

Thermal Isomerizations of Substituted Benzyl Isocyanides: Relative Rates Controlled Entirely by Differences in Entropies of Activation[†]

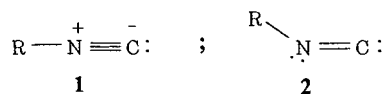
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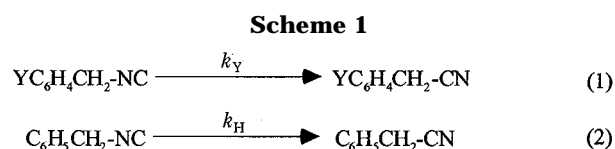
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The absolute and relative rates of thermal rearrangements of substituted benzyl isocyanides were obtained at the temperatures between 170 and 230 °C. The relative rates are independent of temperature and exhibit excellent Hammett correlations ($\rho^+ = -0.24$). The temperature studies yielded activation parameters (ΔH_Y^\ddagger and ΔS_Y^\ddagger) and their differential counterparts ($\Delta\Delta H_{Y-H}^\ddagger$ and $\Delta\Delta S_{Y-H}^\ddagger$). The differential terms were plotted against σ^+ . The secondary α -deuterium kinetic isotope effects ($k_D/k_H = 1.11$) were measured at several temperatures. The rate data can be rationalized with the cyclic TS. The substituent effects on the rates are due to the entropic contributions.

An isonitrile² maintains the alternative structure of **1** or **2** with **1** being responsible for the heterolytic reactions. The thermal isomerization of methyl isocyanide³ in gas phase is a cationotropic 1,2-shift which takes place via a triangular transition state (TS) with concerted bond formation and cleavage. Either ultraviolet radiation⁴ or vibrationally excited ethane molecules⁵ also bring about the same isomerizations without intervention of radicals. The isonitrile–nitrile rearrangements⁶ of several aryl and alkyl isocyanides evidently excluded the carbocations as reaction intermediates. The structure–reactivity relationship⁷ appeared, however, ambiguous for isomerizations of a number of isonitriles. The structural changes of the isonitriles failed to produce equivalent variations of the activation parameters.



However, we were fortunate enough to discover small polar substituent effects controlling rates of the isomerizations in previous work.^{6,7} The rearrangements of substituted phenyl isocyanides⁶ to substituted benzonitriles reveal $\rho = -0.21$ at 200 °C. Similar reactions of substituted benzyl isocyanides⁷ indicate $\rho^+ = -0.24$ at 210 °C. We report herein novel temperature effects on the rates of the isomerizations.



Results and Discussion

Relative Rates, Hammett Constants, Activation Parameters, and Secondary α -Deuterium Kinetic Isotope Effects. The ampoules containing a substituted benzyl isocyanide, chlorobenzene (internal standard), 1,1-diphenylethylene, and benzene (solvent) underwent thermalolysis at several temperatures (170–230 °C). 1,1-Diphenylethylene was added as a safeguard to eliminate the possibility of radical reactions. However, the reactions were unaltered even in the absence of the radical scavenger (Scheme 1). The heating transformed the substituted benzyl isocyanide smoothly into the substituted phenyl acetonitrile without detectable side reactions, which were verified by either GLC or NMR method. The excellent first-order plots ($r \geq 0.98$) and material balances ($\geq 97\%$) again excluded other reaction pathways. The rates at 170, 190, and 210 °C were measured by GLC method. The absolute rate constants (k_Y) have been derived from $\ln C_0/C_t = k_{Y(H)}t$ with C_0 and C_t denoting initial and final concentrations of the substituted benzyl isocyanide, respectively. NMR method was utilized to determine the rates (k_Y) at 230 °C employing $\ln[(C_{At} + C_{Bt})/C_{At}] = k_Y t$ where C_{At} and C_{Bt} are the concentrations of reactant and product, respectively. The rate of isomerization of benzyl isocyanide at 210 °C indicated virtually identical value whether obtained by either NMR or GLC. The relative rates (k_Y/k_H) have been obtained and put into Hammett correlations. The value of $\rho^+ = -0.24$ excellently agrees with the previous one⁷ calculated by us. These rate data are tabulated in Table 1. The rates ($k_Y \times 10^5 \text{ s}^{-1}$) of isomerization of benzyl isocyanide in three solvents at 210 °C measured by NMR method are $45.2 \pm$

[†] We mourn for the late Professor Glen A. Russell who passed away on January 1, 1998.

