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Synthesis and spectral studies of some (E)-N-(substituted benzylidene)-4-methylbenzenesulfonamides

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Abstract

A series of some (E)-N-(substituted benzylidene)-4-methylbenzenesulfonamides have been synthesised using solid SiO2-H3PO4 catalyst under solvent free conditions in microwave irradiation. The synthesised (E)-N-tosylimine purities have been verified by their physical constants and spectroscopic data. The spectral frequencies are correlated with Hammett substituent constants, F and R parameters using linear regression analysis. From the results of statistical analysis the effect of substituents on the group frequencies will be discussed.

Keywords: (E)-N-tosylimines; SiO2-H3PO4; Greener synthesis; Hammett correlations.

Introduction

Imines which possesses the -CH=N-SO_2- moiety and it is bonded with alkyl - aryl or aryl-aryl groups in both sides are known as tosylimines. The *(E)*-N-tosylimines are useful versatile intermediates for organic synthesis [1]. These *(E)*-N-tosylimine intermediates are used as excellent substrates in Diels-Alder reactions and it is called as Aza-Diels-Alder reaction [2]. In this Diels-Alder reactions this intermediates undergo nucleophilic additions [3,4], reductions [5], radical [6] and Baylis-Hillman [7,8]. Generally, these *E*-N-tosylimines were prepared by condensation of aldehydes and 4-methylbenzenesulfonamides or solfonyl chlorides using several methods such as conventional solvent assisted condensation [9,10], greener methods, like microwave assisted condensation [11], isomerization of N-tosylaziridines by palladium [12], tellurium metal assisted oxidation of chloramine-T [9], rearrangement of oxime O-sulfinates by in situ [1,14], reaction of N-trimethylsilylaldimine and solfonyl chlorides [15] and condensation of racemic sulfinylamides with carbonyl compounds followed by oxidation with haloperoxobenzoic acid [16]. For this condensation various catalyst have been utilized such as, $TiCl_4$ [17], aq. HCOOH and Na_2CO_3 [18], Molecular sieves-amberlite [19], claymineral [20], zeolites [7], Lewis acid, protoic acids, base, metal oxides, $AlCl_3$ [21], BF_3-Et_2O [22], sulfamic acid [23], P_2O_5/SiO_2 [24], tetraethyl orthosilicate [25], silphox [26], zirconium sulphate-silica [27], sulfated titania [28], montmorillonite K-10 [29], zirconium oxide-persulfate [30], powdered zinc oxide [31], TFFA [32], $InCl_3$ [10] and ionic liquids [33]. This *(E)*-N-tosylimines have been used for synthesis of many organics

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such as triheteroarylmethanes [2], stereoselective heterocycles [1], co-ordination compounds [34], porphyrins [35], azetidine-2-imines [36], pyrrolidines [37], multisubstituted imidazolidines [38], α,β-diamino acid derivatives [39], aziridines [40], chiral aziridines [41], (Z)-N-(1-bromo-1-alken-2-yl)-*p*-toluenesulfonamides [3], tosylamino alkyl naphthalenols [42], vinyl aziridines [43], 2-benzoyl fumarates and 1-aza dienes [44], complexes containing nitroamines [45], arylgylcene derivatives [46], 2-alikylidenazetidines [47], chiral 1-aryl-1-ethylamines [48], heteroaromatic N-tosyl-α-amino acids [49], carboxylates [50], tosylhexahydropyrimidine-2-imines [51], β-aryl-β-amino acids [4], furyl sulphonamides [52], Baylis-Hillman adducts [7,8], imidazoles [11], and sulphonamide phosphonates [53]. Solvent free methods are very useful for synthesis of various organics [1,54-56]. Organic Chemists and researcher have paid more attention to green synthesis, due to the operational simplicity, lesser times, high yields, easy handling procedure and less hazardous to reaction and environment. The spectroscopic data is useful for analysis ground state molecular equilibration and configuration of organic molecules [57-60]. Also these findings were carried out via spectral correlations. The spectral group frequencies were correlated various substituent constants and F and R parameters gave the effects of the substituents on the group frequency of the corresponding molecule. This type of study was studied only in ketones, esters, imines, acyl halides, pyrazolines, unsaturated aldehydes, acids [61-66]and bicycle ketones [67]. With a view to above, there is no report available in the literature for solvent free synthesis and the study of effects of substituent on the group frequencies of some *(E)-N*-tosylimines by SiO_2-H_3PO_4 catalyzed condensation of substituted benzaldehydes and 4-methyl sulphonamide. Therefore the authors have taken efforts to synthesis of some (*E*)-*N*-(substituted benzylidene)-4-methylbenzenesulfonamides and studied the spectral correlations on the specified group frequencies using Hammett correlation equation.

