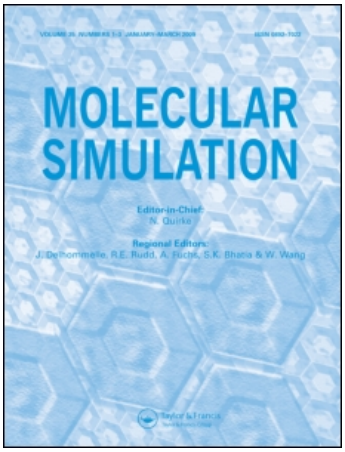

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Kinetic and thermodynamic study of the substituent effect on the amino-Claisen rearrangement of *para*-substituted *N*-allyl-*N*-arylamine: a Hammett study via DFT

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Kinetic and thermodynamic study of the substituent effect on the amino-Claisen rearrangement of *para*-substituted *N*-allyl-*N*-arylamine: a Hammett study via DFT

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In order to find the susceptibility of the amino-Claisen rearrangement and the next proton shift reaction of *N*-allyl-*N*-arylamine to the substituent effects in the *para* position, the kinetic and thermodynamic parameters were calculated at the B3LYP level using the 6-31G** basis set. The calculated activation energies for the rearrangements and proton shift reactions are close to 44.4 and 49.5 kcal mol^{-1}, respectively. The transition states of the rearrangement with electron-donor substituents are more stable than those with electron-withdrawing substituent groups, but for the proton shift reaction, this situation is reversed (with the exception of fluorine atom for the rearrangement and fluorine and chlorine atoms for the proton shift reaction). Negative values for the activation entropy confirm the concerted mechanism for the amino-Claisen rearrangement and proton shift reaction. The Hammett ρ values of -2.4172 and -1.7791 are obtained for σ_p and σ^- (enhanced sigma) in the amino-Claisen rearrangement, respectively. The correlation between $\log(k_X/k_H)$ and σ_p is weaker than that with σ^- (enhanced sigma). A negative Hammett ρ value indicates that the electron-donating groups slightly increase the rate of amino-Claisen rearrangement. A positive Hammett ρ value (2.4921) for the proton shift reaction indicates that electron-withdrawing groups increase the rate of reaction.

Keywords: Hammett; density functional theory; substituent effect; amino-Claisen rearrangement; *N*-allyl-*N*-arylamine

1. Introduction

A typical organic reaction proceeds in a certain mechanism. There might be several proposed mechanisms for a typical organic reaction. Experimental methods have many instrumental limitations, including trapping the intermediates or transition states (TSs) in confirming the mechanism that reactions proceed via it. Computational methods can make the mechanism confirmation easier, cheaper and more exact. For example, the gas-phase kinetics and the mechanism of two retro-cheletropic ene reactions were studied applying computational methods, and therefore the stepwise mechanism was rejected and the concerted mechanism was fully investigated [1].

Among the most efficient reactions in terms of atom economy are the [3,3] sigmatropic shifts, which allow the formation of a C—C bond through the rearrangement of a molecule [2]. The potential of [3,3]-sigmatropic rearrangements (such as Cope and Claisen rearrangements) to create simultaneously two adjacent stereocentres with high levels of diastereoselectivity has been exploited extensively in the synthesis of complex molecular systems [3,4]. The Claisen rearrangement is the example of a [3,3]-sigmatropic rearrangement, first reported in 1912 by Ludwig Claisen [3,5–7]. In this rearrangement, a σ-bond moves across a conjugated π-system to a new site. In fact, a [3,3]-sigmatropic rearrangement includes the cleavage of a C—X (X=O, N, S) σ-bond and formation of a new C—C σ-bond three atoms apart, with the reorganisation of the conjugated π-system [8]. The [3,3]-sigmatropic rearrangement of *N*-allyl-*N*-arylamines, known as the amino-Claisen rearrangement (aza-Cope rearrangement), has received much less attention than its oxygen counterpart, probably because of the more drastic conditions required [9,10] and the concomitant tendency towards side reactions (see Scheme 1).

The amino-Claisen rearrangement has many limitations, such as slow rates, high-temperature requirement and low yield. The thermal, uncatalysed aromatic amino-Claisen rearrangement (aza-Cope rearrangement) requires a temperature of 250–280°C [11]. Undoubtedly, this is due to the high kinetic barrier of the amino-Claisen rearrangement [12]. In general, allylenamine structures require heating to 100–150°C in excess of the temperature for the analogous rearrangement with allyl enol ethers. Charge on the nitrogen atom kinetically facilitates the rearrangement considerably. In fact, the first reports of aza-Cope rearrangements were those of iminium and ammonium salts. Under high temperatures, aromatic *N*-allylamines are not stable; e.g. *N*-allylaniline heated at 275°C gives aniline, propane and tar instead of the expected *ortho*-allylaniline [11]. The same indirect probes of reaction topology as applied to the aromatic Claisen rearrangement suggested a