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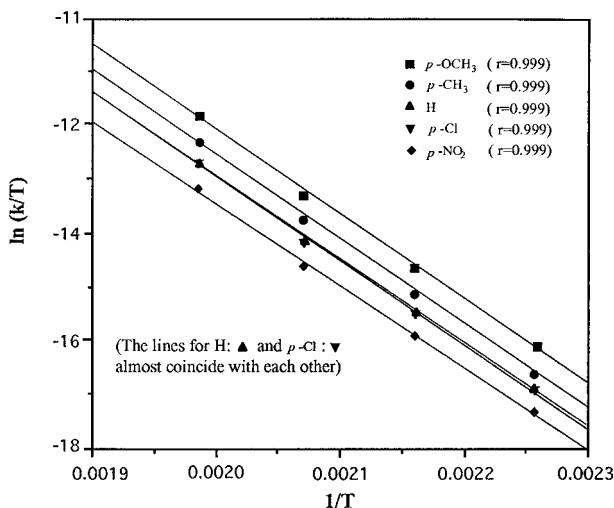
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Table 1. Absolute (Relative) Rates and Hammett Correlations of the Thermal Isomerizations

temp (°C)	$k_Y \times 10^5/s (k_Y/k_H)^{a,b}$ when Y =						$\rho^+ (r)^d$	$\rho (r)^d$
	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>p</i> -NO ₂ ^c			
170 ^e	3.46(1.72)	2.61(1.30)	2.01(1)	1.95(0.97)	1.47(0.73)	-0.24(0.987)	-0.31(0.914)	
190 ^e	16.9(1.70)	13.0(1.31)	9.94(1)	9.54(0.96)	7.26(0.73)	-0.24(0.986)	-0.31(0.919)	
210 ^e	78.6(1.72)	59.4(1.31)	45.2(1) ^g	44.3(0.98)	33.4(0.73)	-0.24(0.986)	-0.31(0.915)	
230 ^f	396(1.74)	295(1.29)	228(1)	226(0.99)	166(0.73)	-0.24(0.987)	-0.31(0.911)	

^a The absolute rates (k_Y) were obtained from the plot of $\ln(C_0/C_t)$ vs time. The correlation coefficients for the slope are always $r > 0.98$. The error limits are far less than 5%. ^b Substituent constants are taken from ref 29. ^c The relative reactivity of *p*-nitrobenzyl isocyanide against benzyl isocyanide has been taken as $k_Y/k_H = 0.73$ from Table 1 of ref 7. ^d Correlation coefficient. ^e The rates were measured by GLC method. ^f The rates were measured by NMR method. ^g The rates were measured in three solvents (C₆H₆, C₆H₅CN, and *n*-C₁₆H₃₄). The analysis of the reaction mixture by GLC and NMR method have produced identical results.

**Figure 1.** Temperature dependence of rates of the isomerizations.

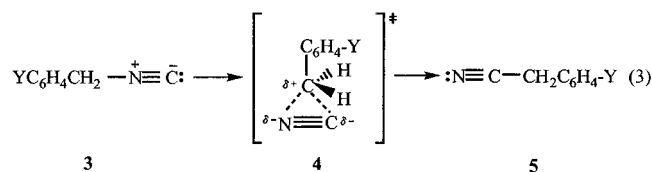
0.5 in C₆H₆, 45.2 ± 0.2 in C₆H₅CN, 47.6 ± 1.4 in *n*-C₁₆H₃₄. Nearly identical rates may indicate that kinetic solvent interactions hardly control cleavage and formation of the bonds in **4**. Therefore the substituent effects should solely perturb the activation process.