Experimental

Materials and Methods

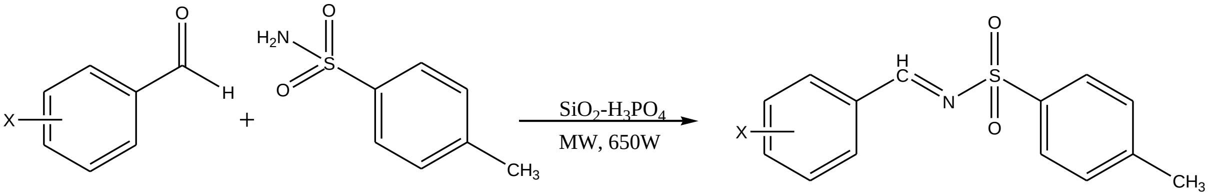
All chemicals used were purchased from Sigma-Aldrich and E-Merck chemical companies. Infrared spectra (KBr, 4000-400cm^{-1}) were recorded on AVATAR-300 Fourier transform spectrophotometer. The NMR spectra of all *(E)*-N-tosylimines were recorded in INSTRUM AV300 NMR spectrometer operating at 500MHz for ^{1}H and 125.46MHz for ^{13}C spectra in DMSO solvent using TMS as internal standard. Mass spectra were recorded on a SIMADZU GC-MS2010 Spectrometer using Electron Impact (EI) techniques.

Synthesis of SiO_2-H_3PO_4 catalyst

The SiO_2-H_3PO_4 catalyst was prepared by procedure published in literature [54].

Synthesis of (*E*)-N-(substituted benzylidene)-4-methylbenzenesulfonamides

To an appropriate mixture of substituted benzaldehydes (2 mmol), 4-methylbenzene sulphonamide (2mmol) and 0.5g of SiO_2-H_3PO_4 were taken in 50 mL glass beaker and covered with lid. This mixture was subjected to microwave heating for 5-8 minutes at 650W(Samsung GW73BD microwave oven, 100-750W, 230V A/C, 2450MHz). The completion of the reaction was monitored by thin layer chromatography. After completion of reaction, dichloromethane (20 mL) was added, followed by simple filtration. The pure product was obtained by the evaporation of dichloromethane and recrystallization with ethanol. The yields of the *(E)*-N-tosylimines are more than 90%. The purities of these *E*-N-tosylimines were persuaded by their physical constants, IR, ^{1}H, ^{13}C NMR and Mass spectral data. Analytical and mass spectral data are presented in TABLE 1.



X= H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH$_3$, 4-CH$_3$, 4-NO$_2$

Scheme 1: Synthesis of substituted (*E*)-*N*-(substituted benzylidene)-4-methyl benzenesulfonamides.

Entry	X	M.F.	M.W.	Yield (%)	m.p. (°C)	Mass (m/z)
1	H	$C_{14}H_{13}NO_2S$	259	96	106-107(105-108) [33]	259 [M+]
2	3-Br	$C_{14}H_{12}BrNO_2S$	339	91	117-118	339 [M^+], 341 [M^{+2}]
3	4-Br	$C_{14}H_{12}BrNO_2S$	339	93	198-199(200-204) [33]	339 [M^+], 341 [M^{+2}]
4	2-Cl	$C_{14}H_{12}ClNO_2S$	293	92	131-132(130-132) [33]	293 [M^+], 295 [M^{+2}]
5	4-Cl	$C_{14}H_{12}ClNO_2S$	293	91	173-174(174-176) [33]	293 [M^+], 295 [M^{+2}]
6	2-F	$C_{14}H_{12}FNO_2S$	277	90	121-122(120-125) [33]	277 [M^+], 279 [M^{+2}]
7	4-OCH$_3$	$C_{15}H_{15}NO_3S$	289	95	125-126(124-128) [33]	289 [M^+]
8	4-CH$_3$	$C_{15}H_{15}NO_2S$	273	94	117-118(116-118) [33]	273 [M^+]
9	4-NO$_2$	$C_{14}H_{12}N_2O_4S$	290	92	113-114(162-170) [33]	290 [M^+]

