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Photobrominations of Substituted Cumenes by *N*-Bromosuccinimide: Charge Delocalizations, Inductive Effects, and Spin Dispersions Triggered by Substituents

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Introdution

Substituents[1] control the rates of radical reactions through charge delocalizations (σ^+), inductive effects (σ), or spin dispersions ($\sigma^\bullet$). The *polar effects* of radical reactions[2−7] are due mainly to the charge delocalizations and involve entropy control of rates.[6c,7] Furthermore, dominance of entropy could maintain the relative rates (k_Y/k_H) either constant or higher with increasing temperature (a violation of reactivity/selectivity principle). The inductive effects[7c,8,9] have been operated only with TS bearing a carbanionic moiety where localization of negative charge occurs on the benzylic carbon atom. Substituents could also provoke spin delocalizations[10−13] to influence the rates of radical reactions.

Photobrominations of substituted cumenes by *N*-bromosuccinimide (NBS)[14] previously showed a Hammett reaction constant ($\rho = -0.38$ at 70 °C). The ρ/σ correlations indicated that the rates were controlled by inductive effects. However, the same brominations of substituted toluenes[6] measured $\rho^+ = -1.40$ at 80 °C and suggested the charge delocalizations taking place with TS. In the present study, we probe functions of substituents that influence the rates. Temperature effects are to be investigated to obtain differential activation parameters telling structures of TS.

Scheme 1

$$\mathrm{YC_6H_4C(CH_3)_2{-}H} + \mathrm{Br}\bullet \xrightarrow{k_Y} \mathrm{YC_6H_4C(CH_3)_2}\bullet + \mathrm{HBr} \qquad (1)$$

$$\mathrm{C_6H_5C(CH_3)_2{-}H} + \mathrm{Br}\bullet \xrightarrow{k_H} \mathrm{C_6H_5C(CH_3)_2}\bullet + \mathrm{HBr} \qquad (2)$$

$$\mathrm{SN{-}Br} + \mathrm{HBr} \longrightarrow \mathrm{SN{-}H} + \mathrm{Br_2} \qquad (3)$$

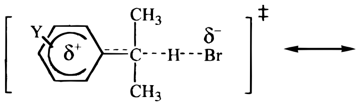
$$\mathrm{Br_2} \longrightarrow 2\,\mathrm{Br}\bullet \qquad (4)$$

(SN–Br = NBS, Y : *p*-OMe, *p*-CH$_3$, H, *p*-Cl, *p*-CN, and *p*-NO$_2$)

$$k_Y/k_H = \log\,(Y_f/Y_i)\,/\,\log\,(H_f/H_i) \qquad (5)$$

Results and Discussion

Competitive photobrominations of pairs of substituted cumene/cumene by NBS were carried out at 10, 40, 60, and 80 °C in CCl$_4$ (Scheme 1). Analysis of the reaction mixtures employed the GLC method. Relative rates (k_Y/k_H) were obtained from eq 5 at each temperature. Y and H indicate concentrations of substituted cumene and cumene, respectively with subscripts f meaning final and i initial concentrations. Hammett plots employed σ^+,[15] σ,[16] and $\sigma^\bullet$ [11] to yield ρ^+, ρ, and $\rho^\bullet$, respectively, that were obtained from Figures 1−3 and the like. Figure 3 exhibits a typical shotgun type of scatter of the points and indicates a breakdown the correlations ($r = 0.198$). Spin delocalizations might occur with **3**. However, the foregoing breakdown suggests that **3** could hardly take place and not influence the rates. Accordingly, the rates should be relatively insensitive to change of bond dissociation energy (BDE) of the bond being broken. Plots of log k_Y/k_H vs 1000/T provided differential activation parameters utilizing Eyring equation[17] (Figure 4). The rate data were altogether tabulated in Table 1. Comparisons of Hammett correlation coefficients (Table 1) and Figures 1−3 advocate the validity of ρ^+/σ^+ correlations that are superior to other correlations (ρ/σ and $\rho^\bullet/\sigma^\bullet$). Accordingly, **1** should be a major TS determining the rates.