The temperature studies employed the Eyring equation⁸ to obtain the activation parameters (ΔH_Y^\ddagger and ΔS_Y^\ddagger) from Figure 1. Table 2 contains the activation terms and their differential ones ($\Delta\Delta H_{Y-H}^\ddagger$ and $\Delta\Delta S_{Y-H}^\ddagger$). Both differential parameters were plotted against σ^+ (Figures 2 and 3). The secondary α -deuterium kinetic isotope effects (k_H/k_D) were measured as $k_H/k_D = 1.11 \pm 0.05$ at 170, 190, and 230 °C. k_D is a rate constant for C₆H₅CD₂NC → C₆H₅CD₂CN.

Mechanistic Highlights of the Isomerizations.

The Hammett constant $\rho^+ = -0.24$ of Table 1 suggests that a modest positive charge occurs on the benzylic carbon atom in **4**. The better correlation with σ^+ indicates dispersion of the positive charge into the phenyl ring. When the bond cleavage slightly outweighs the bond formation in **4**, a fractional positive charge should be left over on the carbon atom. The secondary α -deuterium kinetic isotope effects show $k_H/k_D = 1.11$ for isomerizations of benzyl isocyanide. Typical S_N2 reactions frequently exhibit $k_H/k_D < 1$ with the α -deuterations.⁹ This may suggest that **4** experiences substantial bond cleavage, and the benzylic carbon atom undergoes significant sp²-hybridization to promote a bending vibration of the methylene group.

(+)-*sec*-Butyl isocyanide⁶ undergoes isomerization with retention of configuration at the migrating carbon atom. Numerous anionotropic 1,2-shifts (e.g. Curtius, Hofmann, Lossen, and Schmidt rearrangements)¹⁰ also show similar retention of configuration, which can be due to the cyclic TS structure. "C:" in **3** is a nucleophilic site. The rearrangements can therefore be taken as an intramolecular nucleophilic process where breakage and formation of the bonds occur concurrently on the same side.



The cyclic structure **4** introduces significant angle strains and restricts its internal motions. **3** and **5**, on the contrary, are free of such angular distortions and enjoy the free rotations. If a TS were of an "intermediate configuration" between reactant and product, the rate should be linearly related with the equilibrium to realize the linear free energy relationship (LFER).^{11,12} Therefore the reactivity/selectivity principle¹¹ and the Hammond postulate¹³ should predict the trend of the reactivities. However **4** resembles neither **3** nor **5** and obviously deviates from the aforementioned "intermediacy". The Hammond postulate¹³ should be thus invalidated under the foregoing circumstances. The perpendicular effect¹⁴ has been invoked to describe the deviation of TS occurring in a variety of organic reactions.¹⁵⁻¹⁹ The principle of nonperfect synchronization¹⁸ and "imbalanced TS"²⁰ are other expressions for the deviations. The temperature studies (Table 1) indicate that the absolute rates increase at higher temperatures, but the relative rates (selectivities) persistently remain unaltered. Therefore, the temperature effects disobey the classical reactivity/selectivity principle (RSP).¹¹