Table 1: Analytical, Physical constants and mass fragment data of (*E*)-*N*-(substituted benzylidene)-4-methylbenzenesulfonamides.

Results and Discussion

Spectral linearity

In the present study the Hammett spectral linearity of these synthesised *E*-N-tosylimines has been studied by evaluating the substituent effects [60-65] on the group frequencies. The assigned spectroscopic data of all *(E)*-N-tosylimines such as absorption infrared carbonyl stretches of νC=N and νS=O, (cm^{-1}), NMR chemical shifts δ (ppm) of CH, CH , and C=N have been assigned and these data are correlated with various substituent constants.

IR spectral study

The assigned C=N and S=O frequencies (cm^{-1}) of synthesised *(E)*-N-tosylimines of present study are tabulated in TABLE 2. These data have been correlated with Hammett substituent constants [55-67] and Swain-Lupton constants [68] and are presented in TABLE 3. In this correlation the structure parameter Hammett equation employed is as shown in the following equation:

$$\nu = \rho\sigma + \nu_0 \qquad \ldots (1)$$

Where ν is the carbonyl frequencies of substituted system and ν_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.

Entry	**X**	**IR**		**^{1}H**		**^{13}C**	
		νC=N	**νS=O**	**δC-H**	**δCH_3**	**δC=N**	**δCH_3**
1	H	1657.34	1062.58	8.202	2.416	169.85	23.65
2	3-Br	1657.68	1064.46	8.702	2.716	170.51	24.63
3	4-Br	1658.24	1064.34	8.522	2.733	171.63	24.61
4	2-Cl	1658.44	1063.22	8.401	2.462	172.35	24.01
5	4-Cl	1658.92	1062.45	8.302	2.402	170.65	24.06
6	2-F	1658.73	1062.66	8.491	2.315	169.58	24.38
7	4-OCH_3	1658.02	1061.02	8.011	2.350	175.12	23.08
8	4-CH_3	1658.22	1061.21	8.122	2.371	176.65	23.16
9	4-NO_2	1659.23	1065.95	8.975	2.932	172.87	24.92

Table 2: Infrared stretches(ν, cm^{-1}) and NMR chemical shifts(δ, ppm) of (*E*)-N-(substituted benzylidene)-4-methylbenzenesulfonamides.

The results of single parameter statistical analysis of νC=N stretches with Hammett σ σ^+ and σ_I, substituent constants and R parameters gave satisfactory correlations excluding H, 3-Br, and 4-CH_3 substituents. If these substituents were included in the correlation, the correlations were reduced significantly. The resonance effect components of the substituents were fail in correlation. All correlations gave positive ρ values. This may mean that the normal substituent effect operates in all *(E)*-N-tosylimines. The σ_R constants and R parameters were fail in correlations. This is due to the inability of substituents for prediction of the reactivity on the C=N stretches and associate with conjugation between the substituent and the C=N group in all *E*-N-tosylimines as shown in Figure 1.

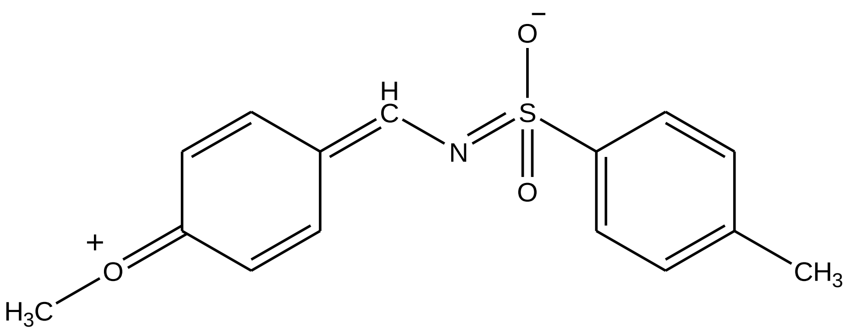


Figure 1: The resonance –conjugative structure.

