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Thermal Isomerizations of Ketenimines to Nitriles: Evaluations of Sigma-Dot ($\sigma^\bullet$) Constants for Spin-Delocalizations

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Rate constants (k_Y) of the isomerizations of 11 diphenyl *N*-(substituted benzyl) ketenimines were measured at 40, 50, 60, and 70 °C. Activation parameters $\Delta H^{\ddagger}_{Y}$ and $\Delta S^{\ddagger}_{Y}$ were obtained using the Eyring equation. The relative rates (k_Y/k_H) were fitted into Hammett single correlations ($\log k_Y/k_H = \rho\sigma$ and $\log k_Y/k_H = \rho^\bullet\sigma^\bullet$). The single correlations have been compared with Hammett dual correlations ($\log k_Y/k_H = \rho\sigma + \rho^\bullet\sigma^\bullet$). Separate treatments of para and meta substituents yielded even better correlations. Para substituents control the rates through spin-delocalizations and inductive effects. The former outweighs the latter when the latter exerts a modest but distinct influence on the rates. On the other hand, inductive effects are the “major” or the sole interactions triggered by meta substituents.

Introduction

The concept of Hammett substituent constants for radical reactions ($\sigma^\bullet$) was introduced for the first time by Streitwieser and Perrin[1] as an index of spin-delocalizations. However, the polar effects[2−5] caused by substituents have been found to outweigh the spin-delocalization effects in determining the rates of numerous radical reactions. Furthermore, separation of the latter from the former engenders extreme difficulty. Recently, substituent effects on rates of radical reactions[6−11] have attracted considerable interest. Numerous $\sigma^\bullet$ scales[12−16] have been devised to address rates of the radical reactions. The $\sigma^\bullet$ scales formulated by Arnold,[14] Creary,[15] and Jiang and Ji[16] could be the least contaminated with polar effects and thereby used as a measure of capacity of spin-delocalizations. Arnold[14] measured α-hydrogen hyperfine coupling constants of substituted benzyl radicals for definition of $\sigma^\bullet_\alpha$. Creary[15] set up the $\sigma^\bullet_c$ scale by measuring rates of rearrangements of methylenearylcyclopropanes. Jiang and Ji[16] derived $\sigma^\bullet_{jj}$ from rates of thermal cycloaddition of α,*β*,*β*-trifluorostyrenes.

Thermal isomerizations of ketenimines to nitriles[17−19] are known to take place via cage recombinations of radical pairs. Subsequently,[20] the rates of isomerizations at 60 °C of various diphenyl *N*-(substituted benzyl)-ketenimines were measured that follow excellent first-order kinetics. The rates are better fitted with Hammett dual correlations indicating concurrent contributions of **1** and **2** to the transition state (TS). Para substituents are capable of spin-delocalizations thereby favoring **1** as a major contributing structure. However the contributions of **2** become important via inductive effects with meta substituents. These are shown in Scheme 1. We wish to now report the temperature dependence of the substituent effects of the isomerizations.

Results and Discussion

Highlights of Kinetic Data. Preparations of numerous substituted ketenimines followed the previous method.[20] All the NMR spectra of ketenimines and nitriles match their structures. Ketenimines were dissolved in $CDCl_3$ and placed into capped NMR tubes that

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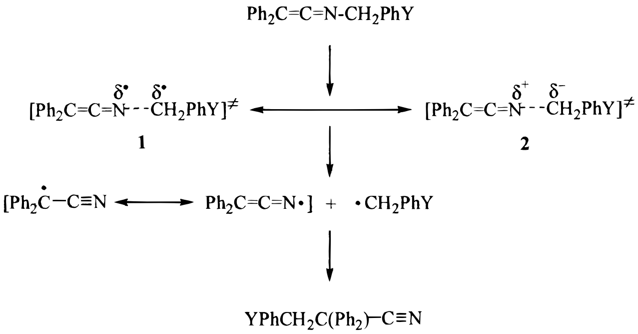
Scheme 1



