치환된 Styryl 4-Methyl-1-naphthyl Ketones에서의 합성과 스펙트럼 linearity

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Synthesis and Spectral Linearity in Substituted Styryl 4-Methyl-1-naphthyl Ketones

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요 약. 치환된 styryl 4-methyl-1-naphthyl ketones [(2E)-1-(4-methyl-1-naphthyl)-3-phenyl-2-propen-1-ones]의 계열은 오븐에서 친환경 촉매 SiO_2-H_2SO_4를 사용하여 solvent free하에서 환경친화적으로 합성되었다. 촉매 실리카는 재사용이 가능하고 chalcones의 수율이 거의 90%이상이다. 이물질을 물리적인 상수, micro분석, 적외선 스펙트럼과 ^1H와 ^{13}C NMR 스펙트럼, mass 스펙트럼 데이터를 통해 구조분석 하였다. 카르보닐기의 s-시스와 s-트란스의 진동, CH의 평면내와 평면외의 진동, -CH=CH-의 평면외, >C=C< 평면외, vinyl부분의 평면외 진동 피크를 적외선 스펙트럼으로 분석하였고, NMR을 이용하여 에틸렌의 수소/탄소 및 카르보닐 탄소의 피크를 확인하였다. 이 스펙트럼 데이터는 다양한 Hammett 치환상수와 연관이 있다. 카르보닐기에서 치환기 효과의 통계적인 분석의 결과로부터 α, β 수소/탄소 및 그들의 변형모드가 설명되어진다.

주제어: Solvent free 합성, 황산실리카, Styryl naphthyl ketones, IR and NMR 스펙트럼, 치환기 효과, 연관 분석

ABSTRACT. A series of substituted styryl 4-methyl-1-naphthyl ketones [*(2E)-1-(4-methyl-1-naphthyl)-3-phenyl-2-propen-1-ones*] were synthesized eco-friendly under solvent free conditions using a green catalyst SiO_2-H_2SO_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 ^1H and ^{13}C and Mass spectral data. From infrared spectra, the *s-cis* and *s-trans* vibrations of carbonyl group and deformation modes CH *in-plane and out of plane*, -CH=CH- *out of plane* and >C=C< *out of plane* of vinyl parts, from NMR spectra the ethylenic 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, α and β 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,[1] Knoevenogel,[2] Aldol[3] and Crossed-aldol,[4] Bayer-Villeger,[5] Michael addition,[6] Oxidative methods[7] and complex reaction like callixrane 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.[8] 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.[9] The basic skeleton of chalcones are widely figured in natural products are known to have multipronged activity.[10] Many of the chalcones are used as agrochemicals, drugs[11] and antimicrobial agents[12] 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[13] and self-condensation of starting molecules.[14]

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.[15] Metal salts of Cp_2ZrH_2 are used for condensation of cycloalkanones.[16] $KF-Al_2O_3$ and bis (p-methoxy phenyl) tellurides are have been used for crossed condensation under microwave irradiation.[17] Anhydrous $RuCl_3$ and $TiCl_3(SO_3CF_3)$ have also been applied for aldol condensation reactions under solvent free conditions.[18] Kalluraya et al.[19] 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.[20] synthesized 60-92% yields of various 2E-3-aryl-1-hetarylprop-2-en-1-ones by crossed aldol condensation reaction in sodium hydroxide-water heterogeneous phase reaction medium. Silica-sulphuric 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-sulphuric 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-Merck 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 ^{13}C of chalcones were recorded using UNITYPLUS-300 "KIBSIPS" 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[21]

4-Methyl-1-naphthyl ketone (2 mmol), m- and p-substituted benzaldehydes and silica-sulfuric acid (1.5 g equal to 4 mmol of H^-) 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 glittering 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 1k 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[22])°C; IR (KBr, cm⁻¹): δ = 1660 (CO s-cis), 1621 (CO s-trans); ^1H NMR(CDCl₃, ppm): v = 8.767(d, 1H, α), 8.247(d,

1H, β), 7.369-7.876 (m, 11H Ar-H), 2.347(s, 3H -CH$_3$); ^{13}C NMR(CDCl$_3$, ppm): δ=122.293(C$_\alpha$) 144.242(C$_\beta$), 191.331(CO), 132.189(C$_1$), 129.193(C$_2$), 126.837(C$_3$), 135.032(C$_4$), 128.305(C$_5$), 126.837(C$_6$), 132.013(C$_7$), 120.912(C$_8$), 131.365(C$_{4a}$), 130.965(C$_{8a}$), 40.125(-CH$_3$), 135.032(C$_{1'}$), 126.837(C$_{2',6'}$), 128.305 (C$_{3',5'}$), 128.119(C$_6$). C$_{20}$H$_{16}$O. MS: m/z = 272[M$^+$], 169,141, 131,127, 103, 77.

