Homolytic Rearrangements of Ketenimines to Nitriles: Employments of Hammett Dual Parameters

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The thermal isomerizations of ketenimines to nitriles involve a "homolytic" transition state (TS) as the major contributor to the structure of the TS. The rates have been fitted to Hammett dual correlations. The magnitudes of $|\rho^{\bullet}/\rho|$ represent the relative weights in the TS assuming homolytic character.

In the absence of steric effects, substituents[2] control the rates of radical reactions through polar effects[3] and spin delocalization. Polar effects have been thoroughly investigated by Kim et al.[4] A polar TS is thus defined as an "imbalanced TS",[5] which features entropy control of rates.[4] The concept of a radical substituent constant ($\sigma^{\bullet}$) was originally proposed by Streitwieser and Perrin.[6] The value of $\sigma^{\bullet}$ may represent the capacity for dispersion of the spin density and the magnitude of $\rho^{\bullet}\sigma^{\bullet}$ is equivalent to the increment of free energy of activation derived therefrom. Recently, numerous $\sigma^{\bullet}$ scales[7−13] have been defined and used in Hammett dual parameters. The pioneering work by Singer[14] indicates that the rearrangement of ketenimines takes place via cage recombination of the radical pairs. Later studies[15,16] corroborate the homolytic nature of the reaction. The previous studies,[14−16] however, neglected investigations of the TS involved. We would like to herein report on the structure of the TS for

the thermal isomerizations of diphenyl N-substituted benzyl ketenimines to the corresponding nitriles (Scheme 1).

Results and Discussion

Various ketenimines were synthesized by known methods[14] with some alterations of reaction conditions (Scheme 2). All the NMR spectra excellently match the structures. Some of them are also consistent with previously reported spectra.[14] Corresponding nitriles show spectral patterns

Table 1. Absolute and Relative Rates of the Isomerizations at 60 °C in CDCl$_3$

$$\text{Ph}_2\text{C=C=N-CH}_2\text{PhY} \xrightarrow{k_Y} \text{YPhCH}_2\text{C(Ph)}_2\text{-CN}$$

$$\text{Ph}_2\text{C=C=N-CH}_2\text{Ph} \xrightarrow{k_H} \text{PhCH}_2\text{C(Ph)}_2\text{-CN}$$

rates (Y)	*p*-Br	*p*-Cl	*p*-OCH$_3$	*m*-F	*m*-Cl
$k_Y \times 10^5$ (s^{-1})[a]	24.3 ± 0.3	21.6 ± 1.0	20.1 ± 0.2	12.5 ± 0.4	12.2 ± 0.7
k_Y/k_H	3.04	2.70	2.51	1.56	1.53

rates (Y)	*p*-CH$_3$	*p*-F	H	*m*-OCH$_3$	*m*-CH$_3$
$k_Y \times 10^5$ (s^{-1})[a]	11.9 ± 0.1	9.17 ± 0.3	8.00 ± 0.2	7.49 ± 0.5	7.17 ± 0.5
k_Y/k_H	1.49	1.15	1.00	0.936	0.896

[a] The rates were measured more than three times.

Table 2. Hammett Single and Dual Correlations for the Isomerizations at 60 °C in CDCl$_3$

$$\log k_Y/k_H = \rho\sigma; \ \log k_Y/k_H = \rho^{\bullet}\sigma^{\bullet}; \ \log k_Y/k_H = \rho\sigma + \rho^{\bullet}\sigma^{\bullet}$$

approach	σ[a]	$\sigma^{\bullet}$	ρ	$\rho^{\bullet}$	$|\rho^{\bullet}/\rho|$	r[b]	n[c]
Exner[17]	σ	−	0.13	−	−	0.145	10
Creary[9]	−	$\sigma_c^{\bullet}$	−	1.34	−	0.698	10
	σ	$\sigma_c^{\bullet}$	0.72	2.19	3.04	0.953	10
	σ_p	$\sigma_c^{\bullet}$	0.61	1.96	3.21	0.976	6
	σ_m	$\sigma_c^{\bullet}$	0.75	1.14	1.52	0.960	5
Arnold[10]	−	$\sigma_{\alpha}^{\bullet}$	−	6.56	−	0.634	8
	σ	$\sigma_{\alpha}^{\bullet}$	0.61	12.7	20.8	0.883	8
	σ_p	$\sigma_{\alpha}^{\bullet}$	0.59	13.8	23.4	0.970	5
	σ_m	$\sigma_{\alpha\bullet}$	0.53	−1.28	2.42	0.998	4
Jiang and Ji[11]	−	$\sigma_{jj}^{\bullet}$	−	1.36	−	0.774	10
	σ	$\sigma_{jj}^{\bullet}$	0.36	1.56	4.33	0.863	10
	σ_p	$\sigma_{jj}^{\bullet}$	0.23	1.70	7.39	0.976	6
	σ_m	$\sigma_{jj}^{\bullet}$	0.58	−0.40	0.69	0.977	5