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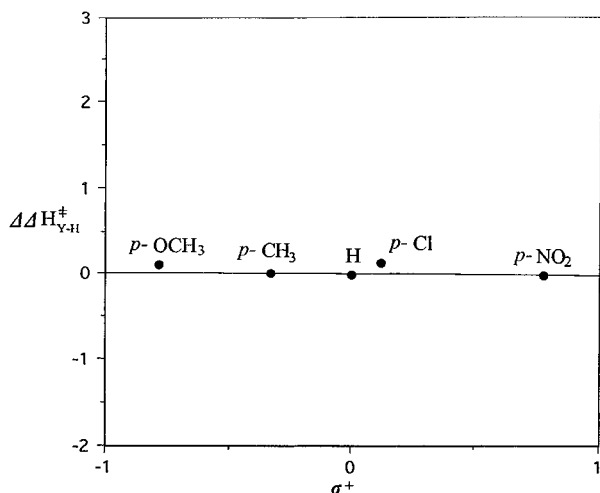
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Table 2. Activation (Differential Activation) Parameters of the Thermal Isomerizations

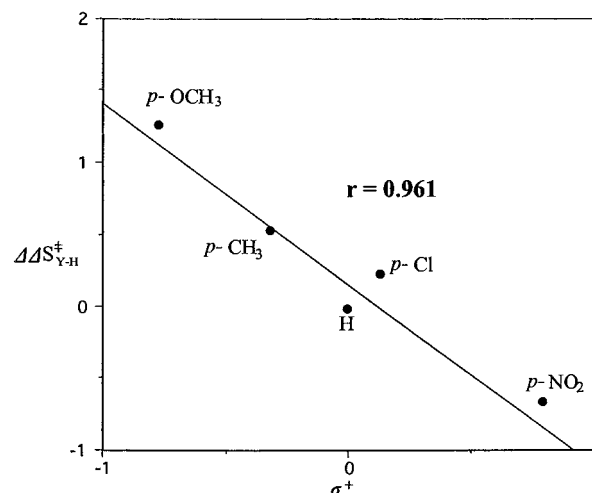
parameters ^a	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>p</i> -NO ₂
$\Delta H_Y^\ddagger (\Delta \Delta H_{Y-H}^\ddagger)^b$	33.95(0.11)	33.83(-0.01)	33.84(0)	34.02(0.18) ^d	33.84(0)
$\Delta S_Y^\ddagger (\Delta \Delta S_{Y-H}^\ddagger)^c$	-3.30(1.31)	-4.10(0.51)	-4.61(0)	-4.25(0.34) ^d	-5.23(-0.62)

^a Refer to the correlation coefficients for the substituents in Figure 1. ^b $\Delta \Delta H_{Y-H}^\ddagger = \Delta H_Y^\ddagger - \Delta H_H^\ddagger$ where ΔH_Y^\ddagger and ΔH_H^\ddagger are the activation enthalpies for substituted and unsubstituted benzyl isocyanides, respectively (unit: kcal/mol). ^c $\Delta \Delta S_{Y-H}^\ddagger = \Delta S_Y^\ddagger - \Delta S_H^\ddagger$ where ΔS_Y^\ddagger and ΔS_H^\ddagger are similarly related as with the above enthalpic terms (unit: eu). ^d The "abnormal" behavior of *p*-Cl has been also noted in a previous work²² and attributed to the dual substituent effects. *p*-Cl could be electron-withdrawing via inductive effects but become electron-donating by resonance effects.

**Figure 2.** Plot of $\Delta \Delta H_{Y-H}^\ddagger$ vs σ^+ for the thermal isomerizations.

Activation Parameters and Rationalization of Constant Selectivities. The enthalpies of activation (ΔH_Y^\ddagger) (Table 2) stay almost invariable (ca. 33.90 kcal/mol) so as to declare sparse substituent effects. Even drastic structural changes of the isonitriles⁷ entail very modest variations of ΔH_Y^\ddagger . The molecular distortion of **4** should be the prime candidate to determine the magnitude of ΔH_Y^\ddagger . The substituents (Y) could exercise only a minor⁹ influence on ΔH_Y^\ddagger because the requirements of bond formation and breakage are opposite. An electron-withdrawing group (Y) facilitates the bond-making but retards the bond-breaking and *vice versa*. Accordingly the differential terms ($\Delta \Delta H_{Y-H}^\ddagger$) become close to zero (Table 2), and a nearly horizontal slope is attained for Figure 2.