were later immersed in a constant-temperature bath for thermal isomerizations. The rates of isomerizations were measured by monitoring variations of the peaks of benzylic protons of the ketenimines and their nitrile counterparts. The former gradually diminished and the latter increased as the reactions progressed. The rates followed excellent first-order kinetics with $\ln(C_{at} + C_{bt})/C_{at} = k_Y t$ where C_{at} and C_{bt} are the peak area of benzylic protons of the ketenimine and the nitrile, respectively, at time t. Absolute rate constants of isomerizations (k_Y) were obtained at 40, 50, 60, and 70 °C. Activation parameters ($\Delta H^{\ddagger}_Y$ and $\Delta S^{\ddagger}_Y$) have been derived from Eyring plot[21] (Table 1). The relative rates (k_Y/k_H) were fitted with a single parameter using either σ^{22} (entries 1−3) or $\sigma^{\bullet\ 14-16}$ (entries 4−6, 10−12, 16−18). Entries 7−9, 13−15, and 19−21 employed both σ^{22} and $\sigma^{\bullet\ 14-16}$ for dual correlations. Furthermore, the correlations have been separately treated as with meta/para substituents (entries 1, 4, 7, 10, 13, 16, 19), para substituents (entries 2, 5, 8, 11, 14, 17, 20), and meta substituents (entries 3, 6, 9, 12, 15, 18, 21). The results at 40 °C are presented as entries 1−21 in Table 2. Similar data at 50, 60, and 70 °C corresponding to Table 2 are given in the Supporting Information.

The variations of rates in Table 1 stay in the range of less than 3-fold. Such modest substituent effects engender differential free energies of activation $\Delta\Delta G^{\neq}_{Y-H}$ of less than 1 kcal mol^{-1}. On the other hand, a larger magnitude of the same entity ($\Delta\Delta G^{\neq}_{Y-H} > 1$ kcal mol^{-1}) was observed for the radical reactions involving polar TS.[5] The modest alterations of the rates suggest that substituent effects may be mainly derived from other than polar interactions via delocalizations of positive charge.[5] Para substituents accelerate the rates (k_Y) regardless of their signs of σ ($\sigma > 0$ or $\sigma < 0$) indicating minor role of inductive effects. Meta substituents reveal even weaker substituent effects on the rates.

Hammett Single Correlations. Entries 1−3 correspond to Figures 1−3, respectively. The Hammett correlations are derived from inductive effects. Figures 1 and 2 exhibit shotgun-type scatter of the points. A satisfactory straight line is recognized only with Figure 3 that reveals Hammett $\rho = 0.602$ ($r = 0.958$). Hydrogen abstractions from substituted toluenes by *tert*-butyl radical[23] also gave a positive value of $\rho = 0.50$ ($r = 0.968$). Tri-*n*-butyltin radical[5d] abstracts cyanide from substituted benzyl isocyanides with $\rho = 0.70$ ($r = 0.999$). Both

Table 1. Absolute Rate Constants and Activation Parameters of the Isomerizations

T (°C)	$k_Y \times 10^5$ s^{-1} [a]										
	p-Cl	*p*-Br	*p*-OMe	*p*-Me	*p*-F	H	*m*-Cl	*m*-Br	*m*-F	*m*-Me	*m*-OMe
40	2.12 ± 0.04	2.07 ± 0.05	1.80 ± 0.03	1.27 ± 0.01	1.01 ± 0.02	0.773 ± 0.017	1.31 ± 0.02	1.28 ± 0.01	1.24 ± 0.02	0.759 ± 0.011	0.746 ± 0.018
50	7.49 ± 0.08	7.43 ± 0.14	6.39 ± 0.11	4.54 ± 0.06	3.69 ± 0.01	2.78 ± 0.03	4.56 ± 0.05	4.53 ± 0.07	4.39 ± 0.03	2.75 ± 0.06	2.72 ± 0.04
60[b]	24.7 ± 0.5	24.5 ± 0.1	22.1 ± 0.5	15.6 ± 0.3	12.6 ± 0.2	9.55 ± 0.39	15.3 ± 0.2	15.3 ± 0.3	14.6 ± 0.2	9.46 ± 0.03	9.16 ± 0.48
70	75.1 ± 1.5	74.3 ± 1.6	67.7 ± 1.8	48.7 ± 0.5	38.8 ± 0.2	29.7 ± 0.5	46.7 ± 0.8	46.6 ± 0.7	45.1 ± 0.6	29.8 ± 0.4	28.2 ± 0.6
$\Delta H^{\ddagger}_Y$ [c]	24.77 ± 0.11	24.85 ± 0.12	25.25 ± 0.13	25.36 ± 0.01	25.36 ± 0.09	25.37 ± 0.11	24.84 ± 0.08	24.99 ± 0.09	24.95 ± 0.08	25.51 ± 0.10	25.23 ± 0.14
$\Delta S^{\ddagger}_Y$ [d]	−1.02 ± 0.33	−0.78 ± 0.36	0.18 ± 0.39	−0.16 ± 0.28	−0.59 ± 0.29	−1.10 ± 0.33	−1.76 ± 0.25	−1.31 ± 0.29	−1.50 ± 0.24	−0.64 ± 0.32	−1.55 ± 0.41