Frequency	**Constants**	**r**	**I**	**ρ**	**s**	**n**	**Correlated derivatives**
νC=N(cm^{-1})	σ	0.905	1658.12	1.037	0.53	7	4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$^+$	0.904	1658.21	0.557	0.56	7	4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$_I$	0.906	1657.72	1.642	0.48	8	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-NO$_2$
	σ$_R$	0.803	1658.33	0.120	0.63	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	F	0.906	1657.70	1.600	0.47	8	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-NO$_2$
	R	0.705	1658.34	0.141	0.63	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
νS=O(cm^{-1})	σ	0.971	1062.70	4.055	1.31	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$^+$	0.908	1062.98	2.519	1.37	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$_I$	0.903	1062.58	2.331	1.80	7	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-NO$_2$
	σ$_R$	0.907	1064.57	6.476	1.34	7	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-NO$_2$
	F	0.901	1062.89	1.414	1.85	6	3-Br, 4-Br, 2-Cl, 4-Cl, 4-OCH, 4-NO$_2$
	R	0.907	1064.68	5.433	1.33	7	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 4-OCH, 4-NO$_2$
δCH(ppm)	σ	0.962	8.551	0.584	0.24	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$^+$	0.962	8.591	0.377	0.24	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$_I$	0.901	8.591	0.195	0.30	7	3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-NO$_2$
	σ$_R$	0.906	8.847	1.050	0.22	6	3-Br, 4-Br, 2-Cl, 4-Cl, 4-OCH, 4-NO$_2$
	F	0.812	8.605	0.148	0.31	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	R	0.869	8.863	0.873	0.42	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
δCH$_3$(ppm)	σ	0.907	2.243	0.548	0.13	7	H, 3-Br, 4-Br, 2-Cl, 4-OCH, 4-CH, 4-NO$_2$
	σ$^+$	0.906	2.475	0.278	0.17	7	H, 3-Br, 4-Br, 2-Cl, 4-OCH, 4-CH, 4-NO$_2$
	σ$_I$	0.850	2.336	0.513	0.19	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$_R$	0.917	2.675	0.750	0.17	7	H, 4-Br, 2-Cl, 4-Cl, 2-F, 4-CH, 4-NO$_2$
	F	0.838	2.394	0.334	0.21	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	R	0.906	2.653	0.573	0.18	7	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 4-CH, 4-NO$_2$
δC=N(ppm)	σ	0.843	172.74	-3.312	2.32	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$^+$	0.853	172.65	-2.909	2.09	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$_I$	0.831	173.55	-3.921	2.38	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$_R$	0.803	172.20	0.391	2.51	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	F	0.904	173.63	-3.945	2.35	8	3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	R	0.803	172.05	-0.358	2.25	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
δCH$_3$(ppm)	σ	0.931	23.70	1.933	0.25	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$^+$	0.922	23.83	1.244	0.26	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$_I$	0.900	23.24	2.250	0.28	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	σ$_R$	0.831	24.24	1.076	0.66	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	F	0.907	23.30	1.986	0.45	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$
	R	0.803	24.26	0.893	0.66	9	H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH, 4-CH, 4-NO$_2$

r= correlation coefficient; I= intercept; ρ=slope; s=standard deviation; n= number of correlated derivatives

Table 3: Results of statistical analysis of infrared absorptions (ν, cm^{-1}) and NMR chemical shifts (δ, ppm) of *(E)*-N-tosylimines with Hammett σ, σ^+, σ_I, σ_R and F and R parameters.