[a] Taken from ref 17. [b] Correlation coefficients. [c] Number of the points.

(1) A postdoctoral fellow (1995−1997) by a grant from Inha University.

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Scheme 1

$$Ph_2C=C=N-CH_2PhY$$

$$\left[Ph_2C=C=\overset{\delta\bullet}{N}\cdots\overset{\delta\bullet}{C}H_2PhY\right]^{\ddagger} \longleftrightarrow \left[Ph_2C=C=\overset{\delta+}{N}\cdots\overset{\delta-}{C}H_2PhY\right]^{\ddagger} \longleftrightarrow \left[Ph_2C=C=\overset{\delta-}{N}\cdots\overset{\delta+}{C}H_2PhY\right]^{\ddagger}$$

$$\mathbf{1} \qquad\qquad\qquad \mathbf{2} \qquad\qquad\qquad \mathbf{3}$$

$$Ph_2\overset{\bullet}{C}-C\equiv N \longleftrightarrow Ph_2C=C=N\bullet \; + \; \bullet CH_2PhY$$

$$YPhCH_2C(Ph)_2-C\equiv N$$

Scheme 2

$$Ph_3P \xrightarrow[\text{benzene}]{\text{1 equiv. Br}_2} Ph_3PBr_2 \xrightarrow[\text{1 equiv. Et}_3N]{\text{1 equiv. NH}_2CH_2PhY} \left[Ph_3PNHCH_2PhY\right]^+ Br^-$$

$$\xrightarrow[\text{liq. NH}_3]{\text{excess NaNH}_2} Ph_3P=NCH_2PhY \xrightarrow[\text{ether}]{Ph_2C=C=O}$$

$$Ph_2C=C=N-CH_2PhY \quad + \quad Ph_3PO$$

consistent with proposed structures. The thermolysis at 60 °C of ketenimines to nitriles proceeds smoothly without side reactions. The rates of the isomerizations follow first-order kinetics and have been measured by monitoring the disappearance and appearance of the benzylic protons of the ketenimine and its nitrile counterpart, respectively. The absolute rate constants (k_Y) were obtained from the equation $\ln(C_{at} + C_{bt})/C_{at} = k_Y t$, C_{at}: magnitude of the benzylic protons of the ketenimine at time t, C_{bt}: the similar entity for the nitrile. The absolute rate constants and relative rates are shown in Table 1. The logarithm of the relative rates were then plotted against σ,[17] $\sigma_c\bullet$,[9] $\sigma_\alpha\bullet$[10] and $\sigma_{jj}\bullet$[11] for the single correlations. For the dual parameter correlations, rates were best fitted to the dual parameter equation $\log k_Y/k_H = \rho\sigma + \rho\bullet\sigma\bullet$ where $\sigma\bullet = \sigma_c\bullet$,[9] $\sigma_\alpha\bullet$[10] or $\sigma_{jj}\bullet$[11] (Table 2).

A plot of $\log k_Y/k_H$ versus σ[17] exhibits a typical shotgun-type scatter of the points and indicates lack of a correlation ($r = 0.145$). Singer et al.[14c] also observed the breakdown of a similar Hammett correlation. The single correlation with the three $\sigma\bullet$ scales shows some improvements but yet plots are not linear ($r = 0.698$,[9] 0.634,[10] and 0.774[11]). The introduction of dual parameter equations, however, gives quite satisfactory plots ($r = 0.953$,[9] 0.883,[10] and 0.863[11]) especially with the Creary approach.[9] The values of $|\rho\bullet/\rho|$ are much larger than unity ($|\rho\bullet/\rho| = 3.04$, 20.8, and 4.33) implicating importance of TS **1** in Scheme 1. The separate treatment of para and meta substituents yields even better correlations ($r \geq 0.960$ for the six cases). $|\rho\bullet/\rho| = 3.21$,[9] 23.4,[10] and 7.39[11] indicate that para substituents promote spin delocalization and stabilize **1** regardless of their electronic character. Most of the meta substituents[9,10] have $\sigma\bullet < 0$ and prevent spin dispersion. Accordingly, the role of **1** is decreased and contributions of **2** begin to emerge. This is clearly shown in the reduction of the magnitude of $|\rho\bullet/$