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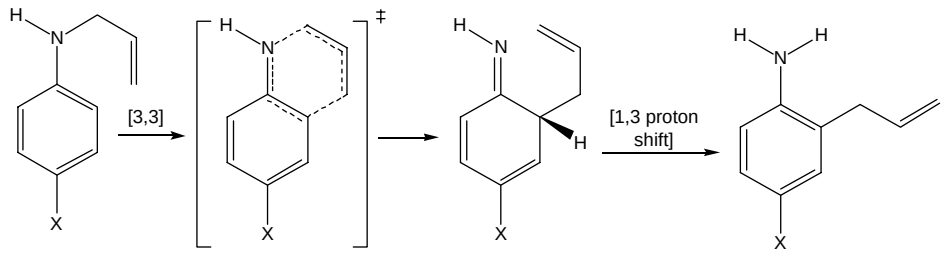


Scheme 1. Amino-Claisen rearrangement of *N*-allyl-*N*-arylamine and 1,3-proton shift of the intermediate. X=H, NO_2, CN, CHO, F, Cl, NH_2, $NHCH_3$, OH, OCH_3 and CH_3.

preferential chair-like TS for the amino analogue [9]. The amino-Claisen rearrangement is promoted in the presence of transition metals, Lewis or protic acids as catalysts. Protic acids such as HCl, H_2SO_4 and H_3PO_4 have been used in certain aromatic aza-Cope rearrangements. But the use of strong protic acids with *N*-allylanilines may lead to the formation of indole and indoline, thereby reducing the effectiveness of this reaction [11].

In the present work, we extended our studies to discover the effect of the substituent on the rearrangement and 1,3-proton shift reaction of *N*-allyl-*N*-arylamine by applying the following Hammett equation [13]:

$$\log \frac{k_X}{k_H} = \rho\sigma, \tag{1}$$

where k_X is the rate constant for a side-chain reaction of a benzene derivative, where a substituent is in *para* or *meta* position with respect to the side chain and k_H is the corresponding quantity for the unsubstituted compound; σ is a Hammett substituent constant, which in principle is characteristic of the substituent and ρ is a reaction constant, which depends on the nature of the reaction. The Hammett equation is an important example of linear free energy relationships, which have been widely used in studies of the chemical reactivity of substituted benzenes [14]. Several compilations of the Hammett σ_p and enhanced σ_p (σ^-) values [15] are tabulated in Table 1.

Table 1. Hammett substituent constant values [15].

X	σ_p	σ^-
H	0	–
NO_2	0.780	1.270
CN	0.650	1.000
CHO	0.450	1.126
F	0.060	–
Cl	0.220	–
NH_2	−0.630	–
$NHCH_3$	−0.840	–
OH	−0.380	–
OCH_3	−0.280	–
CH_3	−0.170	–

2. Computational details

The structures corresponding to the reactants, TSs, intermediates and products (Scheme 1) were optimised, using the Gaussian 03 computational package [16] with the DFT method. The optimised geometries of the stationary points on the potential energy surfaces were performed using Becke's three-parameter hybrid exchange functional with the correlation functional of Lee, Yang and Parr (B3LYP) [17,18] with the 6-31G** basis set. To confirm the nature of the stationary species and evaluate the activation energy barriers, frequency calculations were carried out. For minimum state structures, only real frequency values and for the TSs, only a single imaginary frequency value was accepted. The synchronous transit-guided quasi-Newton method [19] was used to locate the TSs. The activation energies, E_a, and the Arrhenius factors were computed using Equations (2) and (3), respectively, which are derived from the TS theory [20,21]:

$$E_a = \Delta H^{\neq}(T) + RT, \tag{2}$$

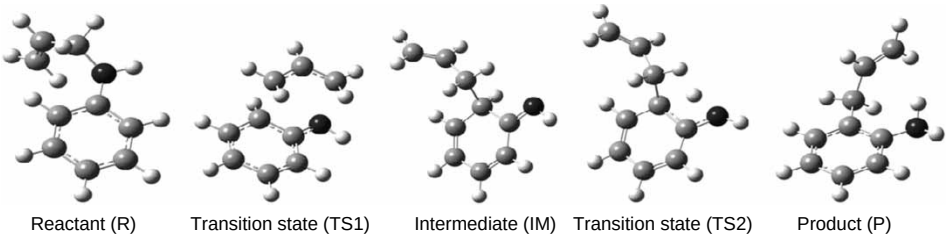
$$A = (ek_B T/h)\exp(\Delta S^{\neq}(T)/R). \tag{3}$$

Here, $\Delta H^{\neq}$, $\Delta S^{\neq}$, R, T and k_B are the activation enthalpy, activation energy, universal gas constant, absolute temperature and the Boltzmann constant, respectively. Kinetic and thermodynamic parameters were calculated at 298.15 K and 1.0 atm.

