Bimolecular Nucleophilic Substitution (S_N2) Reactions of Neopentyl Arenesulfonates with Anilines and Benzylamines in Methanol

Han Joong Koh, Hai Whang Lee and Ikchoon Lee *
Department of Chemistry, Inha University, Inchon 402-751, Korea

Bimolecular nucleophilic substitution (S_N2) reactions of neopentyl arenesulfonates with anilines and benzylamines in methanol at 55.0 °C are reported. The tightness of the transition state (TS) is similar to that for other typical S_N2 processes at a primary alkyl carbon centre based on the magnitude of the cross-interaction constant ρ_{xz} (0.30) between the substituents in the nucleophile (X) and leaving group (Z). The TS variation is in accord with that predicted by the potential energy surface diagram, which in turn is consistent with the positive sign of ρ_{xz}; a later TS is obtained with a weaker nucleophile and nucleofuge. Taft's polar substituent constant, σ^*, for the trimethylsilyl group is estimated to be −0.48 by using a factor of 1.875 for the fall-off of σ^* from the *tert*-butyl to the neopentyl group and extrapolating from the experimental Taft plot.

The relative effect of α-substitution at carbon by a trimethylsilyl (Y = Me_3Si, **1a**) *versus tert*-butyl group (Y = Bu^t, **1b**) on S_N2 reactivities has been the subject of considerable interest recently.[1] The rate enhancement of the α-trimethylsilyl group, **1a**, relative to its carbon analogue, **1b**, is especially strong when the leaving group, LZ, is a strong acceptor such as LZ = *p*-nitrobenzoate or sulfonate in contrast to a small or insignificant effect with LZ = Br^- or I^-.[1c] This has been attributed to a destabilizing effect of the reactant (or ground state) arising from geminal interactions between Y and LZ, the size of the geminal interactions being dependent on the identity of the LZ.[1c,2]

$YCH_2{\cdot}LZ$
1a Y = $(CH_3)_3Si$
1b Y = Bu^t

In previous work,[2] we have shown that the aminolyses of trimethylsilylmethyl arenesulfonates, **1a** with LZ = $OSO_2C_6H_4Z$, in acetonitrile proceed by a clean associative S_N2 process with a relatively tight transition state (TS); the TS tightness in terms of the magnitude of ρ_{XZ}, eqn. (1),[3] was in fact found to be similar to that for other S_N2 processes at a carbon centre of alkyl chains,† *e.g.* Y = H, Me, CH_2CH, CH_2CHMe or Me_3Si; where X and Z denote substituents in the nucleophile and leaving group, respectively.

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \qquad (1)$$

In order to demonstrate experimentally the TS tightness and to estimate Taft's polar substituent constant,[4] σ^*, for $SiMe_3$ from the enhanced S_N2 reactivity of **1a** relative to **1b**, we have carried out the kinetic studies of the aminolysis of **1b** with LZ = $OSO_2C_6H_4Z$ under similar reaction conditions, Scheme 1. Strikingly we found that the reactions of **1b** proceeded with a TS structure which is quite similar to that for **1a** but the rates were much slower than those of **1a**.

$$2XRNH_2 + Bu^tCH_2OSO_2C_6H_4Z \xrightarrow[55.0\,^\circ C]{MeOH} Bu^tCH_2{\cdot}NHRX + XRNH_3^+ + {}^-OSO_2C_6H_4Z$$

R = C_6H_4 or $C_6H_4CH_2$
X = *p*-MeO, *p*-Me, H, *p*-Cl or *m*-Cl
Z = *p*-Me, H, *p*-Cl or *p*-NO_2