(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}): v = 1652 (CO s-cis), 1626 (CO s-trans), 3569 (-NH$_2$). ^{1}H NMR (CDCl$_3$, ppm): δ = 8.132(d, 1H, α), 8.194(d, 1H, β), 7.055-7.876(m, 10H, Ar-H), 4.320(s, 2H -NH$_2$), 2.687(s, 3H -CH$_3$); ^{13}C NMR (CDCl$_3$, ppm): δ = 121.334(C$_\alpha$) 142.624(C$_\beta$), 191.587 (CO). 127.001(C$_1$), 128.001(C$_2$), 106.214(C$_3$), 158.241(C$_4$), 127.999(C$_5$), 127.017(C$_6$), 136.417(C$_7$), 116.111(C$_8$), 124.111(C$_{4a}$), 132.999(C$_{8a}$), 26.993(-CH$_3$), 133.471(C$_{1'}$), 115.172(C$_{2'}$), 141.717(C$_{3'}$), 115.174(C$_{4'}$), 131.471(C$_{5'}$), 115.176(C$_6$). Anal. Calcd. for C$_{20}$H$_{17}$NO$_2$: 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-(4-aminophenyl)-2-propen-1-one (1c) Yield: 96%; m.p.122-123°C; IR (KBr, cm^{-1}): v = 1647 (CO s-cis), 1605 (CO s-trans), 3528(-NH$_2$). ^{1}H NMR (CDCl$_3$, ppm): δ = 8.034(d, 1H α), 8.314(d, 1H, β), 6.760-7.402 (m, 10H, Ar-H), 4.871(s, 2H -NH$_2$), 2.359(-CH$_3$); ^{13}C NMR (CDCl$_3$, ppm): δ = 119.234(C$_\alpha$) 140.606 (C$_\beta$), 189.544(CO), 134.921(C$_1$), 128.992(C$_2$), 127.921 (C$_3$), 135.091(C$_4$), 128.093(C$_5$), 127.940(C$_6$), 132.927 (C$_7$), 125.814(C$_8$), 133.144(C$_{4a}$), 129.124(C$_{8a}$), 26.064 (-CH$_3$), 125.270(C$_{1'}$), 128.770(C$_{2',6'}$), 117.410 (C$_{3',5'}$), 141.730(C$_{4'}$). Anal. Calcd. for C$_{20}$H$_{17}$NO$_2$: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.54; H, 5.94; N, 4.85. MS: m/z = 287[M$^+$], 286, 271, 169, 146, 141, 127, 118, 103.

(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}): v = 1654 (CO s-cis), 1636 (CO s-trans). ^{1}H NMR (CDCl$_3$, ppm): δ = 8.102(d, 1H, α), 8.161(d, 1H, β), 7.342-7.892(m, 10H Ar-H), 2.695(s, 3H -CH$_3$); ^{13}C NMR (CDCl$_3$, ppm): δ = 122.400(C$_\alpha$), 140.818(C$_\beta$), 192.390(CO), 134.100