3. Results and discussion

Scheme 2 shows the optimised structures of the reactant, TSs, intermediate and product for unsubstituted *N*-allyl-*N*-arylamine at the B3LYP/6-31G** level. In Table 2, the resultant thermodynamic parameters are presented for *N*-allyl-*N*-arylamines to their corresponding intermediates (sigmatropic reaction), and for intermediates to corresponding ortho-allylanilines (1,3-proton shift), with different substituents.

The calculations are carried out at the B3LYP/6-31G** level, which include: sum of electronic and thermal enthalpies (H), sum of electronic and thermal Gibbs free energies (G), and entropies (S) for the ground state of



Scheme 2. The optimised structures of reactant, TSs, intermediate and product for the studied reaction.

reactants, products, intermediates and their corresponding TSs in this way, the equilibrium constants (K_{eq}), standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) of both rearrangement and 1,3-proton shift reaction are calculated and collected in Table 3.

The activation energies (E_a), rate constants (k), pre-exponential factors (A), activation enthalpies ($\Delta H^{\neq}$), activation Gibbs free energies ($\Delta G^{\neq}$), activation entropies ($\Delta S^{\neq}$), n_T (the position of the transition structure along the reaction coordinate) and $\log(k_X/k_H)$ for sigmatropic rearrangements and 1,3-proton shift reactions are presented in Tables 4 and 5.

3.1 Kinetic discussion

The results of our calculations showed that the sigmatropic rearrangements with various substituents are endothermic ($\Delta H^\circ > 0$) and the global rearrangement process is not spontaneous ($\Delta G^\circ > 0$). On the other hand, the studied proton shift reactions via all studied substituents are exothermic ($\Delta H^\circ < 0$) and the global proton shift reactions are spontaneous ($\Delta G^\circ < 0$). The values of ΔG° for the sigmatropic rearrangements and proton shift reactions are near to their corresponding calculated ΔH° values (Table 3). As we can see from Table 3, the values of ΔS° are small (near to $2.1\,\mathrm{cal\,mol^{-1}\,K^{-1}}$ for the rearrangements and $6.0\,\mathrm{cal\,mol^{-1}\,K^{-1}}$ for the proton shift reactions). Thus, the entropy effect on the Gibbs free energy value is very small and the $T\Delta S^\circ$ term can be neglected in estimating equilibrium constants. Or the enthalpy term is dominant in evaluating the equilibrium constant. From Tables 4 and 5, one can see that the calculated Gibbs free energy barriers for the sigmatropic rearrangements and proton shift reactions with various substituents are, on average, 45.7 and $49.8\,\mathrm{kcal\,mol^{-1}}$, respectively, which are very similar to the calculated enthalpy barriers. Activation energies for the rearrangements and proton shift reactions are around 44.4 and $49.5\,\mathrm{kcal\,mol^{-1}}$, respectively. The normal range for the experimental activation energies of amino-Claisen rearrangement without any substituent is about $43\,\mathrm{kcal\,mol^{-1}}$. In the rearrangement, the TSs with the electron-donor substituents are more stable than with the electron-withdrawing ones, but in the proton shift reaction, TSs with electron-donor substituents are more unstable than with the electron-withdrawing substituents (with the exception of fluorine atom for the rearrangement and fluorine atom and chlorine atom for the proton shift reaction). Negative values for the activation entropy support the concerted mechanism for the amino-Claisen rearrangement and proton shift reaction.

3.2 Position of the transition structures

Hammond's postulate can be interpreted in terms of the position of the transition structure along the reaction coordinate, n_T (Equation (4)), as defined by Chuang and Lien [22]:

$$n_T = \frac{1}{2 - (\Delta G^\circ / \Delta G^{\neq})}. \quad (4)$$

According to this equation, the position of the TS along the reaction coordinate is to be determined solely by ΔG° (a thermodynamic quantity) and $\Delta G^{\neq}$ (a kinetic quantity). From Table 4, one can see that the values of n_T for the amino-Claisen rearrangement with various substituents are more than 0.5, but for the proton shift reaction with various substituents are less than 0.5. The magnitudes of n_T, which indicate the degrees of similarity between the transition structure and the product, for the rearrangement with an electron-withdrawing substituent, are greater than with an electron-donor substituent, but for the proton shift reaction, the conclusion is reversed. This sequence implies that the transition structures in the rearrangement are more similar to the product than to the reactant, but those in the proton shift reaction have the less resemblance to the product.