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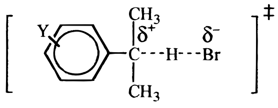

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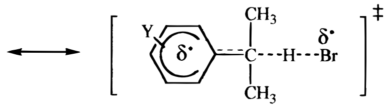

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Hydrogen abstractions[18] from substituted phenols by *tert*-butoxy radical revealed $\rho^+ = -0.90$ at 22 °C. *p*-Methoxyphenol ($k = 1.6 \times 10^9$ M^{-1} s^{-1}) reacted faster than unsubstituted phenol ($k = 3.3 \times 10^8$ M^{-1} s^{-1}). However, the former reaction exhibited higher activation energy ($E_a = 4$ kcal mol^{-1}) than the latter ($E_a = 2.8$ kcal mol^{-1}). *p*-OCH$_3$ stabilizes the cationic site, which may stimulate an increase in the extent of cleavage of phenolic O-H in **4**. An enthalpic increment due to such increase of "heterolytic" bond scission (factor ***a***) could outweigh

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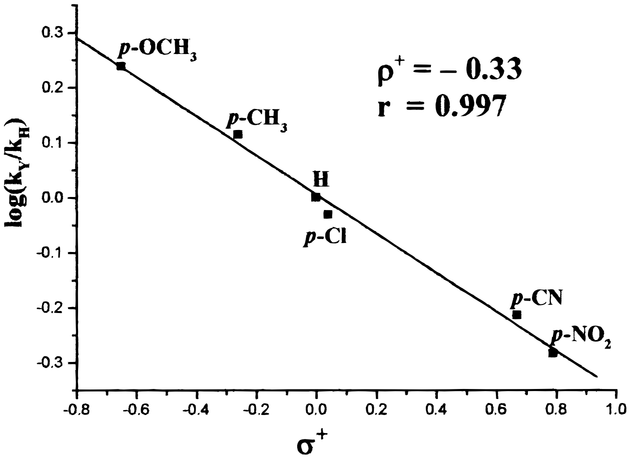


Figure 1. Hammett correlations at 80 °C with σ^{+}.

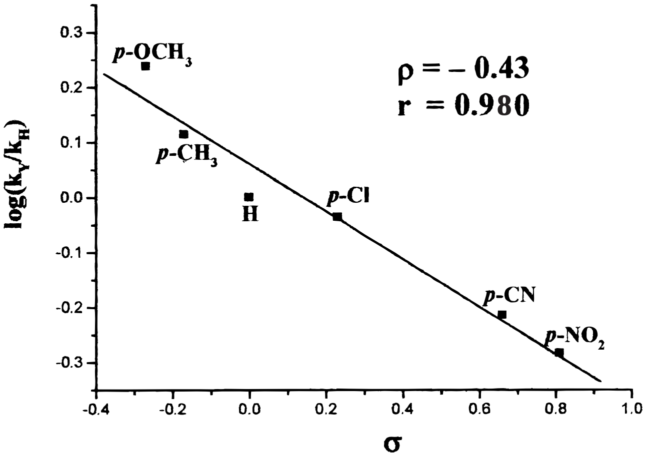


Figure 2. Hammett correlations at 80 °C with σ.

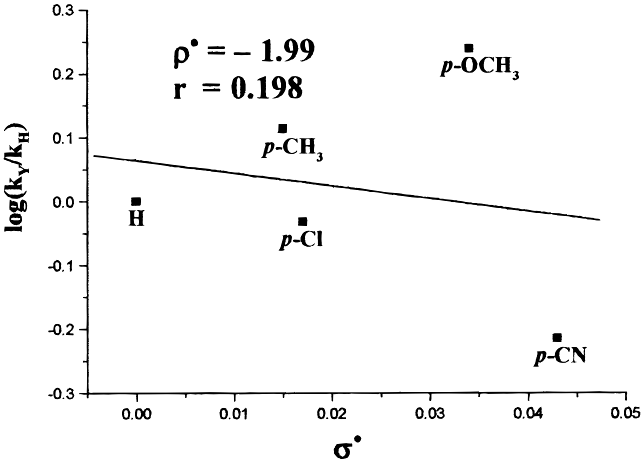


Figure 3. Hammett correlations at 80 °C with $\sigma^{\bullet}$.