(C$_1$), 130.381(C$_2$), 121.630(C$_3$), 136.990(C$_4$), 127.257 (C$_5$), 126.635(C$_6$), 133.363(C$_7$), 121.475(C$_8$), 132.990 (C$_{4a}$), 129.019(C$_{8a}$), 25.632(-CH$_3$), 140.571(C$_{1'}$), 129.553(C$_{2'}$), 123.580(C$_{3'}$), 131.528(C$_{4'}$), 130.998(C$_{5'}$), 124.475(C$_6$). Anal. Calcd. for C$_{20}$H$_{15}$BrO: 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 (1e) Yield: 92%; m.p.97-98°C; IR (KBr, cm^{-1}): v =1657 (CO s-cis), 1629 (CO s-trans). ^{1}H NMR (CDCl$_3$, ppm): δ = 8.315(d, 1H, α), 8.327(d, 1H, β), 7.320-7.843(m, 10H, Ar-H), 2.864 (s, 3H -CH$_3$). ^{13}C NMR (CDCl$_3$, ppm): δ = 123.662(C$_\alpha$) 141.886(C$_\beta$), 192.334(CO), 133.492(C$_1$), 129.188(C$_2$), 126.432(C$_3$), 136.102(C$_4$), 128.414(C$_5$), 126.658(C$_6$), 133.492(C$_7$), 125.778(C$_8$), 131.492(C$_{4a}$), 129.235(C$_{8a}$), 24.247(-CH$_3$), 138.551(C$_{1'}$), 127.006 (C$_2$), 133.492(C$_3$), 128.703(C$_4$), 129.188(C$_5$), 124.656 (C$_6$). Anal. Calcd. for C$_{20}$H$_{15}$ClO: C, 78.30; H, 4.93. Found: C, 78.25; H, 4.86. MS: m/z = 308, 306[M$^+$], 271, 179, 167, 165, 139, 136, 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}): v = 1655 (CO s-cis), 1631 (CO s-trans),. ^{1}H NMR (CDCl$_3$, ppm): δ = 8.174(d, 1H, α), 8.297(d, 1H, β), 7.127-8.000(m, 10H, Ar-H), 2.543 (-CH$_3$); ^{13}C NMR(CDCl$_3$, ppm): δ = 122.966 (C$_\alpha$) 142.997(C$_\beta$), 191.927 (CO), 133.140(C$_1$), 129.289 (C$_2$), 126.034(C$_3$), 136.240(C$_4$), 128.890(C$_5$), 126.834 (C$_6$), 133.020(C$_7$), 125.392(C$_8$), 130.331(C$_{4a}$), 129.817(C$_{8a}$), 25.648(-CH$_3$), 136.230(C$_{1'}$), 127.855 (C$_{2',6'}$), 129.289(C$_{3',5'}$), 135.276(C$_{4'}$). Anal. Calcd. for C$_{20}$H$_{15}$ClO: C, 78.30; H, 4.93. Found: C, 78.28; H, 4.90. MS m/z = 308, 306[M$^+$], 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}): v = 1640 (CO s-cis), 1604 (CO s-trans); ^{1}H NMR(CDCl$_3$, ppm): δ =8.003(d,1H, α), 8.425(d,1H, β), 6.830-7.880(m, 10H, Ar-H), 2.874(s, 3H -CH$_3$), 2.878(s, 6H -(CH$_3$)$_2$). ^{13}C NMR (CDCl$_3$, ppm): δ = 121.659(C$_\alpha$), 140.031 (C$_\beta$), 1879.463(CO), 133.819(C$_1$), 129.889(C$_2$),

126.684(C_3), 136.957(C_4), 127.700(C_5), 126.684(C_6), 133.819(C_7), 124.289(C_8), 131.512(C_{4a}), 130.641 (C_{8a}), 26.023(-CH_3), 126.684($C_{1'}$), 127.565($C_{2',6'}$), 114.659($C_{3',5'}$), 148.654($C_{4'}$), 41.043(-(CH_3)$_2$). Anal. Calcd. for $C_{22}H_{21}NO$: 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, 140, 128, 120, 91, 77, 65.

(2E)-1-(4-Methyl-1-naphthyl)-3-(4-hydroxyphe-nyl)-2-propen-1-one (1h) Yield:91%; m.p.110-111°C; IR (KBr, cm⁻¹): v = 1649 (CO s-cis), 1615 (CO s-trans), 3473(-OH). ¹H NMR (CDCl$_3$, ppm): δ = 8.200(d, 1H, α), 8.318(d, 1H, β), 6.893-7.778(m, 10H, Ar-H), 4.660(s, 1H -OH), 2.507 (-CH$_3$). ¹³C NMR (CDCl$_3$, ppm): δ = 118.997($C_α$), 141.111($C_β$), 190.356(CO), 133.407(C_1), 130.603(C_2), 126.428(C_3), 137.114(C_4), 127.700(C_5), 126.485(C_6), 132.909(C_7), 120.232(C_8), 131.937(C_{4a}), 130.603 (C_{8a}), 24.601(-CH_3), 124.893($C_{1'}$), 127.031($C_{2',6'}$), 118.794($C_{3',5'}$), 157.778($C_{4'}$). Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.50. Found: C, 83.29; H, 5.48. MS: m/z = 288[M⁻], 271, 199, 141, 128, 108, 119, 107, 103, 91.

(2E)-1-(4-Methyl-1-naphthyl)-3-(4-methoxyphe-nyl)-2-propen-1-one (1i) Yield:94%; m.p.106-107°C; IR (KBr, cm⁻¹): v = 1641 (CO s-cis), 1618 (CO s-trans); ¹H NMR(CDCl$_3$, ppm): δ = 8.008 (d,1H, α), 8.037(d, 1H, β), 7.022-7.894(m, 10H, Ar-H), 2.760(s, 3H -CH$_3$), 3.625 (s, 3H, OCH$_3$); ¹³C NMR (CDCl$_3$, ppm): δ = 119.554($C_α$), 140.364($C_β$), 190.573(CO), 133.024(C_1), 130.587(C_2), 125.401(C_3), 139.024(C_4), 127.693(C_5), 126.491(C_6), 132.901(C_7), 120.401(C_8), 131.879(C_{4a}), 130.381(C_{8a}), 24.758(-CH$_3$), 127.498($C_{1'}$), 127.090($C_{2',6'}$), 159.934($C_{3',5'}$), 54.280(-OCH$_3$ Ph), Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.36; H, 5.82. MS: m/z = 302[M⁻], 271, 168, 140,136, 128, 105, 91, 77, 65.