3.3 Hammett study

Figures 1–3 show the plots of $\log(k_X/k_H)$ (Tables 4 and 5) vs. Hammett substituent constant for the rearrangement and proton shift reaction. Despite the enormous success of the original Hammett equation, diversions were observed for systems where the reaction centre is in direct

Table 2. Calculated B3LYP/6-31G** thermodynamic values for the amino-Claisen rearrangement and next proton shift reaction including: sum of electronic and thermal Gibbs free energies (*G*), sum of electronic and thermal enthalpies (*H*), and entropies (*S*) for the ground state of reactants (*R*), products (*P*), intermediates (IM) and their corresponding transition species (TS1 and TS2).

Substituent	State	*G* (Hartree/particle)	*H* (Hartree/particle)	*S* (cal mol^{-1} K^{-1})
H	R	−404.175824	−404.130835	94.687
	TS1	−404.102858	−404.060502	89.146
	IM	−404.140317	−404.094360	96.725
	TS2	−404.061365	−404.017000	93.373
	P	−404.187364	−404.142981	93.411
NO_2	R	−608.684295	−608.631782	110.521
	TS1	−608.607059	−608.557896	103.471
	IM	−608.641677	−608.588924	111.030
	TS2	−608.566996	−608.515939	107.460
	P	−608.694469	−608.643532	107.206
CN	R	−496.426647	−496.376532	105.475
	TS1	−496.350393	−496.303402	98.901
	IM	−496.385319	−496.334760	106.410
	TS2	−496.309703	−496.260741	103.051
	P	−496.437284	−496.388364	102.960
CHO	R	−517.500563	−517.449036	108.448
	TS1	−517.423754	−517.376428	99.606
	IM	−517.460123	−517.409274	107.020
	TS2	−517.384317	−517.334988	103.823
	P	−517.509873	−517.460578	103.750
F	R	−503.415550	−503.368401	99.234
	TS1	−503.343293	−503.298807	93.629
	IM	−503.380318	−503.332384	100.886
	TS2	−503.300208	−503.253679	97.927
	P	−503.427217	−503.380675	97.956
Cl	R	−863.782534	−863.734009	102.131
	TS1	−863.709215	−863.663393	96.441
	IM	−863.746074	−863.696679	103.961
	TS2	−863.666918	−863.619100	100.642
	P	−863.793993	−863.746147	100.700
NH_2	R	−459.515405	−459.467162	101.536
	TS1	−459.445322	−459.399769	95.876
	IM	−459.481988	−459.433177	102.731
	TS2	−459.400047	−459.352435	100.208
	P	−459.527235	−459.479508	100.450
$NHCH_3$	R	−498.797678	−498.745951	108.869
	TS1	−498.728503	−498.679564	103.000
	IM	−498.765774	−498.713665	109.673
	TS2	−498.682818	−498.632068	106.812
	P	−498.809271	−498.758119	107.659
OH	R	−479.390383	−479.342608	100.553
	TS1	−479.319667	−479.274659	94.726
	IM	−479.357558	−479.309187	101.805
	TS2	−479.275767	−479.228748	98.959
	P	−479.402019	−479.354758	99.468
OCH_3	R	−518.669019	−518.617897	107.594
	TS1	−518.599000	−518.550651	101.760
	IM	−518.637760	−518.585868	109.217
	TS2	−518.555191	−518.504870	105.909
	P	−518.680521	−518.629877	106.589
CH_3	R	−443.471580	−443.421361	105.695
	TS1	−443.398371	−443.352128	97.326
	IM	−443.436171	−443.386583	104.367
	TS2	−443.355898	−443.307573	101.707
	P	−443.481270	−443.434417	98.610

Table 3. Changes in thermal Gibbs free energies (ΔG°), thermal enthalpies (ΔH°), entropies (ΔS°) and equilibrium constants (K_{eq}) calculated at the B3LYP/6-31G** level of theory for the amino-Claisen rearrangement and next proton shift reaction.