$\rho|$ for the meta substituents ($|\rho\bullet/\rho| = 1.52$,[9] 2.42,[10] and 0.69[11]). The rates of homolyses of various azoalkanes[18-23] were also treated with similar Hammett dual parameter equations. Here[18] again $|\rho\bullet/\rho|$ is larger than unity; that is $1.04 \leq |\rho\bullet/\rho| \leq 3.60$, which indicates the importance of a TS analogous to **1**. Furthermore the order of substituent effects on rates is very similar in the rearrangement reactions of ketenimines (Table 1) and the pyrolyses of azocompounds.[18] The rates thus increase in the order H $< p$-CH$_3 < p$-OCH$_3 < p$-Cl $< p$-Br. The parallelism could be again due to the similar TS structure for the two reactions.

In conclusion the major substitutent effects on the rates of ketenimine rearrangement are due to spin delocalization. Single correlations with $\sigma\bullet$ alone, however, yield relatively poor correlations. Therefore polar effects in the TS are not to be ignored completely. The role of solvent in forming the polar TS could be unimportant because the polarity[3] has been attributed to factors other than solvent (e.g. electronegativity and heats of reaction). The relative rates (k_Y/k_H in Table 1) can be utilized as a new set of $\sigma\bullet$ constants in reactions which have both polar and radical character in the TS. Further work is in progress in terms of solvent effects and temperature studies.

Experimental Section

Materials. The reagents are commercially available from major suppliers. Liquids were distilled with center-cut col-

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lections, and solids were recrystallized according to standard procedures.[24]

Diphenyl N-substituted benzyl ketenimines were prepared according to a known method[14] with some modifications. Substituted (benzylamino)triphenylphosphonium bromides (0.05 mol) in 300 mL of liquid NH_3 were treated with $NaNH_2$ (0.055 mol). However, previous preparations[14] utilized KOH in anhydrous ether. The method employing $NaNH_2$ in liquid NH_3 improved the yield (90−95%) and shortened the reaction time from 20−40 h to 2−4 h for the preparations of triphenylphosphine substituted benzylimines (Scheme 2).

^{1}H NMR data for the ketenimines ($CDCl_3$ with 0.03% TMS): *p*-Br: 7.0−7.8 (m, 14H) 4.8 (s, 2H); *p*-Cl: 7.0−7.8 (m, 14H) 4.8 (s, 2H); *p*-OCH$_3$: 6.8−7.8 (m, 14H) 4.7 (s, 2H) 3.8 (s, 3H); *m*-F: 7.0−7.4 (m, 14H) 4.8 (s, 2H); *m*-Cl: 7.1−7.4 (m, 14H) 4.7 (s, 2H); *p*-CH$_3$: 7.2−7.8 (m, 14H) 4.8 (s, 2H) 2.4 (s, 3H); *p*-F: 7.1−7.8 (m, 14H) 4.8 (s, 2H); H: 7.3−7.4 (m, 15H) 4.8 (s, 2H); *m*-OCH$_3$: 6.8−7.4 (m, 14H) 4.8 (s, 2H) 3.7 (s, 3H); *m*-CH$_3$: 7.0−7.4 (m, 14H) 4.7 (s, 2H) 3.6 (s, 3H).

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Analytical Procedures. The ketenimine solutions (0.3 M in $CDCl_3$) were placed in capped NMR tubes. The tubes were then placed in a thermostated bath for the thermal reactions. At several time intervals the tubes were quenched in liquid nitrogen, thawed, and transferred to the cavity of a Varian Gemini 2000 NMR spectrometer for ^{1}H NMR measurement. 1:1 correlation was observed in integrated areas for the benzylic protons of the reacted ketenimines and corresponding nitriles produced. The absolute rate constants (k_Y) were calculated using the equation $\ln(C_{at} + C_{bt})/C_{at} = k_Y t$.