(2E)-1-(4-Methyl-1-naphthyl)-3-(4-methylphe-nyl)-2-propen-1-one (1j) Yield: 95%; m.p.122-123°C; IR (KBr, cm⁻¹): v = 1655 (CO s-cis), 1627 (CO s-trans). ¹H NMR (CDCl$_3$, ppm): δ = 8.020(d, 1H, α), 8.274(d, 1H, β), 7.262-7.898(m, 10H, Ar-H), 2.463(s, 3H -CH$_3$), 2.365(s, 3H -CH$_3$, Ph); ¹³C NMR (CDCl$_3$, ppm): δ = 120.262($C_α$), 139.852 ($C_β$), 190.871(CO), 134.253(C_1), 129.408(C_2),

126.538(C_3), 142.253(C_4), 128.661(C_5), 126.378(C_6), 133.017(C_7), 120.476(C_8), 131.253(C_{4a}), 130.489(C_{8a}), 24.421(-CH$_3$), 134.253($C_{1'}$), 126.378($C_{2',6'}$), 129.408 ($C_{3',5'}$), 137.343($C_{4'}$), 24.963(CH$_3$). Anal. Calcd. for $C_{21}H_{18}O$: 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(88²³) °C; IR (KBr, cm⁻¹): v = 1664 (CO s-cis), 1658 (CO s-trans).¹H NMR(CDCl$_3$, ppm): δ = 8.261(d,1H, α), 8.329(d,1H, β), 7.375-8.029(m, 10H. Ar-H), 2.301(s, 3H -CH$_3$); ¹³C NMR (CDCl$_3$, ppm): δ = 124.909($C_α$), 143.137($C_β$), 193.498(CO), 134.185 (C_1), 129.153(C_2), 126.397(C_3), 141.185(C_4), 128.192 (C_5), 126.390(C_6), 133.017(C_7), 120.909(C_8), 131.185 (C_{4a}), 130.708(C_{8a}), 24.247(-CH$_3$), 125.273($C_{1'}$), 148.486($C_{2'}$), 114.415($C_{3'}$), 125.310($C_{4'}$), 123.170($C_{5'}$), 124.930($C_{6'}$). Anal. Calcd. for $C_{20}H_{15}NO_3$: 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): v = 1667 (CO s-cis), 1654 (CO s-trans).; ¹H NMR(CDCl$_3$, ppm): δ = 8.273(d, 1H, α), 8.344 (d,1H, β), 7.335-8.025(m, 10H, Ar-H), 2.803(s, 3H -CH$_3$); ¹³C NMR (CDCl$_3$, ppm): δ = 119.603($C_α$), 145.643($C_β$), 193.309(CO), 133.028 (C_1), 130.578(C_2), 126.443(C_3), 140.925(C_4), 121.350 (C_5), 126.443(C_6), 131.920(C_7), 124.288(C_8), 131.028 (C_{4a}), 130.180(C_{8a}), 26.297(-CH$_3$), 133.079($C_{1'}$), 111.178($C_{2'}$), 145.642($C_{3'}$), 115.038($C_{4'}$), 126.432($C_{5'}$), 121.028($C_{6'}$). Anal. Calcd. for $C_{20}H_{15}NO_3$: 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-nitrolphenyl)-2-propen-1-one (1m) Yield: 95%; m.p.96-97°C; IR (KBr, cm⁻¹): v = 1655 (CO s-cis), 1649 (CO s-trans). ¹H NMR(CDCl$_3$, ppm): δ = 8.299(d, 1H, α), 8.492(d, 1H, β), 7.370-8.092(m, 10H, Ar-H), 2.630(s, 3H -CH$_3$); ¹³C NMR (CDCl$_3$, ppm): δ = 123.703($C_α$), 145.182($C_β$), 193.471(CO), 134.659(C_1), 130.524(C_2), 125.568(C_3), 140.944(C_4), 128.880(C_5), 126.520(C_6), 133.524(C_7), 120.495(C_8), 131.659(C_{4a}),

130.021(C_{8d}), 25.732(-CH₃), 129.644(C_1), 126.190 ($C_{2,6}$), 118.837($C_{3,5}$), 157.831(C_4), Anal. Cacld. for $C_{20}H_{15}NO_2$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.68; H, 4.72; 4.39. MS: m/z = 317[M⁻], 168, 142, 126, 116, 103, 91, 77, 65.