	Rearrangement				Proton shift			
Substituent	ΔG° (kcal mol^{-1})	ΔH° (kcal mol^{-1})	ΔS° (cal mol^{-1} K^{-1})	K_{eq}	ΔG° (kcal mol^{-1})	ΔH° (kcal mol^{-1})	ΔS° (cal mol^{-1} K^{-1})	K_{eq}
H	22.280	22.888	2.038	4.63×10^{-17}	− 29.522	− 30.510	− 3.314	4.39×10^{21}
NO_2	26.743	26.893	0.509	2.47×10^{-20}	− 33.127	− 34.267	− 3.824	1.93×10^{24}
CN	25.933	26.212	0.935	9.72×10^{-20}	− 32.608	− 33.637	− 3.450	8.04×10^{23}
CHO	25.376	24.951	− 1.428	2.49×10^{-19}	− 31.218	− 32.193	− 3.270	7.70×10^{22}
F	22.108	22.601	1.652	6.19×10^{-17}	− 29.429	− 30.303	− 2.930	3.75×10^{21}
Cl	22.879	23.424	1.830	1.68×10^{-17}	− 30.069	− 31.041	− 3.261	1.10×10^{22}
NH_2	20.969	21.325	1.195	4.23×10^{-16}	− 28.392	− 29.073	− 2.281	6.52×10^{20}
$NHCH_3$	20.020	20.259	0.804	2.10×10^{-15}	− 27.294	− 27.895	− 2.014	1.02×10^{20}
OH	20.598	20.972	1.252	7.93×10^{-16}	− 27.899	− 28.596	− 2.337	2.84×10^{20}
OCH_3	19.615	20.098	1.623	4.16×10^{-15}	− 26.832	− 27.616	− 2.628	4.69×10^{19}
CH_3	22.219	21.823	− 1.328	5.13×10^{-17}	− 28.300	− 30.016	− 5.757	5.58×10^{20}

conjugation (Scheme 3) with substituents capable of accepting electrons. This system is inadequately modelled by σ, because the original constants were obtained from benzoic acids, which do not exhibit through-resonance, and hence the two systems are not comparable [23]. In order to overcome these short comings, a new set of parameters, known as σ^-, were introduced [15]. The values of these constants differ from the conventional Hammett substituent constants for electron-accepting substituents (NO_2, CN and CHO). For other substituents that cannot accept electrons by through-resonance, such as halogens, methyl group, NH_2, $NHCH_3$, OH and OCH_3, these differences are less pronounced.

Equations (5)–(7) show our results of a linear regression for $\log(k_X/k_H)$ vs. Hammett σ constant and σ^- for the rearrangement and proton shift reaction:

$$\log\left(\frac{k_X}{k_H}\right)_{\text{Rearrangement}} = -2.4172\sigma_p - 0.0065, \quad R^2 = 0.9007, \tag{5}$$

$$\log\left(\frac{k_X}{k_H}\right)_{\text{Rearrangement}} = -1.7791\sigma^- + 0.2468, \quad R^2 = 0.9461, \tag{6}$$

$$\log\left(\frac{k_X}{k_H}\right)_{\text{Proton shift}} = 2.4921\sigma_p - 0.1928, \quad R^2 = 0.9022. \tag{7}$$

The Hammett ρ values of -2.4172 and -1.7791 (Figures 1 and 2) are obtained for σ_p and σ^- (enhanced sigma) in amino-Claisen rearrangement, respectively. The correlation coefficient between $\log(k_X/k_H)$ and σ_p (0.9007) is smaller than with σ^- (0.9461). In fact, the better correlation between $\log(k_X/k_H)$ and σ^- relative to $\log(k_X/k_H)$ and σ_p is due to insertion of the through-resonance effect in the electron-accepting substituents (NO_2, CN and CHO). A negative Hammett ρ value (-2.4172 for σ_p and -1.7791 for σ^-) indicates that the electron-donating groups moderately increase the rate of amino-Claisen rearrangement. A positive Hammett ρ value (2.4921) for the proton shift reaction indicates that the electron-withdrawing groups increase the rate of reaction.

4. Conclusion

DFT calculations portray a clear picture of the electronic effect on the *N*-allyl-*N*-arylamine rearrangement and its next step (proton shift reaction). The agreement between the numerical values of $\log(k_X/k_H)$ and Hammett substituent constant is fairly excellent and Equations (5)–(7) describe these relationships. A negative Hammett

Table 4. Activation parameters, position of the transition structures and $\log(k_X/k_H)$, calculated at the B3LYP/6-31G** level of theory for the amino-Claisen rearrangement.

Substituent	$\Delta G^{\neq}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})	n_T	E_a (kcal mol^{-1})	log A	k (S^{-1})	$\log(k_X/k_H)$
H	45.786	44.134	−5.541	0.660	44.726	12.012	1.684×10^{-21}	0.000
NO_2	48.466	46.364	−7.050	0.690	46.956	11.685	1.827×10^{-23}	−1.964
CN	47.850	45.889	−6.574	0.685	46.481	11.788	5.169×10^{-23}	−1.512
CHO	48.198	45.562	−8.842	0.678	46.154	11.292	2.872×10^{-23}	−1.768
F	45.341	43.670	−5.605	0.661	44.262	12.000	3.571×10^{-21}	0.326
Cl	46.008	44.312	−5.690	0.665	44.904	11.983	1.158×10^{-21}	−0.162
NH_2	43.977	42.289	−5.660	0.656	42.881	11.989	3.570×10^{-20}	1.326
$NHCH_3$	43.408	41.658	−5.869	0.649	42.250	11.943	9.330×10^{-20}	1.743
OH	44.374	42.638	−5.827	0.651	43.230	11.953	1.826×10^{-20}	1.035
OCH_3	43.937	42.197	−5.834	0.643	42.789	11.950	3.820×10^{-20}	1.355
CH_3	45.939	43.444	−8.369	0.659	44.036	11.396	1.301×10^{-21}	−0.112

Table 5. Activation parameters, position of the transition structures and $\log(k_X/k_H)$, calculated at the B3LYP/6-31G** level of theory for the proton shift reaction.