Entropies of activation²¹ (ΔS_Y^\ddagger) can be closely related with the differences in number and character of the degrees of freedom between **4** and **3**. The cyclic structure of **4** barely allows the internal freedom while **3** enjoys the free rotations. The negative sign of ΔS_Y^\ddagger of Table 2 can be accordingly understood. The small and negative value of $\rho^+ = -0.24$ suggests that bond-breaking slightly exceeds bond-making with net increase in the entropy. The electron-donating substituents tend to increase the extent of bond cleavage leading to a relatively looser TS structure. The differential entropy terms ($\Delta \Delta S_{Y-H}^\ddagger$) should thus be a result of bond scission for a substituted benzyl isocyanide being less than for benzyl isocyanide itself. Figure 3 shows almost linear relations between $\Delta \Delta S_{Y-H}^\ddagger$ and σ^+ which are also featured with our radical reactions.²²⁻²⁴ The values of $\Delta \Delta H_{Y-H}^\ddagger$ are close to zero,

**Figure 3.** Plot of $\Delta \Delta S_{Y-H}^\ddagger$ vs σ^+ for the thermal isomerizations.

and the Gibbs formulation reduces to $\Delta \Delta G_{Y-H}^\ddagger = -T \Delta \Delta S_{Y-H}^\ddagger$. The values of $T \Delta \Delta S_{Y-H}^\ddagger$ at 210 °C have been calculated to be 0.63 and -0.30 kcal/mol for *p*-OCH₃ and *p*-NO₂, respectively. Therefore the rates are delicately controlled through the entropic term derived from the degrees of the bond cleavages.

Figures 2 and 3 are empirical drawings to visualize the substituent effects controlling extent of bond cleavages. The differential substituent effects could be too weak to yield significant alterations of ΔH_Y^\ddagger . Such feeble interactions (equivalent to less than 1 kcal) have been however detected in ΔS_Y^\ddagger . A similar phenomenon concerning the substituent effects on ΔH_Y^\ddagger and ΔS_Y^\ddagger was already observed with the radical reactions involving polar TS (refer to the "Supporting Information").²²⁻²⁴ Others^{25,26} also perceived importance of the entropies with similar radical reactions. The cyclic TS, **4**, and the polar TS²²⁻²⁶ share a structural similarity in that they both escape from the "intermediate configuration" between reactant and product.

Solvolysis of substituted cumyl chlorides (eq 4) and decomposition of the phosphonium chlorides (eqs 5 and

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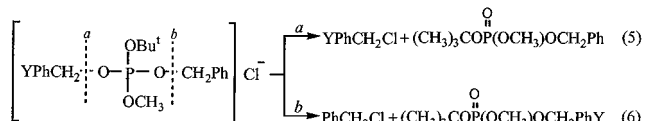
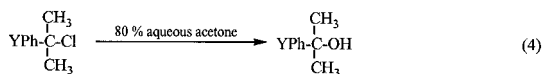
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6) were investigated by us²⁷ to obtain the differential activation parameters ($\Delta\Delta H_{Y-H}^\ddagger$ and $\Delta\Delta S_{Y-H}^\ddagger$). Both reactions showed enthalpy control of reactivities. The structures of TSs must satisfy requirements of the "intermediate configuration". The temperature effects on the relative rates (k_Y/k_H) conformed to RSP. The plots of $\Delta\Delta H_{Y-H}^\ddagger$ vs σ^+ yielded good straight lines with positive slopes (refer to the "Supporting Information"). Therefore the substituent effects systematically control the bond ruptures, which is reflected in variations of ΔH_{Y-H}^\ddagger .