its reduction caused by the stabilization of the positive charge via conjugations making a double bond (factor ***b***). A value of 4−2.8 = 1.2 kcal mol^{-1} is equivalent to the differential enthalpy of activation ($\Delta\Delta H^{\neq}_{Y-H} = \Delta H^{\neq}_{Y} - \Delta H^{\neq}_{H}$, $\Delta H^{\neq}_{Y}$ and $\Delta H^{\neq}_{H}$ are enthalpy of activation when substituents are Y and hydrogen, respectively). The positive sign of $\Delta\Delta H^{\neq}_{Y-H} = 1.2$ kcal mol^{-1} conflicts with the classical concept of a linear free energy relationship (LFER).[19] LFER[19] assumed that the TS structure should be independent of substituent effects. Accordingly, the extent of bond cleavage (e.g., O−H in **4**) was to remain invariable regardless of substituents. However, a positive value of 1.2 kcal mol^{-1} can be justified only when *p*-OCH$_3$ promotes the bond cleavage so that ***a*** may outweigh ***b***. ***a*** tends to increase $\Delta H^{\neq}_{Y}$ while ***b*** acts to reduce it, thereby counteracting with each other to determine $\Delta H^{\neq}_{Y}$ (e.g., *p*-OCH$_3$: $\Delta H^{\neq}_{Y} = 3.42$ kcal mol^{-1}, *p*-H: $\Delta H^{\neq}_{H} = 2.22$ kcal mol^{-1}).[20] Photobrominations of substituted toluenes[6c] also bear similar polar TS resembling **4**. Therefore, the electron-donating substituents again yielded $\Delta\Delta H^{\neq}_{Y-H} > 0$ (e.g., 0.73 kcal mol^{-1} for *p*-methoxytoluene: refer to Table II of ref 6c for $\Delta\Delta H^{\neq}_{Y-H} > 0$ with other electron-donating substituents).

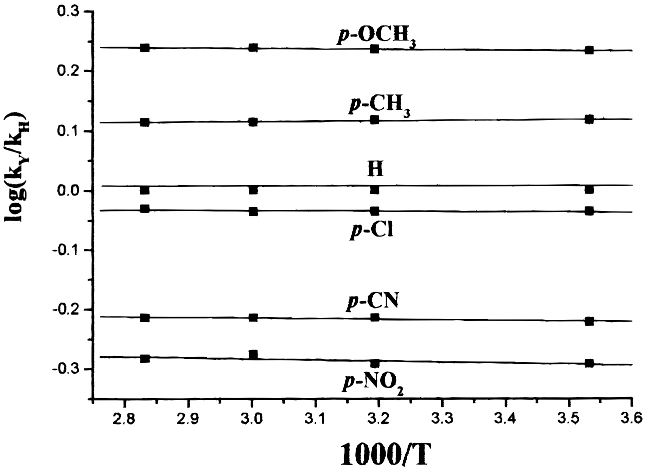
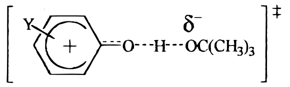


Figure 4. Eyring plot for activation parameters.



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1 and **4** share structural resemblance that should promise similar substituent effects on the bond scission. However, magnitude of the activation parameter ($\Delta H^{\neq}_{Y}$) could be varied by dissimilar molecular structures between cumene and phenol. The approach of Br• to cumylic hydrogen could be retarded by steric crowding of two methyl groups in **1**. The steric hindrance may cause equivalently less extent of C−H cleavage of **1**. Furthermore, cumylic C−H (BDE = 84.4 kcal mol^{-1})[21] is weaker than phenolic O−H (BDE = 88.3 kcal mol^{-1}).[22] The lesser extent of bond breakage and weaker BDE may cooperate to further alleviate substituent effects on disturbance of $\Delta H^{\neq}_{Y}$. Accordingly, values of $\Delta\Delta H^{\neq}_{Y-H}$ became trivial showing almost invariable fluctuations of $\Delta\Delta H^{\neq}_{Y-H}$ against σ^{+} (Figure 5). Similar values of $\Delta\Delta H^{\neq}_{Y-H}$ close to zero were also observed with fragmentation reactions of benzyl methyl substituted benzyl carbinyloxy radicals.[7a]

The enthalpic disadvantage triggered by *p*-OCH$_3$ with **4** ($\Delta\Delta H^{\neq}_{Y-H} = 1.2$ kcal mol^{-1}) has been overcome by a much larger differential entropy term ($\Delta\Delta S^{\neq}_{Y-H} = 6.62$ cal K^{-1} mol^{-1}) to achieve the rate enhancement ($k = 1.6 \times 10^{9}$ M^{-1} s^{-1} for *p*-OCH$_3$; $k = 3.3 \times 10^{8}$ M^{-1} s^{-1} for *p*-H). The differential entropy is expressed as $\Delta\Delta S^{\neq}_{Y-H} = \Delta S^{\neq}_{Y}$