Substituent	$\Delta G^{\neq}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})	n_T	E_a (kcal mol^{-1})	log A	k (S^{-1})	$\log(k_X/k_H)$
H	49.543	48.544	−3.352	0.385	49.136	12.494	2.966×10^{-24}	0.000
NO_2	46.863	45.798	−3.570	0.369	46.390	12.445	2.735×10^{-22}	1.964
CN	47.449	46.447	−3.359	0.372	47.039	12.492	1.017×10^{-22}	1.535
CHO	47.569	46.615	−3.197	0.376	47.207	12.527	8.306×10^{-23}	1.447
F	50.269	49.388	−2.959	0.386	49.980	12.580	8.710×10^{-25}	−0.532
Cl	49.671	48.681	−3.319	0.383	49.273	12.500	2.390×10^{-24}	−0.093
NH_2	51.418	50.666	−2.523	0.391	51.258	12.675	1.252×10^{-25}	−1.374
$NHCH_3$	52.055	51.202	−2.861	0.396	51.794	12.601	4.272×10^{-26}	−1.841
OH	51.324	50.476	−2.846	0.393	51.068	12.604	1.467×10^{-25}	−1.305
OCH_3	51.812	50.827	−3.308	0.397	51.419	12.504	6.439×10^{-26}	−1.663
CH_3	50.372	49.579	−2.660	0.390	50.171	12.645	7.320×10^{-25}	−0.607

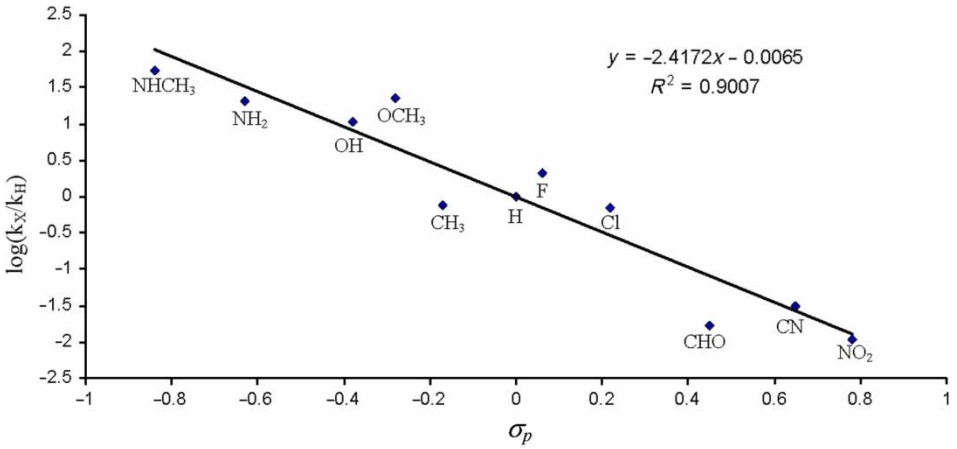


Figure 1. Regression plot between $\log(k_X/k_H)$ and Hammett substituent constant at the *para* position (σ_p) for the amino-Claisen rearrangement.

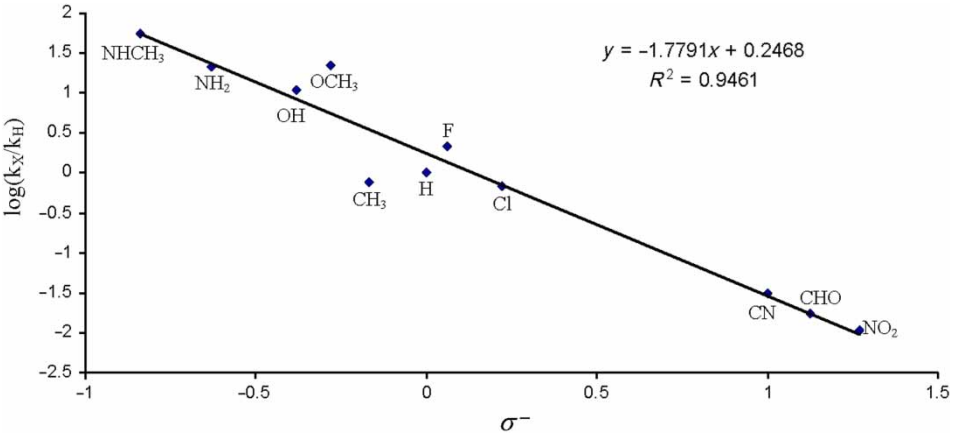


Figure 2. Regression plot of $\log(k_X/k_H)$ vs. enhanced Hammett substituent constant at the *para* position (σ^-) for the amino-Claisen rearrangement.

