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Elimination Reactions of *N*-Alkyl-*N*-chlorothenylamines Promoted by MeONa−MeOH and Et$_2$NH−MeCN. Effect of the *β*-Aryl Group on the Imine-Forming Transition State

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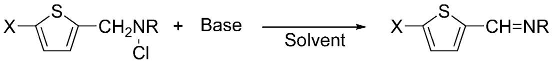
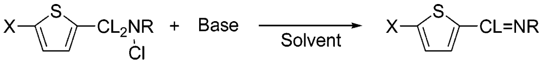


Elimination reactions of *N*-alkyl-*N*-chlorothenylamines **1**−**4** with MeONa−MeOH and Et$_2$NH−MeCN have been studied kinetically. The elimination reactions are regiospecific, producing only the conjugated imines. The reactions are second order and exhibit substantial values of Hammett ρ and k_H/k_D, and an E2 mechanism is evident. The relative rates of elimination for Me/Et/*i*-Pr/*t*-Bu substituents are 1/0.5/0.2/0.02 with MeONa−MeOH and 1/0.4/0.2/0.06 with Et$_2$NH−MeCN. The transition state structure changes toward more product-like as the base is changed from MeONa−MeOH to Et$_2$NH−MeCN. Comparison with existing data reveals that the structure of the transition state is relatively insensitive to the β-aryl group variation.

Extensive studies of the structure−reactivity relationships in the imine-forming elimination reactions from XC$_6$H$_4$CH$_2$N(Y)R have led to the qualitative understanding of the relationship between the reactant structure and the E2 transition state.[1−5] In contrast, virtually nothing is known about the corresponding eliminations involving heterocyclic aromatic compounds.

Earlier, we reported that the nitrile-forming elimination from (*Z*)-ArCH═NOC(O)Ar′ proceeds by the E2 mechanism via a symmetrical transition state.[6,7] When the β-aryl group was changed from Ph to thienyl to furyl, the rates remained nearly the same and the transition state structure changed slightly toward product-like with a larger degree of proton transfer, more negative charge development at the β-carbon, and a greater extent of the leaving group departure. It occurred to us that the effect of the β-aryl group would be more pronounced in the imine-forming eliminations for the following reasons. First, the energy difference between C−N and C═N bonds is significantly larger than that between C═N and C≡N bonds. Second, both the C$_\beta$−H bond and developing partial multiple bonds are parallel to the π-orbital of the β-aryl group in the imine-forming transition state, whereas they are orthogonal to it in the nitrile-forming transition state. Hence, the β-aryl group is expected to stabilize the imine-forming more than the nitrile-forming transition state.

To explore the relative importance of these factors, we have investigated the reactions of *N*-alkyl-*N*-chlorothenylamines **1**−**4** with MeONa−MeOH and Et$_2$NH−MeCN. We have determined k_H/k_D, Hammett ρ, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ values for the elimination from **1**−**4**. The mechanism of the elimination reactions, the effect of base−solvent, and the steric effect have been studied. From these results, the effect of changing the β-aryl group from Ph to thienyl on the imine-forming transition states is assessed.



R = Me (**1**); Et (**2**); *i*-Pr (**3**); *t*-Bu (**4**)
X = H, L = H (**a**); X = H, L = D (**b**); X = Me, L = H (**c**); X = Br, L = H (**d**);
X = NO$_2$, L = H (**e**);
Base-Solvent = MeONa-MeOH; Et$_2$NH-MeCN

Reactions of **1**−**4** with MeONa−MeOH and Et$_2$NH−MeCN produced only *N*-thenylidenealkylamines. Rates of the elimination reactions were measured by monitoring the appearance of the absorption at the λ_{max} for the products. Excellent pseudo-first-order kinetic plots that covered at least 3 half-lives were obtained. Pseudo-first-order rate constants (k_{obs}) are summarized in Tables S1 and S2 in Supporting Information. The plots of k_{obs} versus base concentration for **1**−**4** are straight lines passing through the origin, indicating that the reactions are second-order, first order to the substrate and first order to the base (Figure S1 and S2). The second-order rate constants k_2 were obtained either from the slopes of straight lines or by dividing the k_{obs} by base concentration. Values of k_2 for eliminations from **1**−**4** are summarized in Tables 1 and 2. Relative rates of elimination for **1a**/**2a**/**3a**/**4a** at 25 °C are 1/0.5/0.2/0.02 with MeONa−MeOH and 1/0.4/0.2/0.06 with Et$_2$NH−MeCN.