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Table 1. Rate Data of Photobrominations of Substituted Cumenes by NBS in CCl_4

	$(k_Y/k_H)^a$								
T (°C)	p-OMe	p-Me	H	p-Cl	p-CN	p-NO_2	$\rho^{+\,b}$ (r)	ρ^{b} (r)	$\rho^{\bullet\,c}$ (r)
10	1.71^d	1.31	1	0.92	0.60	0.51	−0.33 (0.998)	−0.43 (0.981)	−2.17(0.215)
40	1.72	1.31	1	0.92	0.61	0.51	−0.33 (0.996)	−0.43 (0.982)	−2.01(0.201)
60	1.73	1.30	1	$(0.92)^f$	$(0.61)^f$	0.53	−0.33 (0.998)	−0.42 (0.980)	−1.97(0.196)
80	1.73^e	1.30	1	0.93^g	0.61^g	0.52	−0.33 (0.997)	−0.43 (0.980)	−1.99(0.198)

	p-OMe	p-Me	H	p-Cl	p-CN	p-NO_2
$\Delta\Delta H^{\neq}_{\mathrm{Y-H}}{}^h$	0.04 ± 0.01	−0.03 ± 0.01	0	0.02 ± 0.02	0.05 ± 0.02	0.08 ± 0.06
$\Delta\Delta S^{\neq}_{\mathrm{Y-H}}\ i$	1.19 ± 0.02	0.45 ± 0.03	0	−0.084 ± 0.06	−0.84 ± 0.06	−1.05 ± 0.20

[a] Error limits were far less than 2% being average deviations of three runs unless otherwise stated. Each sample has been always subject to GLC analysis three times. [b] Hammett substituent constants (σ^+ and σ) were taken from March, J. In *Advanced Organic Chemistry*; Wiley: New York, 1992. [c] $\sigma^\bullet$ was taken from ref 11. [d] An average value of five runs. [e] An average value of nine runs. [f] The values were taken from those at 40 °C. [g] The relative rate ($k_{p\text{-Cl}}/k_{p\text{-CN}}$) at 80 °C has been obtained as $k_{p\text{-Cl}}/k_{p\text{-CN}} = 1.55$ from competition reactions of p-chlorocumene and p-cyanocumene with NBS. A similar value of $(k_{p\text{-Cl}}/k_H)/(k_{p\text{-CN}}/k_H) = 1.52$ was observed to indicate validity of the competition method. [h] Unit: *kcal* mol^{-1}. [i] Unit: *cal* K^{-1} mol^{-1}.

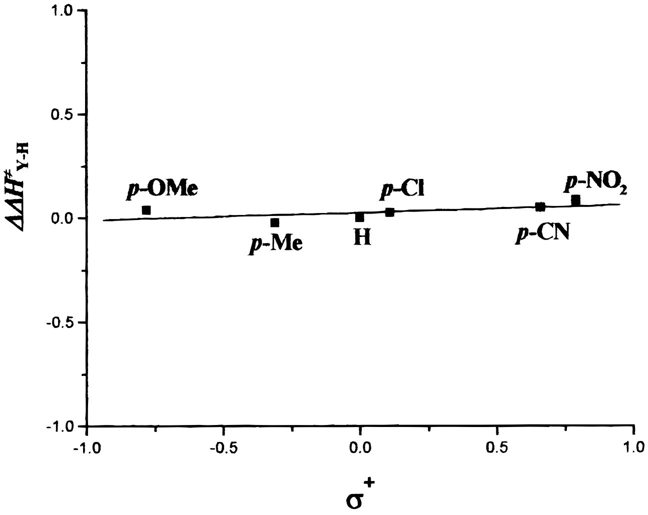

Figure 5. Plot of $\Delta\Delta H^{\ddagger}_{\mathrm{Y-H}}$ vs σ^+.