Based on Hays[24] and Singh[25] infrared carbonyl stretching frequencies of s-*cis* and s-*trans* conformers are assigned. The deformation modes of CH, CH–CH and C–C are assigned based on data reported in the literature.[26] The NMR chemical shifts (ppm) of ethylene α, β protons and carbons are assigned based on reported in earlier literature.[27]

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 SiO_2-H_2SO_4 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. Attempted to the condensation of this ketone with *o*-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]

$$a. \; s = \rho\sigma - s_o; \; b. \; s = \rho_I\sigma_I + \rho_R\sigma_R + s_o; \; c \; s$$
$$= f F + r R - s_o \qquad (1)$$

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

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
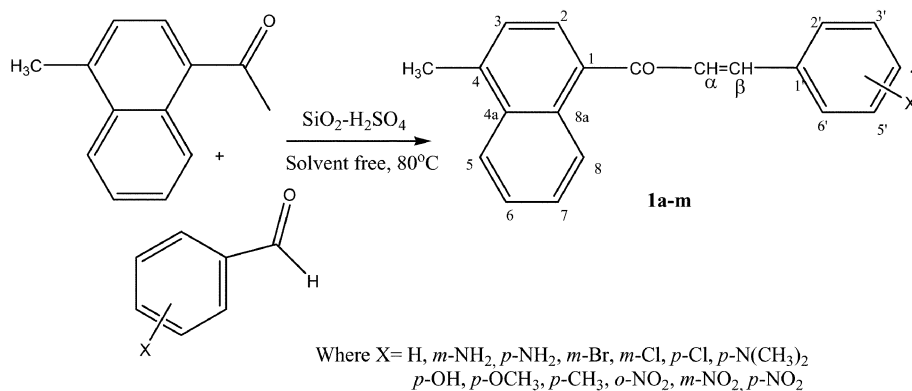
Scheme 1

characteristics, $\sigma_{m/p}$, σ_I, σ_R, F and R are substituent constants, ρ, ρ_I, ρ_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_0 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 equilibrations[29,30] 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 becomes popular for studying transition state study of reaction mechanisms[31] and normal coordinate analysis.[32] Dhami and Stothers[33] have extensively studied the ^{1}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 shieldings, first observed by Lauterber.[34] Savin and coworkers[35] obtained the NMR spectra of unsaturated ketones of the type RC_6H_4-CH=CH-$COCMe_3$ and sought Hammett correlations for the ethylenic protons. Sol-caniova and coworkers[36] have measured ^{1}H and ^{13}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[37] 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[38] investigate elaborately 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-naph-thyl ketones. Hence the author have synthesized thirteen chalcones of the above type using silica-sulphuric acid supported crossed - aldol condensation reaction between 4-methyl-1-napthyl 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[39,40] 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 σ (r = 0.996, I = 1652.2, ρ = 8.74, s = 0.18, n = 13) constants in these compounds implies that through conjugation is less important due to non-co planarity 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 σ_I and σ_R 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 σ (r = 0.995, I = 1648.0, ρ = 6.34, s = 0.13, n = 13) and good correlation with σ$^-$ (r = 0.999, I = 1652.6, ρ = 4.43, s = 0.02, n = 13) constants. The σ_I and σ_R 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 σ constants to produce individually satisfactory correlations, it was thought worthwhile to seek multiple correlations involving collectively either σ_I and σ_R constants or Swain-Lupton's[41] F and R parameters.

The correlation equations generated are in equations (2-4).

$$v_{C=O}(s\text{-}cis) \, (cm^{-1}) = 1652.2(\pm 5.147)$$
$$+ 8.683\sigma_I (\pm 1.581) + 8.2173\sigma_R (\pm 0.878) \, (2)$$
$$(R = 0.998, n = 13, P > 90\%)$$

$$v_{C=O} (s\text{-}cis) \, (cm^{-1}) = 1663.8 \, (\pm 3.777)$$
$$- 8.272F \, (\pm 7.484) + 23.129R \, (\pm 4.739) \quad (3)$$
$$(R = 0.997, n = 13, P > 90\%)$$

$$v_{C=O} (s\text{-}trans)(cm^{-1}) = 1626.9(\pm 6.175)$$
$$+ 31.584F(\pm 10.255) + 26.380R(\pm 6.499) \quad (4)$$
$$(R = 0.998, n = 13, P > 90\%)$$