[a] The rates were measured more than three times. [b] Some values of k_Y are not identical with the previous ones taken from ref 20. However general trends of the correlations are hardly altered. We may propose the present figures to be more accurate entities. [c] Enthalpies of activation for substituents Y. Unit: kcal mol^{-1}. [d] Entropies of activation for substituents Y. Unit: e.u.

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Table 2. Hammett Single and Dual Correlations of the Isomerizations at 40 °C

entry	approach[a]	σ^b	$\sigma^{\bullet c}$	ρ	$\rho^\bullet$	$\lvert\rho^\bullet/\rho\rvert$	r^d	n^e
1	Hammett[22]	σ_p/σ_m		0.137			0.181	11
2		σ_p		0.172			0.209	6
3		σ_m		0.602			0.958	6
4	Creary[15]		$\sigma^\bullet_p/\sigma^\bullet_m$		1.118		0.652	10
5			$\sigma^\bullet_p$		1.205		0.748	6
6			$\sigma^\bullet_m$		−3.102		−0.805	5
7	Hammett[22]/Creary[15]	σ_p/σ_m	$\sigma^\bullet_p/\sigma^\bullet_m$	0.648	1.886	2.91	0.928	10
8		σ_p	$\sigma^\bullet_p$	0.534	1.650	3.09	0.950	6
9		σ_m	$\sigma^\bullet_m$	1.012	2.693	2.66	0.978	5
10	Arnold[14]		$\sigma^\bullet_p/\sigma^\bullet_m$		5.668		0.599	8
11			$\sigma^\bullet_p$		7.908		0.761	5
12			$\sigma^\bullet_m$		−7.892		−0.535	4
13	Hammett[22]/Arnold[14]	σ_p/σ_m	$\sigma^\bullet_p/\sigma^\bullet_m$	0.592	11.20	18.92	0.888	8
14		σ_p	$\sigma^\bullet_p$	0.595	12.35	20.76	0.942	5
15		σ_m	$\sigma^\bullet_m$	0.574	0.178	0.31	0.996	4
16	Jiang and Ji[16]		$\sigma^\bullet_p/\sigma^\bullet_m$		1.134		0.724	11
17			$\sigma^\bullet_p$		1.446		0.936	6
18			$\sigma^\bullet_m$		−0.074		−0.039	6
19	Hammett[22]/Jiang and Ji[16]	σ_p/σ_m	$\sigma^\bullet_p/\sigma^\bullet_m$	0.277	1.266	4.57	0.808	11
20		σ_p	$\sigma^\bullet_p$	0.215	1.468	6.83	0.972	6
21		σ_m	$\sigma^\bullet_m$	0.618	−0.330	0.53	0.974	6

[a] The authors have originally defined the substituent constants. [b] σ is the Hammett substituent constant for the inductive effects taken from ref 22. [c] $\sigma^\bullet$ has been defined by three different scales[14−16] that measure the capacity of spin-delocalizations triggered by substituents. [d] Correlation coefficients. [e] Number of the points (e.g., substituents) forming the correlations.

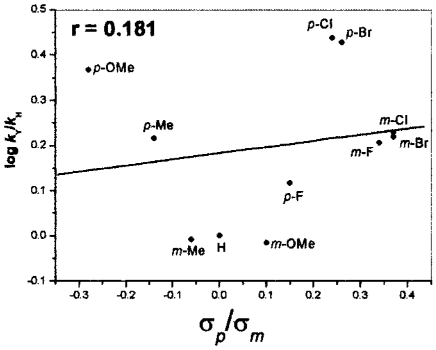

Figure 1. $\log k_Y/k_H = \rho\sigma_{m/p}$.