Scheme 1

Results and Discussion

The rate measurements for the reactions of neopentyl arenesulfonates with anilines were attempted in acetonitrile, but the rates were found to be too slow for our conductivity apparatus. For sulfonates, *ab initio* calculations predict‡ the rate ratio of *ca.* 4 × 10^3 (in the gas-phase) for $k(H_3SiCH_2LZ)/k(EtLZ)$ at 65.0 °C based on the relative strength of geminal interactions. Assuming the same ratio for k_{1a}/k_{1b}, the rate for **1b** with aniline (in aprotic solvent, acetonitrile)§ at 65.0 °C is *ca.* $k_2 \cong 4 \times 10^{-8}$ $dm^3\ mol^{-1}\ s^{-1}$ for X = Z = H, which is indeed too slow for convenient measurement with conventional conductivity apparatus. Therefore we changed the solvent to MeOH in which the rate for X = Z = H at 65.0 °C was obtained as $k_2 = 6.12 \times 10^{-6}$ $dm^3\ mol^{-1}\ s^{-1}$, *ca.* 10^2-fold faster than in MeCN. The rate ratio k_{1a}/k_{1b} of methanolysis at 65.0 °C was ~ 10^3, in good agreement with that predicted by MO theory. In this work, we used methanol as the solvent in the rate measurements for aminolyses of **1b**. The results of k_2 values determined are summarized in Table 1. Methanolysis rate constants, k_1, included in Table 1 are those determined independently. However, the intercepts in the plots of k_{obsd} *vs.* $[XRNH_2]$ agreed well within experimental error with the k_1 values for each neopentyl (Z)-arenesulfonate as shown in Fig. 1. This indicates that the methanolysis proceeds in parallel, but does not interfere, with the aminolysis. Moreover there is no, or insignificant, other reaction, *e.g.* S_N1 process, involved.¶ The rates are faster with a stronger nucleophile and also with a stronger nucleofuge (or LZ), which are consistent with the trends of rate changes expected for a typical S_N2 process.[5] Comparison of the two corresponding k_2 values for aniline (AN) and benzylamine (BA) reveals that the rate ratio, k_{BA}/k_{AN}, increases as the nucleophiles become weaker; the ratios increase from *ca.* 10 for X = *p*-MeO to *ca.* 30 for X = *p*-Cl. In contrast, however, the ratio varies little from one leaving group to

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† We are differentiating the primary alkyl substrates from the primary benzyl substrates.

‡ The geminal interactions in H_3SiCH_2LZ relative to EtLZ for LZ = OSO_2H are more exothermic by 5.6 kcal mol^{-1},[1c] which leads to a rate ratio, $[k(H_3SiCH_2LZ)/k(EtLZ)]$ of 4 × 10^3 at 65.0 °C.

§ The difference in the geminal interactions is based on *ab initio* MO calculations,[1c] and hence the relative reactivity refers to the gas-phase. However, since acetonitrile is an aprotic solvent, comparison of relative reactivity may not be totally unjustified.

¶ If there is a parallel S_N1 pathway, the intercepts should represent both the S_N1 and methanolysis rates, and will not coincide with the methanolysis rate constants.

Table 1 Second-order rate constants, $k_2/10^{-6}$ dm^3 mol^{-1} s^{-1}, for reactions of Z-substituted neopentyl arenesulfonates with X-substituted anilines and benzylamines in MeOH at 55.0 °C

		Z			
Nucleophile	X	*p*-Me	H	*p*-Cl	*p*-NO_2
	(MeOH)[a]	(0.121)	(0.309)	(1.15)	(29.4)
Aniline	*p*-MeO	11.9	18.1	34.9	128
	p-Me	7.43	11.3	22.7	93.5
	H	3.71	6.12	12.5	56.8
	p-Cl	1.56	2.62	5.19	22.8
	m-Cl	0.795	1.45	3.31	15.1
Benzylamine	*p*-MeO	115	184	335	1459
	p-Me	96.6	150	294	1265
	H	75.7	122	231	1016
	p-Cl	53.0	86.0	169	759

[a] Methanolysis rate constants, $k_1/10^{-7}$ s^{-1}, are given in parentheses at 55.0 °C.