The influence of the *N*-alkyl group upon the rates for the MeONa-promoted eliminations from **1a**−**4a** correlated reasonably well with Charton's equation using ν' values.[12,13] On the other hand, the rate data for the

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TABLE 1. **Rate Constants for Elimination from 5-X-$C_4H_2(S)CL_2N(Cl)R^a$ Promoted by MeONa−MeOH^b**

			$10^2\ k_2$, $M^{-1}\ s^{-1\ c,d}$			
X	L	temp, °C	R = Me	R = Et	R = *i*-Pr	R = *t*-Bu
H	H	25.0	1.59	0.821	0.389	0.0277
H	H	35.0	3.67	1.57	0.917	0.0546
H	H	45.0	7.74	3.51	2.11	0.136
H	D	25.0	0.244	0.154	0.0867	0.0126
CH_3	H	25.0	1.04			
Br	H	25.0	7.55			
NO_2	H	25.0	406			

[a] [Substrate] = 1.0 × 10^{-5} M. [b] [Base] = 1.2 × 10^{-4} to 1.50 × 10^{-1} M. [c] Average of three or more kinetic runs. [d] Estimated uncertainty, ±3%.

TABLE 2. **Rate Constants for Elimination from 5-X-$C_4H_2(S)CL_2N(Cl)R^a$ Promoted by Et_2NH−MeCN^b**

			$10^3\ k_2$, $M^{-1}\ s^{-1\ c,d}$			
X	L	temp,°C	R = Me	R = Et	R = *i*-Pr	R = *t*-Bu
H	H	25.0	8.51	3.49	2.04	0.494
H	H	35.0	16.6	8.27	7.44	1.21
H	H	45.0	28.2	13.4	12.1	2.85
H	D	25.0	2.15	0.926	0.889	0.332
CH_3	H	25.0	3.05			
Br	H	25.0	25.7			
NO_2	H	25.0	847			

[a] [Substrate] = 1.0 × 10^{-5} M. [b] [Base] = 1.2 × 10^{-4} to 1.50 × 10^{-1} M. [c] Average of three or more kinetic runs. [d] Estimated uncertainty, ±3%.

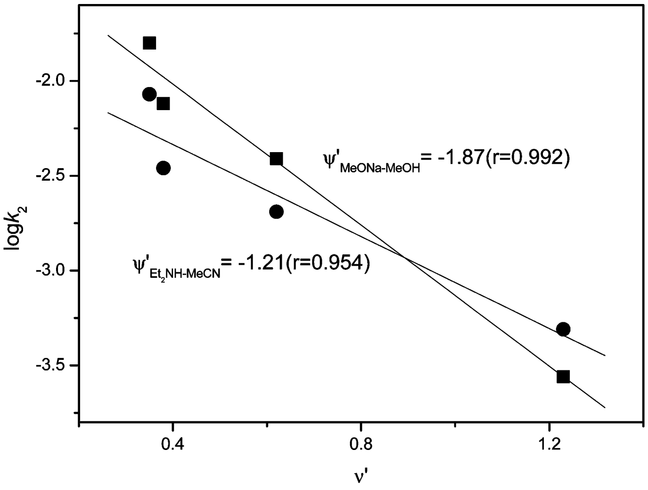

FIGURE 1. Charton's plots for base-promoted eliminations from $C_4H_3(S)CH_2N(Cl)R$. Base−solvents are the following; MeONa−MeOH (■) and Et_2NH−MeCN (●).

Et_2NH-promoted eliminations scattered significantly from the Charton plot (Figure 1). Charton's ψ' values are summarized in Table 3.

