ (13)

$$\delta_{\text{H}_\delta}^{\text{(ppm)}} = 8.269(±0.147) + 0.142F(±0.128) + 0.071R(±0.065)$$

$(R = 0.998, n = 13, P > 90\%)$ (14)


\(^{13}\text{C}\) NMR Spectra

From \(^{13}\text{C}\) NMR spectra the observed \(^{13}\text{C}\) chemical shifts of \(\text{C}_a\), \(\text{C}_b\) and carbonyl carbons are presented in Table 2. These chemical shifts of \(\text{C}_a\), \(\text{C}_b\) are correlated with various Hammett substituent constants. From the results of statistical analysis the correlation of \(\text{C}_a\), carbon chemical shifts are failed with all sigma constants. \(\text{C}_b\) carbon chemical shifts are produce fair degree of correlation obtained with Hammett \(\sigma\) and \(\sigma_r\) sigma constants \[\sigma(r = 0.901, I = 142.233, \rho = 1.27, s = 1.02, n = 13); \sigma_r(r = 0.996, I = 144.410, \rho = 1.273, s = 0.63, n = 13)\] others failed to produce the correlation is due to the reasons stated earlier. The degree of transmission of electronic effects is found to be lower with \(\text{C}_a\) carbon than \(\text{C}_b\) carbon.

Uniformly \(\sigma_i\) and \(\sigma_{r_i}\) parameters or \(F\) and \(R\) values are adequately explained the substituent effects in all chalcones are evidenced from the correlation equations (15-17).

\[
\delta_{\text{C}_a}^{13\text{NMR}} = 123.07(\pm 1.289) - 0.870F(\pm 2.554) + 3.168R(\pm 1.617) \\
(R = 0.967, n = 13, P > 90\%)
\]  
(15)

\[
\delta_{\text{C}_b}^{13\text{NMR}} = 142.19(\pm 1.101) + 0.327\sigma(\pm 0.973) + 1.755\sigma_r(\pm 0.113) \\
(R = 0.997, n = 13, P > 90\%)
\]  
(16)

\[
\delta_{\text{C}_b}^{13\text{NMR}} = 146.72(\pm 1.002) + 1.405F(\pm 1.091) + 5.722R(\pm 0.041) \\
(R = 0.998, n = 13, P > 90\%)
\]  
(17)

The \(^{13}\text{C}\) chemical shifts of carbonyl carbons of these ketones are correlated with various Hammett \(\sigma\) constants. The result of statistical analysis shows good and satisfactory correlation with \(\sigma\) and \(\sigma^*\) constants. \[\sigma(r = 0.998, I = 191.351, \rho = 3.194, s = 0.02, n = 13); \sigma^*(r = 0.976, I = 191.844, \rho = 2.428, s = 0.08, n = 13)\] Hammett \(\sigma_i\) and \(\sigma_{r_i}\) constants are failed for produce the correlation due to the carbon oxygen double bond character was converted into single bond character \(>\text{C}-\text{O}\). This is largely affect the electronic effect of substituent as shown in conjugative structure in (III). There is a satisfactory correlation obtained with field, resonance and inductive effects of substituents generated the equations (18 and 19).

\[
\delta_{\text{C}_a,\text{C}_b}^{13\text{NMR}} = 190.441(\pm 0.469) + 4.014\sigma(\pm 0.105) + 0.913\sigma_r(\pm 0.018) \\
(R = 0.914, n = 13, P > 90\%)
\]  
(18)

\[
\delta_{\text{C}_a,\text{C}_b}^{13\text{NMR}} = 191.341(\pm 0.423) + 2.523\rho(\pm 0.873) + 1.917F(\pm 0.513) \\
(R = 0.943, n = 13, P > 90\%)
\]  
(19)
CONCLUSION

This method is a very efficient and selective protocol for crossed-aldo condensation of 4-methyl-1-naphthyl ketones and aldehydes to produced high yield of 4-methyl-1-naphthyl chalcones in the presence of a reusable and environmentally beginning catalyst silica-sulphuric acid. Operative simplicity, easy work-up procedure, better yield including washing the mixture followed by evaporation of the solvent is another advantage of this method. In correlation analysis of infrared carbonyl frequencies both conformers produce fair and satisfactory correlations with \( \sigma \) constants. A good correlation obtained with \( \sigma^2 \) constants and carbonyl frequencies of \( \text{m-trans} \) conformers. Adequately a satisfactory correlation obtained in both the conformers with inductive, field and resonance effects. Deformation modes are produced good, satisfactory and fair degree of correlations with Hammett \( \sigma \) constants. The proton chemical shifts (ppm) of \( H_\alpha \) protons produce satisfactory correlation with all Hammett \( \sigma \) constants than the \( H_\beta \) proton chemical shifts. The inductive and resonance effects of the substrates are predicting the reactivity collectively well on \( H_\alpha \) and it produce good correlation with field and resonance effects. The substrates were fails for prediction of reactivity on \( C_\beta \) carbon chemical shifts. A fair degree of correlation obtained for \( C_\beta \) chemical shifts with \( \sigma \) and \( \sigma^2 \). Collectively field and resonance effects are give satisfactory correlation on both carbons. The carbonyl carbon chemical shifts are produce good and satisfactory correlation with \( \sigma \) constant through single and multiparameter statistical analysis.

REFERENCES