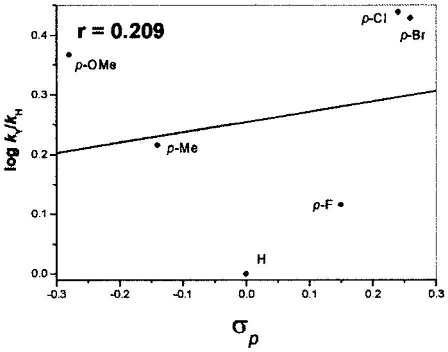

Figure 2. $\log k_Y/k_H = \rho\sigma_p$.

abstraction reactions by nucleophilic radicals[5d,23] maintain polar TS structure with the partial negative charge being localized[24] on the benzylic carbon atom. The correlation coefficient $r = 0.958$ could be considered fair when comparing with $r = 0.968$[23] and $r = 0.999$.[5d] However an excellent linearity ($r = 0.999$) is attained

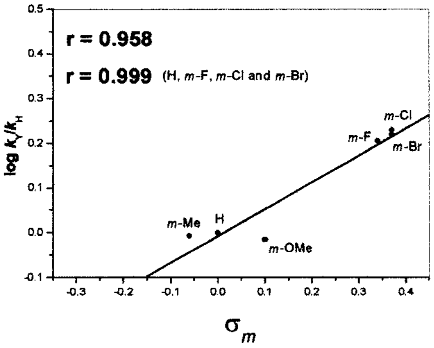

Figure 3. $\log k_Y/k_H = \rho\sigma_m$.

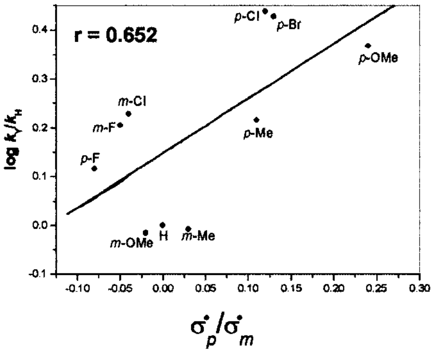

Figure 4. $\log k_Y/k_H = \rho^\bullet\sigma^\bullet_{m/p}$.

with *m*-Cl(*m*-Br), *m*-F, and H showing the weight of inductive effects on the rates illustrated by **2**.

Entries 4−6 utilize $\sigma^\bullet$ defined by Creary[15] while entries 10−12 and 16−18 indicate the correlations with $\sigma^\bullet$ scales invented by Arnold[14] and by Jiang and Ji,[16] respectively. *Entries 4−6, 10−12* and 16−18 disclose surprisingly parallel trend of variations of $\rho^\bullet$ and r. Entries 4−6 correspond to Figures 4−6, respectively. Figure 4 shows a poor linear relation ($r = 0.652$) that could be, however, better than $r = 0.181$ of Figure 1. Such poor improvement nonetheless suggests that spin-delocalization could be somewhat more important than inductive effects. The Hammett plot was further reformed in Figure 5 ($r =$

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(24) Deprotonations of nitroalkanes traverse “carbanionic” TS structure where the negative charge is also localized on the carbon atom (Bordwell, F. G.; Boyle, W. J., Jr.; Yee, K. C. *J. Am. Chem. Soc.* **1970**, *92*, 5926.). The conjugation may not occur when the reorganization (from sp^3 to sp^2) energy can be hardly compensated by delocalization of negative charge on carbanion (Impastato, F. J.; Walborsky, H. M. *J. Am. Chem. Soc.* **1962**, *84*, 4838).

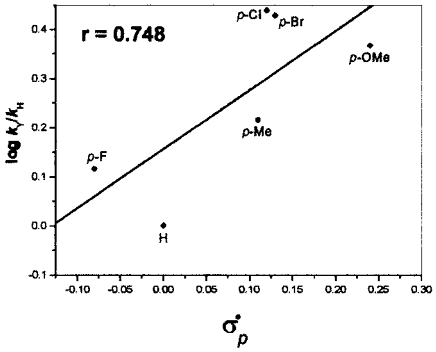

Figure 5. log k_Y/k_H $= \rho^{\bullet}\sigma^{\bullet}_p$.