From the equations (2-4) it is inferred that in most of the cases the correlation is significant with either σ_I or σ_R or with F and R parameters together. The s-trans isomer was failed to produce the correlation with σ_I or σ_R constants. This may treated 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 parameters 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.[12] They prepared several substituted styryl 9H-fluorenyl ketones and studied the effects of substitutents on CH, CH=CH and >C=C< deformation modes of vinyl portion with various Hammett σ constants and Swain-Lupton constants using linear regression analysis. In their investigation, they observed satisfactory correlation with ρ constants. Inductive and Resonance effects are failed to produce the correlation individually due to methylene resonance. But collectively σ_I, σ_R 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 -CH out of plane, in-plane, -CH=CH- out of plane and >C=C< out of plane stretches (cm^{-1}) of

Table 1. Infrared spectral data v (cm^{-1}) of substituted styryl 4-methyl-1-naphthyl ketones

Entry	$CO_{s\text{-}cis}$	$CO_{s\text{-}trans}$	$\text{-}CH_{ip}$	$\text{-}CH_{op}$	$CH=CH_{op}$	$C=C_{op}$
1a	1660	1621	1154	744	1038	563
1b	1652	1626	1155	742	1037	564
1c	1641	1605	1132	715	1028	536
1d	1654	1636	1166	761	1046	580
1e	1657	1629	1165	773	1044	578
1f	1655	1631	1161	765	1045	573
1g	1640	1604	1132	713	1206	535
1h	1649	1615	1143	720	1029	549
1i	1641	1618	1145	725	1033	552
1j	1665	1627	1149	735	1035	556
1k	1664	1658	1179	784	1055	598
1l	1667	1654	1177	787	1051	594
1m	1655	1649	1179	792	1053	597

vinyl part of these ketones are presented in Table 1. These modes are separately analyzed using single and multi linear regression analysis through Hammett equation with various σ constants. All the correlation data are pertaining to single parameter correlation and they gave positive ρ values in all cases. These modes produce good, satisfactory and fair degree of correlation with σ and σ^+ constants. [vCHop (ρ: r = 0.995, I = 754.72, ρ = 3.02, s = 1.5, n = 13); (σ^+: r = 0.992, I = 755.54, ρ = 5.60, s =1.8, n = 13)]; [vCHip (σ: r = 0.999, I = 1153.91, ρ = 2.90, s = 0.15, n = 13); (σ^+: r = 0.997, I = 1159.68, ρ = 3.83, s = 0.83, n = 13); (σ_I: r = 0.980, I = 1139.81, ρ = 2.98, s = 1.57, n = 13)]; [v-CH=CH-op (σ: r = 0.989, I = 1038.11, ρ = 6.90, s = 1.3, n = 13); (σ^-: r = 0.959, I = 1041.75, ρ = 7.59, s = 2.01, n = 13)]; [v>CH=CH<op (σ: r = 0.999, I = 563.62, ρ = 7.82, s = 0.15, n = 13); (σ^+: r = 0.980, I = 571.25, ρ = 5.14, s = 1.05, n = 13)]. Individually the Hammett σ_I and σ_R constants are failed to produce correlation because the vinyl part is affected by the conjugative structure in (III) 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).

$$v_{CH_{ip}}(cm^{-1}) = 725.250(\pm 0.832) + 85.685\sigma_I(\pm 2.091)$$
$$+ 8.14.278\sigma_R(\pm 1.725) \quad (5)$$
$$(R = 0.983, n = 13, P > 95\%)$$

$\nu_{CH_{op}}(cm^{-1}) = 743.880(\pm 1.015) + 54.49F (\pm 1.783)$
$\qquad + 38.752R(\pm 1.053)$ (6)
$\qquad (R = 0.921, n = 13, P > 90\%)$

$\nu_{CH=CH_{op}}(cm^{-1}) = 1038.432 (\pm 2.052) +$
$17.623F(\pm 0.527) + 14.533R(\pm 0.331)$ (7)
$\qquad (R = 0.942, n = 13, P > 90\%)$

$\nu_{CH_{ip}}(cm^{-1}) = 1143.513(\pm 5.398) + 46.613\sigma_I (\pm 2.137)$
$\qquad + 11.645\sigma_R (\pm 1.033)$
$\qquad (R = 0.900, n = 13, P > 90\%)$ (8)

$\nu_{CH_{ip}}(cm^{-1}) = 1153.890(\pm 4.618) + 29.595F (\pm 0.193)$
$\qquad + 23.808R (\pm 0.356)$ (9)
$\qquad (R = 0.953, n = 13, P > 90\%)$