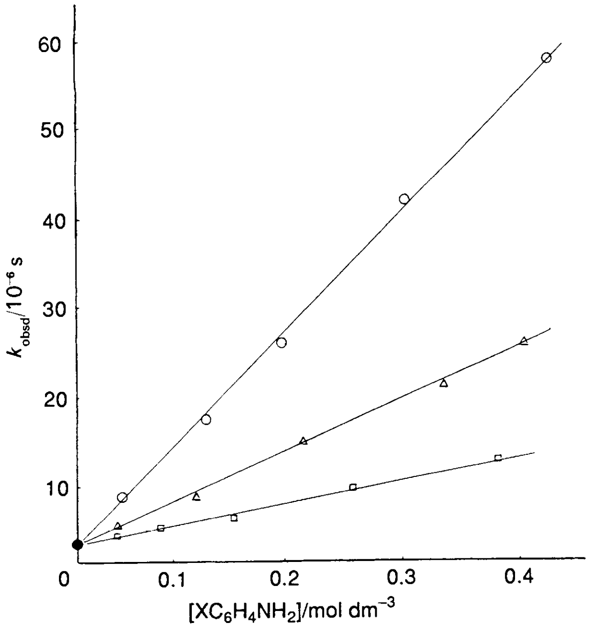

Fig. 1 Plots of pseudo-first order rate constants (k_{obsd}) *vs.* nucleophile concentration for reactions of neopentyl *p*-nitroarenesulfonate with X-anilines in methanol at 55.0 °C: (○), X = *p*-MeO; (△), X = H; (□), X = *p*-Cl; (●), pure MeOH

another. This rate ratio change is in line with an associative type of S_N2 process, since bond making by the nucleophile is more advanced and hence is more important than bond cleavage of the leaving group in such processes.[6] In an associative S_N2 process, the TS is rather tight and the ρ_{XZ} value in eqn. (1), which can be given alternatively as eqn. (2),[3] is positive.[3] When ρ_{XZ} is positive, the TS variation conforms to the predictions

$$\rho_{XZ} = \frac{\partial \rho_Z}{\partial \sigma_X} = \frac{\partial \rho_X}{\partial \sigma_Z} \qquad (2)$$

by the More O'Ferrall and Jencks[7] or potential energy surface (PES)[8] diagram. The predictions by the PES diagram [and also eqn. (2)] invariably leads to a later TS with a greater degree of bond-making and -breaking for a weaker nucleophile and nucleofuge, *i.e.* $\rho_{XZ} > 0$ when $\delta\sigma_X > 0$ and $\delta\rho_Z > 0$ and/or when $\delta\sigma_Z < 0$ and $\delta\rho_X < 0$.

This is supported by the trends of variations of $\rho_X(\rho_{nuc})$ and $\rho_Z(\rho_{lg})$ in Table 2 and kinetic isotope effects (k_H/k_D) involving deuteriated aniline nucleophiles ($XC_6H_4ND_2$) in Table 3 with changes in substituents Z and X. Examination of Table 2 reveals that the magnitude of ρ_X (and β_X) and ρ_Z (and β_Z) increases with a weaker nucleophile (X = *m*-Cl) and nucleofuge (Z = *p*-Me) for both aniline and benzylamine nucleophiles; since within a series of reaction, the magnitude of ρ_X and ρ_Z can be a measure of the degree of bond-making and -breaking,[9] the trends of changes in $|\rho_X|$ and ρ_Z above are in accord with a later TS for a weaker nucleophile and nucleofuge. We note that the $|\rho_X|$ values for benzylamine are less than half of the corresponding values for aniline. This is due to an intervening CH_2 group between the substituent, X, and the reaction centre, N, in benzylamine.[3] Since one such group is known to reduce the ρ values by *ca.* 2.8-fold,[4,10] the magnitude of ρ_X for benzylamine becomes similar to that for aniline when corrected for the fall-off factor. Otherwise the magnitudes of $\rho_X(\beta_X)$ and $\rho_Z(\beta_Z)$ are similar for the corresponding values of aniline and benzylamine. Since no such fall-off factor is involved in β_X, β_Z and β_{XZ},[3] these values are listed together with the corresponding ρ values for comparison.