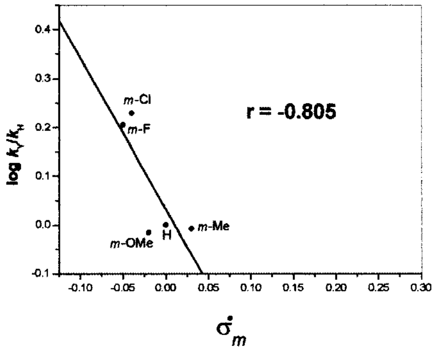

Figure 6. log k_Y/k_H $= \rho^{\bullet}\sigma^{\bullet}_m$.

0.748) when only para substituents were engaged suggesting promotion of spin-delocalizations via **1**. However, meta substituents seem to be incapable of spin-delocalizations to break down the correlations (Figure 6). The values of $\sigma^{\bullet}$ of electron-withdrawing meta substituents devised by Fisher,[13] Arnold,[14] and Creary[15] carry negative signs ($\sigma_m^{\bullet} < 0$). Free radicals are in principle electron-deficient groups and can be destabilized[7,8,11,13] by the inductive effects of electron-attracting groups.

Hammett Dual Correlations. Entries 7–9, 13–15, and 19–21 use dual substituent constants incorporating inductive effects (σ) and spin-delocalizations ($\sigma^{\bullet}$) into log $k_Y/k_H = \rho\sigma + \rho^{\bullet}\sigma^{\bullet}$.[25] Once again, a similar tendency of variations of ρ, $\rho^{\bullet}$, and r can be deciphered in the three groups of entries, respectively. Entries 7–9 are illustrated in Figures 7– 9, respectively. Figure 7 shows improved Hammett correlations ($r = 0.928$) compared to Figures 1 ($r = 0.181$) and 4 ($r = 0.652$). The linear correlations are further improved when para and meta substituents were separately treated. Accordingly, Figures 8 and 9 exhibit good Hammett correlations with $r = 0.950$ and $r = 0.978$, respectively.

p-Cl and *p*-Br exhibit faster rates than *p*-OMe, although the former carry much smaller spin-delocalization constants ($\sigma_c^{\bullet} = 0.12$ for *p*-Cl and 0.13 for *p*-Br)[15] than the latter ($\sigma_c^{\bullet} = 0.24$).[15] This “anomaly” can be explained by consideration of participation of inductive effects of the substituents ($\sigma = 0.24$ for *p*-Cl, 0.26 for *p*-Br, and -0.27 for *p*-OMe).[22] Figure 5 shows a negative deviation for *p*-Me ($\sigma_c^{\bullet} = 0.11$; $\sigma = -0.14$)[15,22] and a positive one for *p*-F ($\sigma_c^{\bullet} = -0.08$; $\sigma = 0.15$).[15,22] The directions of deviation match sign of σ of the substituents indicating again the secondary role of inductive effects. Therefore, rates triggered by para substituents are determined mainly by contribution of **1**, which is supplemented partly with role of **2**.

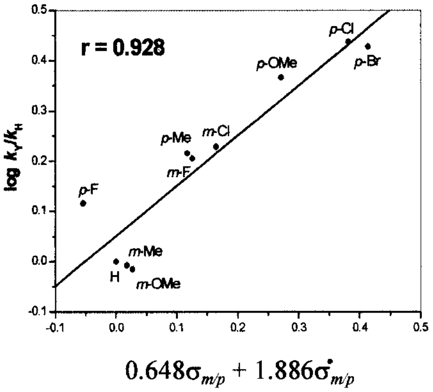

Figure 7. log k_Y/k_H $= 0.648\sigma_{m/p} + 1.886\sigma^{\bullet}_{m/p}$.