The correlation of νC=S stretches with Hammett substituent constants, F and R parameters gave satisfactory r values [σ (r=0.906), σ^+(r=0.906), σ_I(r=0.903), σ_R(r=0.907), F (0.901) and R(0.907)] excluding H, 2-F and 4-CH_3 substituents. If these substituents were included in the correlation, the correlations were reduced significantly. All correlations gave positive ρ values and it is evident for the normal substituent effects operates in all systems. The failure in correlation is due the conjugation between the substituent and the C=S group in all *(E)*-N-tosylimines as shown in Figure 1.

In view of the inability of some of the σ constants to produce individually satisfactory correlations, it was thought that worthwhile to seek multiple correlations involving either σ_I and σ_R constants or Swain-Lupton's [68] F and R parameters. The correlation equations for νC=N and νC=S are given in equations (2-5).

$$\nu C{=}N(cm^{-1}) = 1657.75(\pm 0.364)+1.651(\pm 0.771)\sigma_I+0.222(\pm 0.092)\sigma_R \quad \ldots\textbf{(2)}$$

$$(R = 0.965,\ n=9,\ P>95\%)$$

$$\nu C{=}N(cm^{-1}) = 1657.78(\pm 0.321)+1.725(\pm 0.703)F+0.577(\pm 0.075)R \quad \ldots\textbf{(3)}$$

$$(R = 0.970,\ n=9,\ P>95\%)$$

$$\nu C{=}S(cm^{-1}) = 1063.66(\pm 0.882)+2.613(\pm 1.887)\sigma_I+6.638(\pm 2.304)\sigma_R \quad \ldots\textbf{(4)}$$

$$(R = 0.978,\ n=9,\ P>95\%)$$

$$\nu C{=}S(cm^{-1}) = 1063.79(\pm 0.861)+2.736(\pm 1.757)F+6.125(\pm 1.897)R \quad \ldots\textbf{(5)}$$

$$(R = 0.980,\ n=9,\ P>95\%)$$

^{1}H NMR spectral study

Deuterated dimethylsulphoxie was used for recording the ^{1}H NMR spectra of synthesized (*E)*-N-tosylimines employing tetramethylsilane (TMS) as internal standard. The CH and CH_3 proton signals of the (*E)*-N-tosylimines were obtained as a singlet and assigned from their spectra. The assigned CH and CH_3 proton chemical shifts δ(ppm) of all (*E)*-N-tosylimines were presented in TABLE 2.

In nuclear magnetic resonance spectra, the proton or the ^{13}C chemical shifts (δ) depends on the electronic environment of the nuclei concerned. The assigned vinyl proton chemical shifts (ppm) have been correlated with reactivity parameters using Hammett equation in the form of

$$\text{Log}\ \delta = \text{Log}\ \delta_0 + \rho\sigma \quad \ldots\ \textbf{(6)}$$

where δ_0 is the chemical shift of unsubstitued ketones.

The assigned CH proton chemical shifts (ppm) were correlated with Hammett σ constants and F and R parameters [54-67]. The results of statistical analysis [54-67] are presented in TABLE 3. The obtained correlations were satisfactory for CH chemical shifts with Hammett σ substituents excluding H, 2-F and 4-CH_3 substituents. When these substituents were included in the correlations, they reduced the r values significantly. The F and R parameters gave poor correlation. All correlation gave positive ρ values and it is evident for the normal substituent effectsoperates in all correlations. The failure in correlation was due to the weak and incapable of resonance and field effects of substituents for prediction of the effects on the CH chemical shifts in all systems and it is associated with the resonance-conjugates structure shown in Figure 1.

The assigned CH_3 proton chemical shifts (ppm) were correlated with Hammett σ constants and F and R parameters [54-67]. The results of statistical analysis [54-67] are presented in Table 3. The obtained correlations were satisfactory for CH_3 chemical shifts with Hammett σ, σ+, σ_R constants and R parameters excluding H, 2-F and 4-CH_3 substituents. When these substituents were included in the correlations, they reduced the r values significantly. The σ_I and F parameters gave poor correlation. All correlation gave positive ρ values and it is evident for the normal substituent effect operates in all correlations. The failure in correlation was due to the weak and incapable of inductive and field effects of substituents for prediction of the effects on the CH_3 chemical shifts in all systems and it is associated with the resonance-conjugates structure shown in Figure 1.