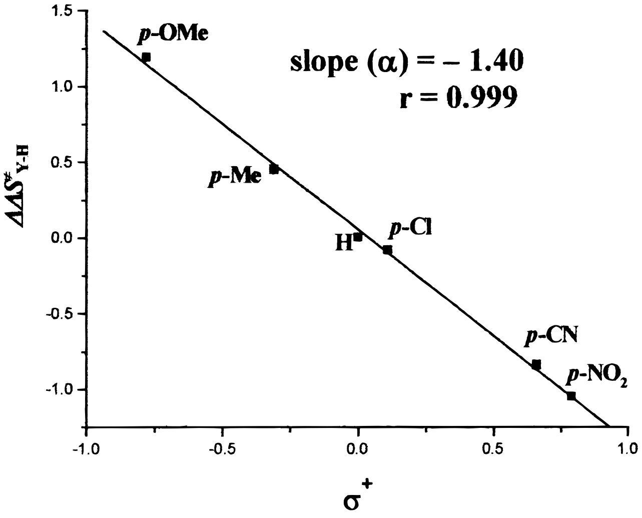

Figure 6. Plot of $\Delta\Delta S^{\ddagger}_{\mathrm{Y-H}}$ vs σ^+.

$- \Delta S^{\neq}_{\mathrm{H}}$, where entropy terms with subscripts are defined similarly as with their enthalpic partners. Entropy of activation with **4** was calculated by us from previous data[18] as $\Delta S^{\neq}_{\mathrm{Y}} = -5.10$ cal K^{-1} mol^{-1} for p-OCH_3 and $\Delta S^{\neq}_{\mathrm{H}} = -11.72$ cal K^{-1} mol^{-1} for p-H. The positive sign of the differential entropy term ($\Delta\Delta S^{\neq}_{\mathrm{Y-H}} = -5.10 + 11.72 = 6.62$ cal K^{-1} mol^{-1}) tells again that p-OCH_3 engenders more bond cleavage than does p-H. The bond scission yields *translational entropy*.[23] $\Delta\Delta S^{\neq}_{\mathrm{Y-H}} = 6.62$ cal K^{-1} mol^{-1} is equivalent to neat increment of *translational entropy* derived from further bond cleavage invoked by p-OCH_3. Therefore, both differential activation parameters ($\Delta\Delta H^{\neq}_{\mathrm{Y-H}} = 1.2$ kcal mol^{-1}, $\Delta\Delta S^{\neq}_{\mathrm{Y-H}} = 6.62$ cal K^{-1} mol^{-1}) argue for p-OCH_3 to increase degree of breakage of O−H in **4**. Our previous radical reactions[6c,7] also involved a similar polar TS showing $\rho^+ < 0$ and indicated entropy control of rates. Plots[24] of $\Delta\Delta S^{\neq}_{\mathrm{Y-H}}$ vs σ^+ gave good linear lines with negative slopes. The negative entities repeatedly suggest that electron-donating substituents (e.g., p-OCH_3) promote bond breakings to loosen TS structures. Quite similar loosening of TS has been also detected by secondary α-deuterium kinetic isotope effects occurring in thermolysis of *tert*-butyl phenylperacetates.[7e]

The same logics for the substituent effects can be applied to **1** in order to explain values of $\Delta\Delta S^{\neq}_{\mathrm{Y-H}}$. The entropic perturbations have been equated as $\Delta\Delta S^{\neq}_{\mathrm{Y-H}} = \alpha\sigma^+ + c$ (Figure 6). The negative slope ($\alpha = -1.40$) in Figure 6 indicates that TS could become loosened by electron-donating substituents (e.g., p-OCH_3). α may represent intensity of substituent effects controlling degree of bond cleavage. Accordingly α and ρ^+ are relevant entities measuring looseness of TS structure. Present reactions (eq 1) reveal $\rho^+ = -0.33$ at 80 °C and $\alpha = -1.40$. Brominations of substituted toluenes (YC_6H_4-CH_2−H + Br• → $YC_6H_4CH_2$• + HBr)[6c] gave much larger values ($\rho^+ = -1.40$ at 80 °C and $\alpha = -10.8$) because of the less steric hindrance allowing bromine atom to easily gain access to benzylic hydrogen for greater bond-breaking. Values of $\Delta\Delta G^{\neq}_{\mathrm{Y-H}}$ at 80 °C were calculated as −0.38 and 0.45 kcal mol^{-1} for p-OMe and p-NO_2, respectively. The rates are therefore delicately controlled through the entropic term derived from bond cleavage creating *translational motions*.[23] When $Q = \ln k_Y/k_H$ and $\ln k_Y/k_H = -(\Delta G^{\neq}_{\mathrm{Y}} - \Delta G^{\neq}_{\mathrm{H}})/RT = -\Delta\Delta G^{\neq}_{\mathrm{Y-H}}/RT$, $Q = -\Delta\Delta G^{\neq}_{\mathrm{Y-H}}/RT$ can be divided into entropy and enthalpy terms. Since $\Delta\Delta H^{\neq}_{\mathrm{Y-H}}/RT$ is close to zero, eq 6 becomes $Q = \Delta\Delta S^{\neq}_{\mathrm{Y-H}}/R$, which is devoid of temperature term and