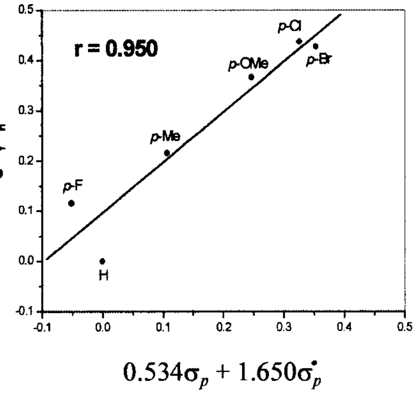

Figure 8. log k_Y/k_H $= 0.534\sigma_p + 1.650\sigma^{\bullet}_p$.

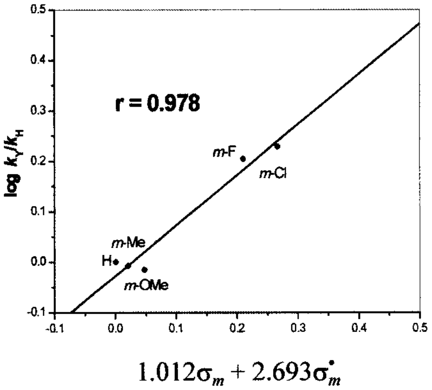

Figure 9. log k_Y/k_H $= 1.012\sigma_m + 2.693\sigma^{\bullet}_m$.

m-Cl, *m*-Br, and *m*-F share very comparable rates that are *ca.* 1.7 times larger than that for H. The three substituents retain a negative spin-delocalization constant (e.g., $\sigma^{\bullet} = -0.04$ for *m*-Cl and $\sigma^{\bullet} = -0.05$ for *m*-F).[26] The rate enhancements could be explained only when inductive effects ($\sigma = 0.37$ for *m*-Cl and *m*-Br, and $\sigma = 0.34$ for *m*-F) eminently outweigh spin-delocalizations. The points for *m*-Cl(*m*-Br), *m*-F, and H show better

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[25] The dual formalism appears similar to Yukawa-Tsuno equation, $\log(k_Y/k_H) = \rho\sigma + \rho^r(\sigma^+ - \sigma)$. The equation expresses LFER derived from normal and extra resonance effects. ρ^r/ρ is a measure of relative contributions of polar and resonance effects, that could be equivalent to $\rho^{\bullet}/\rho$ in our reactions. (a) Tsuno, Y.; Ibata, T.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 960, 965, and 971. (b) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238; **1979**, *101*, 3288 and 4678.

[26] Spin-delocalization constant ($\sigma^{\bullet}$) of *m*-Br has not been reported. However $\sigma^{\bullet}$ of *m*-Br could be comparable in magnitude with that of *m*-Cl.

Table 3. Activation Parameters of Homolysis of Initiators

initiators	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (eu)
$C_6H_5C(O)OOC(CH_3)_3$ [a]	37.5	16.1
$(CH_3)_3COOC(CH_3)_3$ [b]	37.8	13.8
$CH_3C(O)OO(O)CCH_3$ [c]	31.3	11.6
$C_6H_5CH_2N{=}NCH_2C_6H_5$ [d]	34.3	5.6
$(C_6H_5)_2C{=}C{=}NCH_2C_6H_5$	25.4	−1.1

[a] Taken from ref 30. [b] Taken from ref 31. [c] Taken from ref 32. [d] Taken from ref 28.

linearity ($r = 0.999$) than the case including all the substituents ($r = 0.958$) in Figure 3. This may suggest contribution of **2** as a sole element determining the rates. On the contrary, *m*-Me ($\sigma^\bullet = 0.03$ and $\sigma = -0.06$) and *m*-OMe ($\sigma^\bullet = -0.02$ and $\sigma = 0.12$) mark slightly smaller rates than rate for H. If inductive effects prevailing in **2** were implicated, *m*-OMe should show somewhat faster rates than *m*-Me. However the isomerization rates of *m*-OMe are always slightly slower than those of *m*-Me. Accordingly, the role of substituent effects is reversed when spin-delocalizations occurring in **1** emerge to influence the rates. The relative importance of **1** and **2** can be also verified from values of $|\rho^\bullet/\rho|$[27] in Table 2. Para substituents (entries 8, 14, 20) show much larger values of $|\rho^\bullet/\rho|$ than corresponding meta substituents (entries 9, 15, 21).