Application of Swain-Lupton's [68] treatment to the relative chemical shifts (δ,ppm) of CH and CH_3 with F and R values is successful with resonance, inductive effect generates the multi regression equations (7-10).

$\delta_{CH}{}^{(ppm)} = 8.763(\pm0.164)+0.239(\pm0.035)\sigma_I + 1.065(\pm0.429)\sigma_R$ …**(7)**

(R = 0.97 , n=9, P>95%)

$\delta_{CH}{}^{(ppm)} = 8.747(\pm0.149) +0.356(\pm0.032) F + 0.964(\pm0.034) R$ …**(8)**

(R = 0.975, n=9, P>95%)

$\delta_{CH3}{}^{(ppm)} = 2.463(\pm0.076)+0.548(\pm0.164)\sigma_I + 0.784(\pm0.200)\sigma_R$ …**(9)**

(R = 0.989, n=9, P>95%)

$\delta_{CH3}{}^{(ppm)} = 2.497(\pm0.095) +0.485(\pm0.204) F + 0.696(\pm0.220) R$ …**(10)**

(R = 0.98 , n=9, P>95%)

^{13}C NMR spectral study

Physical organic chemists, researchers, organic chemists, spectral analysts, and scientists [54-67] have made extensive study of ^{13}C NMR spectral correlations of ketones, enones, acyl chlorides, bromides, esters, imines, pyrazolines and styrenes. The assigned C=N and CH_3 carbon chemical shifts(δ, ppm) are presented in TABLE 2. The results of statistical analysis are given IN TABLE 3. The C=N chemical shifts (δ, ppm) gave satisfactory correlation with R parameters. The Hammett substituent constants and F parameters were fail in correlations. Most of the correlations produced negative ρ values. This means that the reserved substituent effect operates in all correlations. This is due to reasons stated earlier with the resonance conjugative structure shown in Figure 1.

The results of statistical analysis of CH_3 chemical shifts(δ, ppm) of synthesized tosylimines with Hammett substituent constants, R and R parameters were presented in Table 3. The CH_3 chemical shifts (δ, ppm) gave satisfactory correlation with Hammett σ, σ^+, σ_I and F parameters. The Hammett σ_R constant and R parameters were fail in correlations. All correlations gave positive ρ values. This means that the normal substituent effect operates in all systems. The failure in correlation is due to the reasons stated earlier and it is associated with the resonance conjugative structure shown in Figure 1.

The Swain Lupton's [68] parameter correlations of C=N and CH_3 carbon chemical shifts(δ, ppm) were satisfactorily and the generated regression equations are given in (9-12).

$\delta C{=}N^{(ppm)} = 173.57(\pm1.802) - 3.915(\pm0.385)\sigma_I + 0.151(\pm0.041)\sigma_R$ …**(9)**

(R = 0.938, n=9, P>95%)

$\delta C{=}N^{(ppm)} = 173.42(\pm 1.692) - 4.255(\pm 0.364)F - 1.433(\pm 0.319)R$ …**(10)**

($R = 0.94$, n=9, P>90%)

$\delta CH_3{}^{(ppm)} = 23.43(\pm 0.238) + 2.301(\pm 0.509)\sigma_I + 1.219(\pm 0.622)\sigma_R$ …**(11)**

($R = 0.938$, n=9, P>95%)

$\delta CH_3{}^{(ppm)} = 23.51(\pm 0.201) + 2.301(\pm 0.413)F + 1.474(\pm 0.467)R$ …**(12)**

($R = 0.99$, n=9, P>90%)

Conclusions

We have synthesised more than 90% yields of some *(E)*-N-tosylimines using SiO_2-H_3PO_4 acid catalyst by solvent free condensation of 4-mehylbenzensulfonamide and substituted benzaldehydes under microwave irradiation. The effects of substituent on the group frequencies (ν, cm^{-1}) such as C=N, S=O and the chemical shifts(δ, ppm) of CH,CH_3 and C=N of all the *(E)*-N-tosylimines have been studied. Most of the single and multi-regressions produced satisfactory correlations.

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