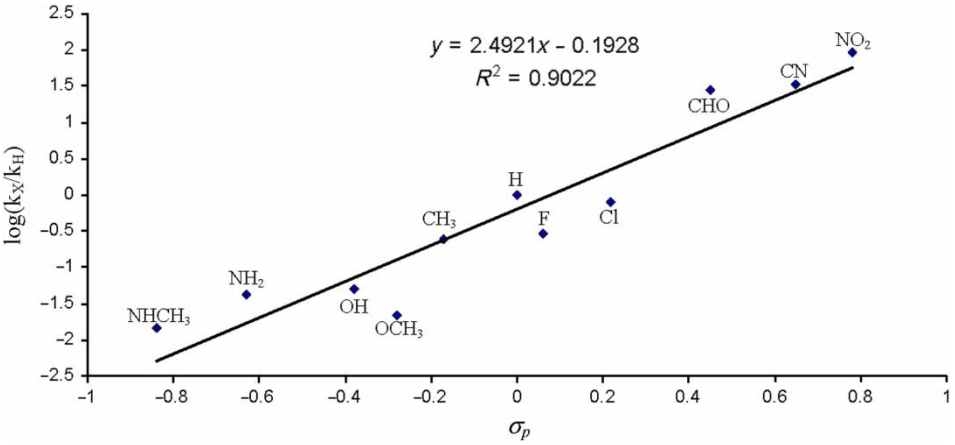
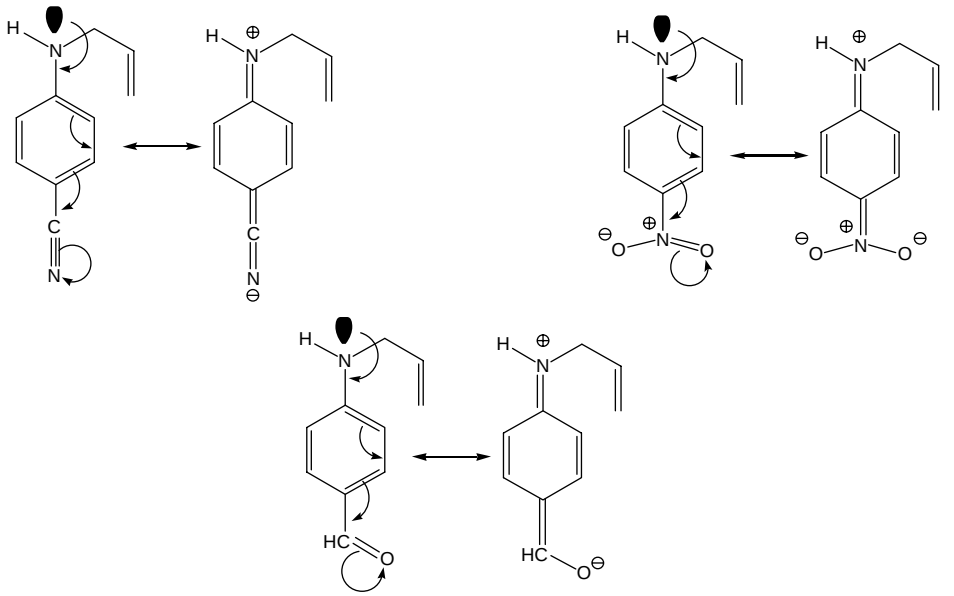


Figure 3. Regression plot of $\log(k_X/k_H)$ vs. Hammett substituent constant at the *para* position (σ_p) for the proton shift reaction.



Scheme 3. Through-resonance structure for *para*-substituted *N*-allyl-*N*-arylamines.

ρ value for the amino-Claisen rearrangement indicates that the electron-donating groups moderately increase the rate of the reaction; on the other hand, a positive value indicates that the electron-withdrawing groups increase the proton shift reaction rate. Because of through-resonance in the reactant, we used enhanced Hammett substituent constant (σ^-) instead of original Hammett substituent constant (σ_p), for NO_2, CN and CHO substituents and consequently the correlation coefficient was improved.

Note

1. Ph.D. Student.

References

[1] M.R. Gholami and M. Izadyar, *Gas phase kinetics and mechanism of 2,2-dimethyl but-3-enal and 1-methyl-6-methylenecyclohexa-2,4-diene-1-carbaldehyde retro-cheletropic ene reaction*, J. Mol. Struct. (THEOCHEM) 672 (2004), pp. 61–66.