Rates of elimination from **1a**−**4a** promoted by MeONa−MeOH and Et_2NH−MeCN were measured at three temperatures spanning 20 °C. The Arrhenius plots are linear with excellent correlations (Figures S3 and S4). Calculated enthalpies and entropies of activation are summarized in Tables 3 and 4. For a given base, $\Delta H^‡$ and $\Delta S^‡$ values increase with a bulkier alkyl substituent.

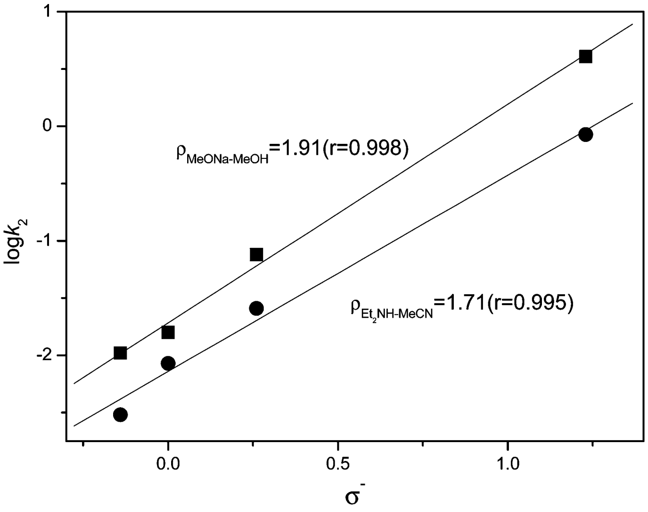

FIGURE 2. Hammett plots for eliminations from 5-X-C_4H_2-(S)$CH_2N(Cl)Me$ promoted by MeONa−MeOH (■) and Et_2NH−MeCN (●).

The influence of aryl substituents upon the elimination rates gave excellent correlations with σ^- values (Figure 2). Hammett ρ values are given in Table 3. The ρ value decreases when the base is changed from MeONa−MeOH to Et_2NH−MeCN. From the rate coefficients for eliminations from **1a**−**4a** and their deuterated analogues **1b**−**4b** at 25 °C, primary deuterium isotope effect values were calculated. The values are listed in Table 3. The k_H/k_D value decreases when base−solvent is changed from Et_2NH−MeCN to MeONa−MeOH (Table 3). For a given base, the k_H/k_D value decreases with a bulkier *N*-alkyl group (Table 4).

Mechanism and Transition State Structure for Eliminations from 1−4 Promoted by MeONa−MeOH and Et_2NH−MeCN. Results of kinetic investigations and product studies reveal that the reactions of **1**−**4** with MeONa−MeOH and Et_2NH−MeCN proceed by the E2 mechanism. Since the reactions produced only elimination products and exhibited second-order kinetics, all but bimolecular pathways can be ruled out. In addition, an E1cb mechanism is negated by the similarities in the transition state parameters to those for eliminations from $XC_6H_4CH_2N(Cl)R$, which is known to proceed by the E2 mechansim.[2−4,14,15,18,19]

Table 3 shows that the Hammett ρ value for MeONa-promoted eliminations from **1** is 1.91. This indicates that a significant amount of negative charge is developed at the β-carbon in the transition state. In addition, the observation of the large k_H/k_D value indicates an extensive proton transfer. The combined results are consistent with an E2-central transition state.

The transition state structure changes significantly when base−solvent is changed from MeONa−MeOH to Et_2NH−MeCN, even though pK_a values of the bases are nearly the same (Table 3). The Hammett ρ value decreases slightly as the base−solvent is changed from MeONa−MeOH to Et_2NH−MeCN, indicating a slight decrease in negative charge density at the β-carbon in the transition state. Moreover, k_H/k_D decreases from 6.5 to 4.0 by the same variation of the base−solvent. In view of the prediction that the maximum isotope effect occurs

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TABLE 3. Transition State Parameters for Imine-Forming Eliminations from $ArCH_2N(Cl)Me$ Promoted by MeONa−MeOH and Et_2NH−MeCN