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(23) Absolute rate theory (ref 17) postulates that a vibration of the bond being broken is replaced by a *translational mode*. One of the reviewers has kindly pointed out that the *translation* should be better termed loose vibration/internal rotation. Therefore, the *translation* is spelled as italics to deliver such notions. S.S.K. is very grateful to the reviewer for the very instructive comments.

(24) See the Supporting Information.

explains why the relative rates (k_Y/k_H) are independent of temperature.

$$Q = \Delta\Delta S^{\neq}{}_{Y-H}/R - \Delta\Delta H^{\neq}{}_{Y-H}/RT \qquad (6)$$

Conclusion

Substituents control extent of the bond cleavage, which is followed by formation of partial double bond. Bond scission creates *translational entropy* while double bond formation reduces rotational entropy. Creation of *translational entropy* outweighs loss of rotational one to determine entropy of activation. The substituent effects perturb free energy of activation in the range of less than 1 kcal mol^{-1}. The entropy term is 1000 times more sensitive than its enthalpic partner to detect such delicate changes of bond scission caused by substituents.

Experimental Section

Materials and Methods. Substituted cumenes (Y: *p*-Me, *p*-H, *p*-NO$_2$) and other organic materials were purchased from the major suppliers. Liquids were distilled with center-cut collection. NBS was rapidly recrystallized from boiling water and dried in a dark vacuum oven for 3 days at ambient temperature (purity 99.8% by iodometric titration). A Varian 3300 gas chromatograph and Varian Gemini 2000 NMR spectrometer were employed.

***p*-Methoxy-, *p*-cyano-, and *p*-chlorocumenes** were prepared by the known methods:[25,26] ^{1}H NMR (CDCl$_3$, 200 MHz) *p*-OMe, δ 1.2 (d, 6H, CH$_3$), 2.9 (m, 1H, CH), 3.83 (s, 3H, OCH$_3$), 6.9 (d, 2H, C$_6$H$_4$), 7.2 (d, 2H, C$_6$H$_4$); *p*-CN, δ 1.2 (d, 6H, CH$_3$), 2.9 (m, 1H, CH), 7.3 (d, 2H, C$_6$H$_4$), 7.6 (d, 2H, C$_6$H$_4$); *p*-Cl, δ 1.2 (d, 6H, CH$_3$), 2.9 (m, 1H, CH), 7.1 (d, 2H, C$_6$H$_4$), 7.3 (d, 2H, C$_6$H$_4$).

Kinetic Studies. Substituted cumene (1−4 mmol), cumene (1−4 mmol), and nitrobenzene (1 mmol) were dissolved in CCl$_4$ to give a total volume of 3 mL. This mixture and NBS (3 mmol) were placed into sealed, degassed Pyrex ampules by a freeze−pump−thaw method. The ampules were then immersed in a constant-temperature bath and irradiated with a 250 W incandescent lamp. The reaction conditions (e.g., substrate concentrations, light intensity, and reaction time) were arranged so that consumption of the substrates may stay within range of 10−20%. After reactions, the tubes were quenched by cooling in the dark, opened, and worked up by filtering the liquid from the residual insolubles. The solutions were then stored in small vials wrapped with foil until GLC analysis. The photolyzed solutions were analyzed on 30 m DB-1 capillary column with FID and temperature programming from 80 to 190 °C.

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Supporting Information Available: Plot of $\Delta\Delta S^{\ddagger}{}_{Y-H}$ vs σ^+ for various radical reactions involving polar TS. This material is available free of charge via the Internet at http://pubs.acs.org.

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