Reference to Table 3 indicates that the secondary α-deuterium kinetic isotope effects (k_H/k_D) involving deuteriated aniline nucleophiles are inverse type, *i.e.*, $k_H/k_D < 1.0$, reflecting an increase in steric crowding, and hence a vibrational frequency (N–H stretching as well as bending) increase,[11] in the TS as the aniline–substrate bond is formed. The k_H/k_D values are indeed smaller with a weaker nucleophile (X = *m*-Cl) and nucleofuge (Z = *p*-Me) in agreement with a later TS, *i.e.*, a greater degree of bond formation resulting in a greater degree of steric crowding.

The kinetic solvent isotope effects (KSIE), k_{SOH}/k_{SOD}, observed with deuteriated methanol are presented in Table 4. The k_{SOH}/k_{SOD} values are all greater than unity, and decrease with a weaker nucleofuge (Z = *p*-Me). It has been shown that KSIEs for S_N2 processes are greater than unity due to general base catalysis[12] by a second solvent molecule, MeOH, in which the solvent nucleophile becomes partially deprotonated. This effect becomes stronger as the degree of bond cleavage is smaller *i.e.*, with Z = *p*-NO_2, as predicted by the PES diagram; this means that a closer approach by a more deprotonated solvent nucleophile ($^-$OMe) with a greater KSIE value is required when the degree of bond cleavage of the leaving group is small in the S_N2 TS. Thus the order of increasing KSIE value from Z = *p*-Me to *p*-NO_2 reflects the order of decreasing degree of bond cleavage in the TS predicted by the PES diagram.

Finally the ρ_{XZ} values determined by subjecting the k_2 values in Table 1 to multiple regression analyses using eqn. (1)[3] are given in Table 5 together with those for other similar reactions. We note that the solvent effect (MeOH *vs.* MeCN) is

Table 2 Hammett (ρ_X and ρ_Z) and Bronsted (β_X and β_Z) coefficients for reactions of Z-substituted neopentyl arenesulfonates with X-substituted anilines and benzylamines

Nucleophile	Z	ρ_X[a]	β_X[b]	X	ρ_Z[a]	β_Z[b]
Aniline	*p*-Me	−1.80	0.63	*p*-MeO	1.09	−0.30
	H	−1.68	0.59	*p*-Me	1.17	−0.32
	p-Cl	−1.59	0.56	H	1.24	−0.34
	p-NO_2	−1.48	0.52	*p*-Cl	1.23	−0.33
				m-Cl	1.34	−0.36
Benzylamine	*p*-Me	−0.67	0.65	*p*-MeO	1.14	−0.31
	H	−0.61	0.61	*p*-Me	1.18	−0.32
	p-Cl	−0.61	0.60	H	1.19	−0.32
	p-NO_2	−0.56	0.55	*p*-Cl	1.22	−0.33

[a] The σ values were taken from ref. 24. The correlation coefficients were better than 0.994 in all cases. [b] The pK_a values were taken from: J. A. Dean, *Handbook of Organic Chemistry*, McGraw-Hill, New York, 1987, table 8 for anilines; and from R. V. Hoffman and J. M. Shankweiler, *J. Am. Chem. Soc.*, 1986, **108**, 5536 for arenesulfonates involving methyl transfers. X = *p*-MeO is excluded from the Brönsted plot for β_X (benzylamine) due to an unreliable pK_a value listed. The correlation coefficients were better than 0.993 in all cases.