	MeONa−MeOH (pK_a 18.3)[a]		Et_2NH−MeCN (pK_a 18.7)[b]	
	Ar = thienyl	Ar = phenyl[c]	Ar = thienyl	Ar = phenyl[d]
rel rate	1.4	1.0	1.1	1.0
ρ	1.91 ± 0.09	1.58	1.71 ± 0.13	0.92
k_H/k_D	6.5	6.4	4.0	7.8
$\Delta H^‡$, kcal/mol	14.4 ± 0.6	14.2	9.2 ± 0.7	7.4
$\Delta S^‡$, eu	−18.4 ± 0.4	−19.9	−37.0 ± 0.3	−43.4
ψ' [e]	−1.87 ± 0.16	−2.11	−1.21 ± 0.27	−1.58

[a] Reference 16. [b] Reference 17. [c] Reference 18. [d] Reference 19. [e] $ArCH_2N(Cl)R$ (R = Me, Et, *i*-Pr, and *t*-Bu).

TABLE 4. Effect of the *N*-Alkyl Group on the Imine-Forming Transition-State for Eliminations from $C_4H_3(S)CL_2N(Cl)R$ Promoted by MeONa−MeOH and Et_2NH−MeCN

	k_H/k_D		$\Delta H^‡$, kcal/mol		$\Delta S^‡$, eu	
R	MeONa−MeOH	Et_2NH−MeCN	MeONa−MeOH	Et_2NH−MeCN	MeONa−MeOH	Et_2NH−MeCN
Me	6.5	4.0	14.4	9.16	−18.4	−37.0
Et	5.3	3.8	15.4	11.6	−16.9	−30.3
i-Pr	4.5	2.3	15.9	16.1	−16.2	−16.2
t-Bu	2.2	1.5	19.2	18.2	−11.5	−13.1

with 0.38 and 0.42 proton transfers for reactions of a carbon acid with an oxygen base and a nitrogen base, respectively, this result could be interpreted as similar extents of proton transfer in both transition states.[2,20] This interpretation is supported by the smaller values of $\Delta H^‡$ and $\Delta S^‡$. Since the C=N bond is approximately 75 kcal/mol stronger than the corresponding single bond and the bond dissociation energy of the N−Cl bond is approximately 60 kcal/mol,[21] the enthalpy of activation should decrease if the extent of C_β−H bond cleavage remains nearly the same and more of the π-bond is formed. This would predict a decrease in the Hammett ρ value, because more of the charge density would be transferred from the β-carbon to the C−N bond to increase the double bond character. The much smaller value of $\Delta S^‡$ is also consistent because more solvent reorganization would be required to solvate the charged transition state with an aprotic solvent. Therefore, the transition state structure for eliminations from **1** appears to change toward more product-like with similar extent of proton transfer, smaller negative change density at the β-carbon, and more double bond character between C−N as the base−solvent is changed from MeONa−MeOH to Et_2NH−MeCN.

Steric Effect. Table 3 shows that Charton's $|\psi'|$ value for eliminations from **1**−**4** decreases from 1.90 to 1.21 by the change in the base−solvent from MeONa−MeOH to Et_2NH−MeCN. Considering the large increase in the base steric effect, this indicates a remarkable decrease in the alkyl group steric effect. It is well established that the origin of the steric effect in the imine-forming eliminations from $XC_6H_4CH_2N(Cl)R$ is the steric interaction between the attacking base and *N*-alkyl group.[19] Hence, the steric effect is expected to decrease as the transition state double bond character increases. Therefore, the smaller $|\psi'|$ value with Et_2NH−MeCN provides additional evidence for the product-like transition state (vide supra).

For eliminations from **1**−**4** promoted by MeONa−MeOH and Et_2NH−MeCN, k_H/k_D decreases and $\Delta H^‡$ and $\Delta S^‡$ increase as the substrate steric effect is increased (Table 4). This indicates that a bulky alkyl substituent hinders the approach of the base to the C_β−H in the transition state to decrease the extent of C_β−H bond cleavage. The increase in $\Delta H^‡$ and $\Delta S^‡$ values is also consistent, because the extent of base−proton bond and π-bond formation would be decreased in the transition state, and the latter will be less associated with respect to the base−proton bond.[1,19]