The selectivity (Q) can be defined as $Q = \ln(k_Y/k_H)$ and $\ln(k_Y/k_H) = -(\Delta G_Y^\ddagger - \Delta G_H^\ddagger)/RT = -\Delta\Delta G_{Y-H}^\ddagger/RT$. $Q = -\Delta\Delta G_{Y-H}^\ddagger/RT$ can be divided into entropy and enthalpy term.

$$Q = \Delta\Delta S_{Y-H}^\ddagger/R - \Delta\Delta H_{Y-H}^\ddagger/RT \quad (7)$$

Since $\Delta\Delta H_{Y-H}^\ddagger/RT$ is close to zero, eq 7 becomes $Q = \Delta\Delta S_{Y-H}^\ddagger/R$ which is devoid of the temperature. The constant selectivities against the temperature gradient are thereby verified.

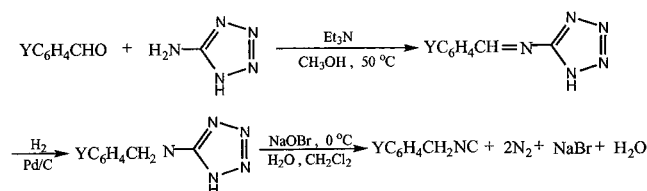
Conclusion

The isomerizations belong to the cationotropic 1,2-shifts, which have been rarely studied.¹⁰ The structure of TS should characterize the reactivities. The cyclic TS can be defined as an "imbalanced TS"²⁰ which confines the validity of Hammond postulate¹³ and reactivity/selectivity principle,¹¹ and engenders the entropy control of reactivities. An absence of temperature effects is rationalized and established in terms of the entropic contribution. The entropy term is 1000 times more sensitive than its enthalpic mate in order to recognize the substituent effects on the bond fissions. The activation parameters fail to follow the isokinetic relationship²⁸ and to show compensation effects.

Experimental Section

Materials and Methods. Substituted benzaldehydes, 5-aminotetrazole, palladium on activated carbon, triethylamine, lithium aluminum deuteride, formic acid, and other reagents were purchased from the major suppliers. Liquids were distilled with center-cut collection, and solids were recrystallized according to the standard procedures³⁰ when necessary. A Varian 3300 gas chromatograph and a Varian Gemini 2000 NMR spectrometer were used for the analysis of the reaction mixtures.

Substituted benzyl isocyanides ($\text{YC}_6\text{H}_4\text{CH}_2\text{NC}$, $\text{Y} = p\text{-OCH}_3$, $p\text{-CH}_3$, H , and $p\text{-Cl}$) were prepared by the literature method.³¹



The stretching vibration of $-\text{N}=\text{C}$ is shown at 2184 cm^{-1} for all the isocyanides ($\text{YC}_6\text{H}_4\text{CH}_2\text{NC}$). The chemical shifts are indicated as follows: $^1\text{H NMR}$ (200 MHz, CDCl_3) δ : $\text{Y} = \text{H}$, 7.38 (m, 5H), 4.64 (s, 2H); $\text{Y} = p\text{-OCH}_3$, 7.29–7.24 (d, 2H), 6.94–6.89 (d, 2H), 4.56 (s, 2H), 3.81 (s, 3H); $\text{Y} = p\text{-CH}_3$, 7.19 (dd, 4H), 4.54 (s, 2H), 2.34 (s, 3H); $\text{Y} = p\text{-Cl}$, 7.40–7.36 (d, 2H), 7.31–7.26 (d, 2H), 4.62 (s, 2H).

Deuterated benzyl isocyanide ($\text{C}_6\text{H}_5\text{CD}_2\text{NC}$)³² was obtained via dehydration of $\text{C}_6\text{H}_5\text{CD}_2\text{NDCHO}$ derived from the reaction of $\text{C}_6\text{H}_5\text{CD}_2\text{ND}_2$ with HCO_2H . Reduction of $\text{C}_6\text{H}_5\text{CN}$ with LiAlD_4 gave $\text{C}_6\text{H}_5\text{CD}_2\text{ND}_2$.³³ The percent deuteration was over 98%.