Table 3 The kinetic isotope effects (k_H/k_D) for the reaction of Z-neopentyl arenesulfonates with deuteriated X-anilines ($XC_6H_4ND_2$) in MeOD at 55.0 °C

X	Z	MeOH/dm^3 mol^{-1} s^{-1}	MeOD/dm^3 mol^{-1} s^{-1}	k_H/k_D
p-MeO	*p*-NO_2	(128 ± 1)[a] $\times 10^{-6}$	$(130 \pm 0.6) \times 10^{-6}$	$0.98_5 \pm 0.00_8$[b]
p-MeO	*p*-CH_3	$(11.9 \pm 0.1) \times 10^{-6}$	$(12.4 \pm 0.2) \times 10^{-6}$	$0.96_0 \pm 0.00_9$
m-Cl	*p*-NO_2	$(15.1 \pm 0.1) \times 10^{-6}$	$(15.6 \pm 0.2) \times 10^{-6}$	$0.96_8 \pm 0.00_7$
m-Cl	*p*-Me	$(0.795 \pm 0.007) \times 10^{-6}$	$(0.835 \pm 0.005) \times 10^{-6}$	$0.95_2 \pm 0.00_8$

[a] Standard deviation. [b] Standard error.[28]

Table 4 The kinetic solvent isotope effects for the solvolyses of neopentyl arenesulfonates in MeOH and MeOD at 55.0 °C

Z	MeOH/s^{-1}	MeOD/s^{-1}	k_{SOH}/k_{SOD}
p-CH_3	(0.121 ± 0.001)[a] $\times 10^{-7}$	$(0.101 \pm 0.001) \times 10^{-7}$	1.20 ± 0.010[b]
H	$(0.309 \pm 0.002) \times 10^{-7}$	$(0.235 \pm 0.001) \times 10^{-7}$	1.31 ± 0.009
p-Cl	$(1.15 \pm 0.002) \times 10^{-7}$	$(0.732 \pm 0.001) \times 10^{-7}$	1.57 ± 0.003
p-NO_2	$(29.4 \pm 0.1) \times 10^{-7}$	$(16.1 \pm 0.2) \times 10^{-7}$	1.83 ± 0.008

[a] Standard deviation. [b] Standard error.[28]

Table 5 Cross-interaction constants, ρ_{XZ} and β_{XZ}, for some nucleophilic substitution reactions

Reaction	Solvent	*T*/°C	ρ_{XZ}	β_{XZ}
$XC_6H_4NH_2 + MeOSO_2C_6H_4Z$[13]	MeOH	65	0.30	0.18
	MeCN	65	0.32	0.20
$XC_6H_4NH_2 + EtOSO_2C_6H_4Z$[13]	MeOH	65	0.33	0.19
	MeCN	65	0.34	0.21
$XC_6H_4NH_2 + Pr^iOSO_2C_6H_4Z$[17]	MeCN	65	0.10	0.06
$XC_6H_4NH_2 + PhCH_2CHMeOSO_2C_6H_4Z$[15]	MeOH	65	0.16	0.02
$XC_6H_4NH_2 + CH_2{=}CHCH_2OSO_2C_6H_4Z$[14]	MeCN	45	0.37	0.21
$XC_6H_4NH_2 + CH_2{=}CMeCH_2OSO_2C_6H_4Z$[16]	MeCN	45	0.40	0.24
$XC_6H_4NH_2 + PhCH_2OSO_2C_6H_4Z$[9]	MeOH	30	−0.10	−0.06
$XC_6H_4NH_2 + Me_3SiCH_2OSO_2C_6H_4Z$[2]	MeOH	65	0.31	0.18
	MeCN	65	0.33	0.20
$XC_6H_4CH_2N_2 + Me_3SiCH_2OSO_2C_6H_4Z$[2]	MeCN	65	0.08	0.12
$XC_6H_4NH_2 + Bu^tCH_2OSO_2C_6H_4Z$[a]	MeOH	55	0.31	0.18
			(0.999)[b]	(0.993)
$XC_6H_4CH_2NH_2 + Bu^tCH_2OSO_2C_6H_4Z$[a]	MeOH	55	0.11	0.15
			(0.999)	(0.992)

[a] This work. [b] The values in parentheses are the correlation coefficients at 99% confidence level.