[2] I. González, I. Bellas, A. Souto, R. Rodríguez, and J. Cruces, *Microwave-assisted aza-Cope rearrangement of* N*-allylanilines*, Tetrahedron Lett. 49 (2008), pp. 2002–2004.

[3] S.G. Davis, A.C. Garner, R.L. Nicholson, J. Osborne, E.D. Savory, and A.D. Smith, *Double diastereoselective [3,3]-sigmatropic aza-Claisen rearrangements*, Chem. Commun. (2003), pp. 2134–2135.

[4] P.S. Mariano, D.D. Mariano, and P.L. Huesmann, *Amino-Claisen rearrangements of* N*-vinylisoquinuclidenes in novel approaches to the synthesis of hydroisoquinolines and hydrophenanthridines*, J. Org. Chem. 44 (1979), pp. 124–133.

[5] L. Claisen, *Über Umlagerung von Phenol-allyläthern in C-Allyl-phenole*, Berichte der Deutschen Chemischen Gesellschaft (A and B Series) 45 (1912), pp. 3157–3166.

[6] L. Claisen and E. Tietze, *Über den Mechanismus der Umlagerung der Phenol-allyläther*, Berichte der Deutschen Chemischen Gesellschaft (A and B Series) 58 (1925), pp. 275–281.

[7] L. Claisen and E. Tietze, *Über den Mechanismus der Umlagerung der Phenol-allyläther (2. Mitteilung)*, Berichte der Deutschen Chemischen Gesellschaft (A and B Series) 59 (1926), pp. 2344–2351.

[8] S. Crotti, L. Stella, I. Munari, F. Massaccesi, L. Cotarca, M. Forcato, and P. Traldi, *Claisen rearrangement induced by low-energy collision of ESI-generated, protonated benzyloxy indoles*, J. Mass Spectrom. 42 (2007), pp. 1562–1568.

[9] R.P. Lutz, *Catalysis of the Cope and Claisen rearrangements*, Chem. Rev. 84 (1984), pp. 205–247.

[10] A.M.M. Castro, *Claisen rearrangement over the past nine decades*, Chem. Rev. 104 (2004), pp. 2939–3002.

[11] A. Chaskar, V. Padalkar, K. Phatangare, K. Patil, A. Bodkhe, and B. Langi, *Heteropoly acids as useful recyclable heterogeneous catalysts for the facile and highly efficient aza-Cope rearrangement of* N*-allylanilines*, Appl. Catal. A: Gen. 359 (2009), pp. 84–87.

[12] S. Jolidon and H.-J. Hansen, *Untersuchungen über aromatische amino-Claisen-Umlagerungen*, Helv. Chim. Acta 60 (1977), pp. 978–1032.

[13] C. Öğretir, E. Açíkkalp, and T. Güray, *Investigation of the acidity constants and Hammett relations of some oxazolo[4,5-b]pyridin derivatives using semiempirical AM1 quantum chemical calculation method*, J. Mol. Struct. (THEOCHEM) 538 (2001), pp. 107–116.

[14] M. Segala, Y. Takahata, and D.P. Chong, *Geometry, solvent, and polar effects on the relationship between calculated core-electron binding energy shifts (ΔCEBE) and Hammett substituent (σ) constants*, J. Mol. Struct. (THEOCHEM) 758 (2006), pp. 61–69.

[15] K.A. Connors, *Chemical Kinetics 'The Study of Reaction Rates in Solution'*, VCH Publishers, Inc., New York, 1990.

[16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, *Gaussian 03*, Revision B.03, Gaussian Inc., Pittsburgh, PA, 2003.

[17] A.D. Becke, *Density-functional exchange-energy approximation with correct asymptotic behaviour*, Phys. Rev. A 38 (1988), pp. 3098–3100.

[18] C. Lee, W. Yang, and R.G. Parr, *Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density*, Phys. Rev. B 37 (1988), pp. 785–789.

[19] H.B. Schlegel, C. Peng, P.Y. Ayala, and M.J. Frisch, *Using redundant internal coordinates to optimize equilibrium geometries and transition states*, J. Comput. Chem. 17 (1996), pp. 49–56.

[20] S. Glasstone, K.J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.

[21] K.J. Laidler, *Theories of Chemical Reaction Rates*, McGraw-Hill, New York, 1941.

[22] C.-H. Chuang and M.-H. Lien, *Computational study on the effects of substituents and functional groups in the isomerization of 1- and 2-substituted propenes, acetaldimines, and aldehydes*, Eur. J. Org. Chem. 2004 (2004), pp. 1432–1443.

[23] P.J. Smith and P.L.A. Popelier, *Quantum chemical topology (QCT) descriptors as substitutes for appropriate Hammett constants*, Org. Biomol. Chem. 3 (2005), pp. 3399–3407.