$\nu_{C=C_{op}}(cm^{-1}) = 562.800(\pm 5.831) + 41.057F (\pm 1.216)$
$\qquad + 30.81R (\pm 1.778)$ (10)
$\qquad (R = 0.946, n = 13, P > 90\%)$

Substituent effects from NMR spectra
¹H NMR Spectra

The ¹H NMR spectral signals of ethylenic protons in all chalcones investigated are assigned. The chemical shifts of H_α protons are at higher field than those of H_β protons in all chalcones. The ethylenic proton signals give 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* 2. The observation that H_α protons appear at higher field than that

Table 2. ¹H and ¹³C nuclear magnetic resonance chemical shifts(ppm) of H_α, H_β protons C_α, C_β and Carbonyl carbon data of substituted styryl 4-methyl-1-naphthyl ketones

Entry	H_α	H_β	C_α	C_β	CO
1a	8.167	8.274	122.293	144.242	191.331
1b	8.132	8.194	121.334	142.624	491.587
1c	8.034	8.314	119.234	140.606	189.544
1d	8.102	8.161	122.400	140.818	192.390
1e	8.315	8.327	123.662	141.886	192.334
1f	8.174	8.297	122.966	142.997	191.927
1g	8.003	8.125	121.659	140.031	189.463
1h	8.200	8.318	118.997	141.111	190.356
1i	8.081	8.370	119.554	140.364	190.573
1j	8.020	8.274	120.262	139.852	190.871
1k	8.261	8.329	124.909	143.137	193.498
1l	8.278	8.344	119.603	145.643	193.309
1m	8.299	8.492	123.703	145.182	193.473

of H_β 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 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 operates 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 were produce a significant correlation with σ^+ (r = 0.996, I = 8.131, ρ = 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 H_β proton cases the correlation with σ and σ^- values is slightly better. [σ (r = 0.991, I = 8.244, ρ = 0.080, s = 0.25, n = 13); σ^-(r = 0.992, I = 8.299, ρ = 0.08, s = 0.34, n = 13)]. That the correlation with σ_I and σ_R parameters is good implies that this values are capable for predicting the substituent effects through chemical shifts individually [σ_I (r = 0.999, I = 8.266, ρ = 0.77, s = 0.26, n = 13); σ_R (r = 0.997, I = 8.320, ρ = 0.77, s = 0.85, n = 13)].

The multiple correlations involving either σ_I and σ_R 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).

$\delta_{H-\alpha}^{(ppm)} = 8.061(\pm 0.037) + 0.279\sigma_I(\pm 0.084)$
$\qquad + 0.036\sigma_R(\pm 0.071)$ (11)
$\qquad (R = 0.999, n = 13, P > 90\%)$

$\delta_{H-\alpha}^{(ppm)} = 8.103(\pm 0.004) + 0.221F (\pm 0.089)$
$\qquad + 0.092R(\pm 0.056)$ (12)
$\qquad (R = 0.996, n = 13, P > 90\%)$

$\delta_{H-\beta}^{(ppm)} = 8.274(\pm 0.092) + 0.122\sigma_I(\pm 0.099)$
$\qquad + 0.150\sigma_R(\pm 0.327)$ (13)
$\qquad (R = 0.999, n = 13, P > 90\%)$

$\delta_{H-\beta}^{(ppm)} = 8.209(\pm 0.147) + 0.142F(\pm 0.128)$
$\qquad + 0.071R(\pm 0.005)$ (14)
$\qquad (R = 0.998, n = 13, P > 90\%)$

^{13}C NMR Spectra

From ^{13}C NMR spectra the observed ^{13}C chemical shifts of C_α, C_β and carbonyl carbons are presented in Table 2. These chemical shifts of C_α, C_β are correlated with various Hammett substituent constants. From the results of statistical analysis the correlation of C_α carbon chemical shifts are failed with all sigma constants. C_β carbon chemical shifts are produce fair degree of correlation obtained with Hammett σ and σ_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 C_α carbon than C_β carbon.