relatively small but the values are slightly greater in MeCN. As mentioned above, ρ_{XZ} is positive so that a later TS is expected,[3] and is indeed observed, by a weaker nucleophile (X = *p*-Cl) and nucleofuge (Z = *p*-Me). A quite surprising result emerges from comparison of the ρ_{XZ} values in Table 5. Reference to this Table reveals that the ρ_{XZ} values are all positive and of similar, relatively large, magnitude ($\rho_{XZ} \cong 0.30$) for S_N2 displacement at a primary alkyl carbon centre (*vs.* benzyl) *i.e.*, **1** with Y = H (methyl),[13] Me (ethyl),[13] CH_2CH (allyl),[14] CH_2CHMe (2-methylallyl),[15] SiMe (trimethylsilylmethyl)[2] and Bu^t (neopentyl). This forms a striking contrast with a smaller, *ca.* one-third, value ($\rho_{XZ} = 0.10$) observed for isopropyl arenesulfonates,[17] a secondary alkyl substrate. Since, the greater the $|\rho_{XZ}|$, the tighter is the TS,[3] the difference in the magnitude in fact correctly reflects a much tighter TS for the S_N2 reactions of the primary alkyl substrates.[3] It is well known

Table 6 The k_2 (10^4 dm^3 mol^{-1} s^{-1}) values for the reactions of $R'OSO_2Ph$ with aniline at 65.0 °C in MeCN ($R' = CH_2Y$)

R'	Y	k_2	$\sigma^*{}_Y{}^a$	Ref.
Me_3SiCH_2	Me_3Si	1.69	-0.48^b	2
Bu^tCH_2	Bu^t	0.0341	-0.30	*b*
Me_2CH	Me	0.411	0.0	17
Et	Me	0.676	0.0	13
$PhCH_2CH_2$	$PhCH_2$	0.847	0.22	*b*
Me	H	7.47	0.49	13
Pr^i	CH_2CH	100	0.56	14
$PhCH_2$	Ph	137	0.60	9

[a] Taft's polar substituent constant for Y from ref. 5. [b] This work.

that the S_N2 TS for a primary substrate is characterized by a strong nucleophile attachment with strong coupling of bond-making and -breaking (an associative S_N2)[6,18] in contrast to a much looser TS with a less strong nucleophile attachment and more advanced bond breaking (a dissociative S_N2)[6,18] for a secondary substrate.[19] The fact that **1a** and **b** have the TSs of similar tightness with those of methyl and ethyl compounds is quite unexpected; the bulky *tert*-butyl and trimethylsilyl groups should certainly have much larger steric requirement than the H and CH_3 groups, and we would have expected somewhat looser TS for **1a** and **b** to relieve the steric congestion.

The results in Table 5 lead us to conclude that the TS tightness is influenced more by the electronic rather than steric requirement. The actual structure of the TS may differ between Y = H and **1a** and **b**; for the former, the TS will have a trigonal bipyramidal (TBP) five-coordinate structure,[20] whereas for the latter, N–C_α–LZ will be bent upward avoiding the steric hindrance to the bulky Y group.[21] In this way the TS structure can be kept to a certain degree of tightness satisfying the electronic requirement but at a rather expensive cost of steric as well as entropic energy leading to much slower rates for the bulky Y groups.

Another unexpected result in Table 5 is that the ρ_{XZ} values for allyl systems (Y = CH_2CH and CH_2CHMe) are similar to those of other primary substrates if we allow for a slight decrease in the magnitude of ρ_{XZ} with a 20 °C rise in temperature to 65.0 °C. *Ab initio* MO calculations at the HF/6–31 + + G** level indicated that the reaction shown in Scheme 2(*a*) provides a good model for the reaction of Scheme 2(*b*) indicating that a vinyl group is electronically similar to a phenyl

$$H^- + H\cdot CH_2CHCH_2 \rightleftharpoons CH_2CHCH_2\cdot H + H^- \qquad (a)$$

$$H^- + H\cdot CH_2Ph \rightleftharpoons PhCH_2\cdot H + H^- \qquad (b)$$

Scheme 2

group.[22] However we note that ρ_{XZ} of *ca.* 0.30 for allyl differs significantly from that of −0.10 for benzyl in Table 5. Perhaps the similarity in the electronic effect between allyl and benzyl may be limited to identity hydride substitution reactions [Scheme 2(*a*) and (*b*)].