Activation Parameters Mirroring TS Structures. Enthalpies of activation show very little variation and stay in the range of $\Delta H^\ddagger_Y = 25.0$ kcal mol^{-1} (Table 1). Thermolysis of diphenylazomethanes[28] and thermal rearrangements of methylenecyclopropanes[29] involve "homolytic" TS structures resembling **1**. Both reactions[28,29] also showed minor substituent effects on the magnitude of $\Delta H^\ddagger_Y$. Homolysis of several initiators[30−32] usually shows positive large entropy of activation ($\Delta S^\ddagger_Y$) (Table 3). However the reactions of the ketenimines reveal $\Delta S^\ddagger_Y <$ 0. This may be due to hindered rotations of phenyl ring[33] taking place by formations of double bonds through conjugation occurring in **1** and **2**. *m*-Cl, *m*-Br, and *m*-F show slightly more negative values of $\Delta S^\ddagger_Y$ than para substituents. The positive charge in **2** could be more effectively delocalized into the two phenyl groups compared to spin-delocalizations occurring in **1**. The rotations of phenyl rings could be more vigorously restricted in **2** than in case of **1**. Similar effects[28] were also observed in the thermolysis of benzyl diazenes.

Conclusion

$\sigma^\bullet_\alpha$, $\sigma^\bullet_c$, and $\sigma^\bullet_{jj}$ are derived from different scales whose values are not identical with each other (e.g., $\sigma^\bullet_\alpha = 0.017$, $\sigma^\bullet_c = 0.12$, and $\sigma^\bullet_{jj} = 0.22$ for *p*-Cl). Nonetheless, the correlations utilizing three different parameters give remarkably parallel tendency with Hammett single and dual equations. The parallelism supports the $\sigma^\bullet$ as bona fide spin-delocalization constants. Spin-delocalizations and inductive effects cooperate to determine the rates. The former is favored by para substituents and the latter by meta substituents. *m*-Cl, *m*-Br, and *m*-F exert solely inductive effects to control the rates. Perturbations of the activation parameters ($\Delta H^{\neq}_Y$ and $\Delta S^{\neq}_Y$) by substituents are too small to elucidate TS structure. However, the negative values of $\Delta S^{\neq}_Y$ may be due to restriction of bond rotation in the TS.

Experimental Section

Materials. The reagents are commercially available and were purified, if necessary, according to standard procedures.[34] The preparations of diphenyl *N*-(substituted benzyl)ketenimines were described in a previous paper.[20]

^{1}H NMR Data for Ketenimines ($CDCl_3$ with 0.03% TMS). Diphenyl *N*-(*m*-bromobenzyl) ketenimine gave ^{1}H NMR: 7.0−7.8 (m, 14H), 4.8 (s, 2H). The other ketenimines were described previously.[20]

Kinetic Procedures. Measurements of rates of the isomerizations are analogous to those previously described.[20] Solutions of ketenimines (0.3 M in $CDCl_3$) were placed in tightly capped NMR tubes. The tubes were then placed in a constant-temperature bath for the thermal reactions. At several intervals the tubes undergoing thermolysis were quenched in liquid nitrogen, thawed, and transferred to the cavity of a Varian Gemini 2000 NMR spectrometer for ^{1}H NMR measurements. A 1:1 correspondence was observed for the integrated peak areas for benzylic protons of ketenimines (δ: 4.7−4.8) and corresponding nitriles (δ: 3.6−3.8) indicating the amount of a ketenimine reacted was equal to quantity of a nitrile produced. Peak areas of the benzylic protons were used for concentrations of a ketenimine and its nitrile isomer. Therefore the rates can be measured with $\ln(C_{at} + C_{bt})/C_{at} = k_Y t$. C_{at} and C_{bt} are the magnitudes of the benzylic protons of a ketenimine and corresponding nitrile at reaction time t, respectively. First-order rate constants (k_Y) were determined by standard least-squares method. Correlation coefficients for the linearity are greater than $r = 0.9990$.

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Supporting Information Available: Comparison of the Hammett single and dual correlations for the isomerizations at 40, 50, 60, and 70 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Magnitude of $|\rho^\bullet/\rho|$ may deliver only qualitative significance because $\sigma^\bullet$ and σ were formulated with different scales.

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