Effect of the *β*-Aryl Group on the Imine-Forming Transition State. The rate of MeONa-promoted elimination from $ArCH_2N(Cl)Me$ increases slightly as the β-aryl group is changed from Ph to thienyl, despite the large difference in the aromatic resonance energy. In addition, k_H/k_D, $\Delta H^‡$, and $\Delta S^‡$ values for the two reactions are almost the same. The only significant differences are smaller $|\psi'|$ and larger Hammett ρ values determined for thienyl than Ph derivatives (Table 3). This can be attributed to the relative size and π-orbital energy of the β-aryl group. Because the thienyl group is smaller than the phenyl group, the $|\psi'|$ value should be smaller. Moreover, the 5-thienyl substituent is closer to the β-carbon than the phenyl substituents and the aromatic resonance energy of thiophene is smaller than that of benzene. Both of these factors would favor more efficient electronic transmission from the β-carbon to the substituents of the thienyl derivatives.[7] Therefore, the slightly larger value of Hammett ρ determined for **1** than the Ph derivatives should be attributed to these factors, not to

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(15) A reviewer argued that the E2 mechanism is not conclusively demonstrated because the $E1cb_{irr}$ mechanism cannot be excluded with the existing data. The distinction between the two mechanisms can be made by using the eaving group element effect.[14] For the reactions of $XC_6H_4CH_2N(Cl)R$ with MeONa−MeOH and Et_2NH−MeCN, the $E1cb_{irr}$ mechanism was negated by the substantial values of k_{Br}/k_{Cl}.[2−4,18,19] Unfortunately, however, we could not determine the k_{Br}/k_{Cl} values for this reaction because $XC_4H_2(S)CH_2N(Br)R$ was not stable enough for the rate measurement. On the other hand, if one has to make a mechanistic decision with the available data, E2 is the most likely mechanism because (i) the $E1cb_{irr}$ mechanism has never been observed in elimination reactions from $XC_6H_4CH_2N(Y)R$ and (ii) the mechanistic parameters determined for $XC_4H_2(S)CH_2N(Cl)R$ and $XC_6H_4CH_2N(Cl)R$ are very similar.

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an increase in the negative charge density at the β-carbon. A similar result is observed for Et_2NH-promoted eliminations. The Hammett ρ value increases from 0.92 to 1.71 as the β-aryl group is changed from Ph to thienyl. Although the increase is larger than that observed in MeOH, it is due to the poorer solvating ability of MeCN than MeOH for the negative charge density at the β-carbon. The k_H/k_D values of 7.8 and 4.0 for both substrates can also be interpreted with similar extents of proton transfer as discussed above. The similar values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ provide supporting evidence for this interpretation. Combined together, the transition state structures for the imine-forming eliminations from $ArCH_2N(Cl)Me$ appear to be very similar for both compounds.

Earlier, we reported that transition states for the imine-forming eliminations from $XC_6H_4CH(R)N(Cl)Me$ are relatively insensitive to the change in R group from H to Me to Ph, and base−solvent from MeONa−MeOH to t-BuOK−t-BuOH.[4] For amine-promoted eliminations from the same substrates, the transition state moved along the parallel direction in the reaction coordinate diagram by the change in base strength.[2] On the other hand, the transition state for eliminations from $XC_6H_4CH_2N(OSO_2Ar)R$ changed toward E1-like when the base was changed to a weaker one and the leaving group was changed to a better one.[3] As the steric effect of the N-alkyl group was increased, the transition state changed gradually toward E1-like until it reached an extreme, where the solvolytic elimination competes with E2 when R = t-Bu.[5] Therefore, it seems reasonable to conclude that the structure of the transition state for the imine-forming eliminations from $XC_6H_4CH(R)N(Y)Me$ is insensitive to the reactant structure variation, when the transition state is E2-central where the formation of the partial C═N bond is important, whereas it is sensitive when the transition state is E1-like where the cleavage of the N−X bond is important. The similar transition state structures noted for eliminations from $ArCH_2N(Cl)Me$ with the β-aryl group variation provide additional support for this conclusion.