Uniformly σ_I and σ_R parameters or F and R values are adequately explained the substituent effects in all chalcones are evidenced from the correlation equations (15-17).

$$\delta_{C-\alpha}^{(ppm)} = 123.07(+ 1.289) - 0.870F(+ 2.554) + 3.168R(+ 1.617) \quad (15)$$
$$(R = 0.967, n = 13, P > 90\%)$$

$$\delta_{C-\beta}^{(ppm)} = 142.191(\pm 1.101) + 0.327\sigma_I(\pm 0.973) + 1.755\sigma_R(\pm 0.113) \quad (16)$$
$$(R = 0.997, n = 13, P > 90\%)$$

$$\delta_{C-\beta}^{(ppm)} = 146.72(\pm 1.002) + 1.405F(\pm 1.091) + 5.7227R(\pm 0.041) \quad (17)$$
$$(R = 0.998, n = 13, P > 90\%)$$

The ^{13}C chemical shifts of carbonyl carbons of these ketones are correlated with various Hammett σ constants. The result of statistical analysis shows good and satisfactory correlation with σ and σ^- constants. [$\sigma(r = 0.998, I = 191.351, \rho = 3.194, s = 0.02, n = 13)$; σ^+ $(r = 0.976, I = 191.844, \rho = 2.428, s = 0.08, n = 13)$]. Hammett σ_I and σ_R constants are failed for produce the correlation due to the carbon oxygen double bond character was converted into single bond character >C-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).
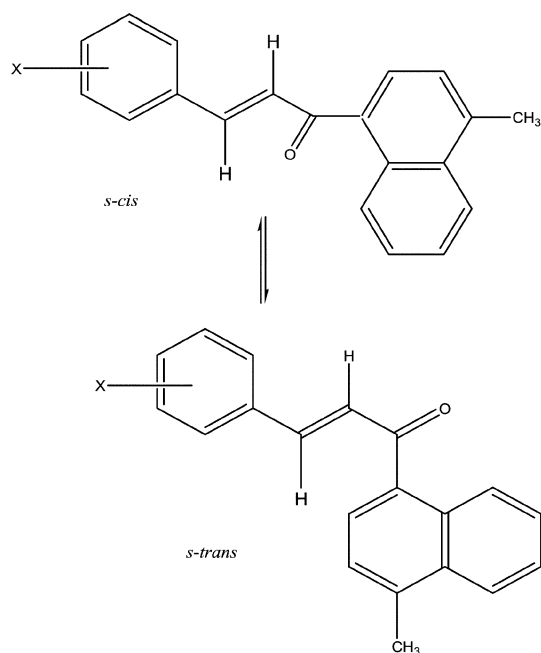
$$\delta_{C=O}^{(ppm)} = 190.441(\pm 0.469) + 4.011\sigma_I(\pm 0.105) + 0.913\sigma_R(\pm 0.018) \quad (18)$$
$$(R = 0.914, n = 13, P > 90\%)$$
$$\delta_{C=O}^{(ppm)} = 191.341(\pm 0.423) + 2.523F(\pm 0.873) + 1.917R(\pm 0.513) \quad (19)$$
$$(R - 0.943, n - 13, P > 90\%)$$

s-cis

s-trans

Where X= H, m-NH$_2$, p-NH$_2$, m-Br, m-Cl, p-Cl, p-N(CH$_3$)$_2$, p-OH, p-OCH$_3$, p-CH3, o-NO$_2$, m-NO$_2$, p-NO$_2$

(I)

Where X= H, m-NH$_2$, p-NH$_2$, m-Br, m-Cl, p-Cl, p-N(CH$_3$)$_2$, p-OH, p-OCH$_3$, p-CH3, o-NO$_2$, m-NO$_2$, p-NO$_2$

(II)

(III)
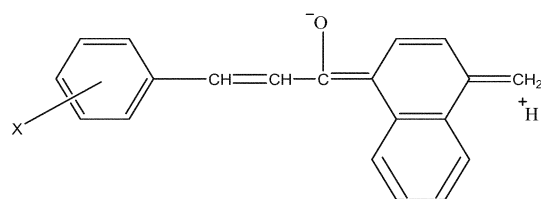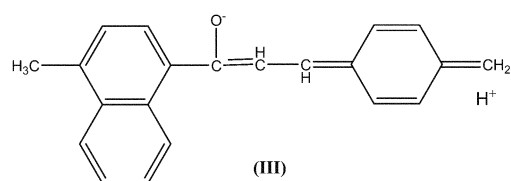
CONCLUSION

This method is a very efficient and selective protocol for crossed-aldol 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 σ constants. A good correlation obtained with σ^+ constants and carbonyl frequencies of s-$trans$ 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_β protons produce satisfactory correlation with all Hammett constants than the H_α proton chemical shifts. The inductive and resonance effects of the substituents are predicting the reactivity collectively well on H_β and it produce good correlation with field and resonance effects. The substituents were fails for prediction of reactivity on C_α carbon chemical shifts. A fair degree of correlation obtained for C_β chemical shifts with σ and σ_R. Collectively field and resonance effects are gave satisfactory correlation on both carbons. The carbonyl carbon chemical shifts are produce good and satisfactory correlation with substituent constants through single and multiparameter statistical analysis.

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