Thermal Reactions. A substituted benzyl isocyanide ($\text{YC}_6\text{H}_4\text{CH}_2\text{NC}$, 0.6 M), 1,1-diphenylethylene (0.4 M), and chlorobenzene (internal standard, 0.2 M) were dissolved in benzene. The benzene solutions were divided into several Pyrex ampules, which were degassed and sealed by the freeze-pump-thaw method. Before the thermolysis, the ampules were prewarmed at 170°C for 5 min to shorten the time of thermal equilibrium. The control experiment indicated no isomerizations taking place during the period of 5 min. Less than 10 s was required for the warming up to 230°C . The ampules were then exposed to the thermal reactions at the temperatures and quenched with ice/water at several intervals.

Analytical Procedures. The solutions having undergone the thermal reactions were analyzed on 30 m DB-1 capillary column utilizing FID and temperature programming from 40 to 210°C . The GLC analysis provided the final concentrations of $\text{YC}_6\text{H}_4\text{CH}_2\text{NC}$ and $\text{YC}_6\text{H}_4\text{CH}_3\text{CN}$, which always showed excellent material balances ($\geq 97\%$). The absolute rate constants have been derived from plot of $\ln(C_{A0}/C_{At})$ vs t , with C_{A0} and C_{At} representing the initial and final concentration of $\text{YC}_6\text{H}_4\text{CH}_2\text{NC}$ at time t , respectively. The rate constants (k_Y) at 170, 190, and 210°C were obtained as follows. Each sample was analyzed more than two times to locate a point in the plot of $\ln C_{A0}/C_{At}$ vs time. More than four points make a straight line with a correlation coefficient, $r \geq 0.980$. The figure ($r \geq 0.980$) should indicate that the isomerization is the sole reaction taking place during the thermolysis. Each rate constant (k_Y) was obtained from the average slopes of more than two straight lines. The rates at 230°C were measured by NMR method. The NMR spectra showed the peaks only for $\text{YC}_6\text{H}_4\text{CH}_2\text{NC}$ and $\text{YC}_6\text{H}_4\text{CH}_2\text{CN}$ which indicated that no side reactions occurred during the reactions. The disappearance of $\text{YC}_6\text{H}_4\text{CH}_2\text{NC}$ also matched the formation of $\text{YC}_6\text{H}_4\text{CH}_2\text{CN}$. The rate equation can be written down as $\ln[(C_{At} + C_{Bt})/C_{A0}] = k_Y t$ where C_{At} and C_{Bt} are concentrations of $\text{YC}_6\text{H}_4\text{CH}_2\text{NC}$ and $\text{YC}_6\text{H}_4\text{CH}_2\text{CN}$ at reaction time t , respectively. The integration of the methylene peaks of $\text{YC}_6\text{H}_4\text{CH}_2\text{NC}$ and $\text{YC}_6\text{H}_4\text{CH}_2\text{CN}$ were used as the substitute for the concentrations, i.e., C_{At} and C_{Bt} . Therefore the rate equation exempts employment of an internal standard and guarantees the better precision of the data. Separate samples were measured at various intervals to determine the location of the points in the

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plots. More than four points were obtained to make one straight line. The plots of $\ln[(C_{At} + C_{Bi})/C_{At}]$ vs time gave straight lines with excellent correlation coefficient, i.e., $r \geq 0.980$. Several representative plots of the rate equation are given in the Supporting Information.

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Supporting Information Available: Several plots (e.g. $\Delta\Delta H_{Y-H}^\ddagger$ vs σ^+ or σ and $\Delta\Delta S_{Y-H}^\ddagger$ vs σ^+ or σ) that compare the reactivities controlled by the entropies and enthalpies; $\ln(\text{concn})$ vs time plots that indicate accuracy of the measurements of the absolute rates; the examples of material balance of the isomerizations (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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