In conclusion, we have studied elimination reactions from **1**−**4** promoted by MeONa−MeOH and Et_2NH−MeCN. The reactions proceed by the E2 mechanism via an E2-central transition state. The structure of the transition state changes toward more product-like with concomitant decrease in the substrate steric effect as base−solvent is changed from MeONa−MeOH to Et_2NH−MeCN. Noteworthy is relative insensitivity of the imine-forming transition state to the β-Ar group variation.

Experimental Section

Materials. N-Alkylthenylamines were prepared by reductive amination as described elsewhere.[8,9] To a solution of anhydrous alkylamine in methanol (75 mL) was added methanolic HCl (60 mmol) followed by the substituted thiophene-2-carboxaldehyde (30 mmol) and $NaBH_3CN$ (18 mmol). The resulting solution was stirred at room temperature for 3−4 days. For product workup, concentrated HCl was added until pH <2, and the methanol was removed in vacuo. The residue was taken up in 20 mL of water and extracted with three 20 mL portions of ether. The aqueous solution was brought to pH >10 with solid KOH, saturated with NaCl, and extracted with five 20 mL portions of ether. The product was vacuum distilled. The deuterated compounds **1b**, **2b**, **3b**, and **4b** were prepared by reduction of the corresponding N-alkylthienylamides with $LiAlD_4$ in dry ether.[10,11]

N-Thenylidenealkylamines [$C_4H_3(S)CH{=}NR$] were prepared by stirring 1:1 mixtures of thiophene-2-carboxaldehyde and appropriate alkylamines for 1 h at RT.[4,5] The product was extracted with ether and purified by vacuum distillation. When R = i-Pr and t-Bu, the products contained appreciable amounts of thiophene-2-carboxaldehyde (Supporting Information).

All of the compounds were oily products and difficult to obtain as analytically pure products. However, the spectral and HRMS data of the compounds were consistent with those of the proposed structures (Supporting Information).

The absorption spectra of N-thenylidenealkylamines showed λ_{max} at 280 nm in MeOH and MeCN. When R = i-Pr and t-Bu, the mole fraction of the imine in the product mixture was determined by gas chromatography before measuring the molar extinction coefficients (ϵ). The ϵ values of $C_4H_3(S)CH{=}NR$ are 9720, 10 400, 11 100, 10 500 in MeOH, and 9560, 9680, 10 200, 10 100 in MeCN, respectively, when R = Me, Et, i-Pr, and t-Bu.

The substituted N-alkyl-N-chlorothenylamines were prepared by the reaction of N-alkylthenylamines with N-chlorosuccinimide in pantane as described.[4] Solutions of MeONa−MeOH and Et_2NH−MeCN were prepared as reported.[17,18]

Kinetic Studies. Reactions of **1**−**4** with MeONa−MeOH or Et_2NH−MeCN were followed by monitoring the increase in the absorbance of the imines at 280−300 nm with a UV−vis spectrophotometer as described.[2] Due to the instability of **1e**, a freshly prepared solution of **1e** was used for all kinetic runs.

Product Studies. For reactions of N-alkyl-N-chlorothenylamines **1**−**4** with MeONa−MeOH or Et_2NH−MeCN, the absorbance of infinity samples from the kinetic reactions was compared with those of an authentic sample of N-thenylidenealkylamine. On the basis of the starting N-alkylthenylamines, the yields of imine were in the range of 82−99%.

The products of reactions of **4** with MeONa−MeOH were identified by using more concentrated solutions and gas chromatographic analysis outlined previously.[2] The products were N-thenylidene-*tert*-butylamine (64.5%) and thiophene-2-carboxaldehyde (19.6%). The latter is the hydrolysis product.

Control Experiments. The stabilities of N-chloroamines were determined as reported earlier.[4] Solutions of N-chloroamines **1a**−**d** and **2a**−**4a** were stable for at least 3 weeks in MeOH or MeCN solution at room temperature. However, the solution of **1e** was stable for only 2 days.

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Supporting Information Available: Rate constants for eliminations from **1**−**4** promoted by MeONa−MeOH and Et_2NH−MeCN, plots of k_{obs} vs base concentration, Arrhenius plots, and spectroscopic and analytical data for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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