There exists some confusion as to the assignment of a substituent constant for trimethylsily group.[2] Recent theoretical as well as experimental studies have led to a general acceptance that the silyl group is a relatively strong inductive electron donor.[1a,23] One available source[24] of the Taft's polar substituent constants σ^* lists $\sigma^* = -0.81$ for the Me_3Si group. This represents a quite large electron donating polar effect. On the other hand, the fall-off factor of 2.8 for a CH_2 group[10] seems to fit well for various σ^* constants in alkyl compounds.[4b,10] For example one CH_2 group causes an almost regular fall-off of 2.8 in a series of σ^* values:[4b] Ph (0.60)→CH_2Ph (0.215)→$[CH_2]_2Ph$ (0.08)→$[CH_2]_3Ph$ (0.02); CH_2Cl (1.05)→$[CH_2]_2Cl$ (0.385); MeCO (1.65)→MeCOMe (0.60); CF_3CH_2 (0.92)→$CF_3[CH_2]_2$ (0.32)→$CF_3[CH_2]_3$ (0.12). However, one CH_2 addition to Bu^t seems to cause a fall-off of σ^* by 1.875; Bu^t (−0.30)→CH_2Bu^t (−0.16).[25] If we assume a fall-off factor of 2.8 the value for $SiMe_3$ will be $\sigma^* = -0.73$ using the $\sigma^* = -0.26$ for CH_2SiMe_3,[4b] while assuming the fall-off factor of 1.875 based on σ^* for $Bu^t \rightarrow Bu^tCH_2$, we get $\sigma^* = -0.49$ for $SiMe_3$. In any case the two estimates give lower σ^* values than that of $\sigma^* = -0.81$, which was taken from the only listed source.[24]

We have collected the experimental k_2 values for eight substrates with different Y groups (in **1**) in Table 6 and attempted a Taft's polar plot,[4] eqn. (3), with seven points

$$\log k_2 = \rho^*\sigma^* \qquad (3)$$

excepting Y = Me_3Si. The linearity of the plot is only fair (r = 0.957) with $\rho^* = 3.76$. Extrapolation using the theoretical rate ratio of $k(H_3SiCH_2LZ)/k(EtLZ) \cong 4 \times 10^3$ with LZ = OSO_2H and the observed k_2 value of 1.69×10^{-4} dm^3 mol^{-1} s^{-1} for Y = CH_2SiMe_3 in Table 6, we arrive at $\sigma^* \cong -0.48$ for $SiMe_3$ on the Taft plot. This seems almost a fortuitous agreement between the two estimated σ^* values ($\sigma^* = -0.49$ *vs.* −0.48), considering that quite a lot of approximations are involved in the estimates. However, the ($\sigma^* = -0.48$) value obtained seems to provide a far more reliable σ^* value for the trimethylsilyl group on the more accountable basis. The agreement also tells us that the effect of $SiMe_3$ is much more similar to that of Bu^t than any other groups, since the fall-off factor of 1.875 not 2.8 gave the more acceptable σ^* (= −0.49) value.

Experimental

Materials.—Merck analytical grade methanol was used without further purification. The nucleophiles, aniline, (Aldrich G.R.) were redistilled or recrystallized before use. Preparation of deuteriated anilines were as described previously.[6,14] The analysis (NMR spectroscopy) of the deuteriated anilines showed more than 99% deuterium content, so no corrections to kinetic isotope effects for incomplete deuterium were made. Substrates, neopentyl arenesulfonates, were prepared by reacting Aldrich G.R. neopentyl alcohol with benzenesulfonyl chlorides.[26] The substrates synthesized were confirmed by spectral and elementary analyses as follows. Neopentyl arenesulfonate; ν_{max}(neat)/cm^{-1} 1360, 1190 (SO_2), 1020 (SO) and 815 (S–O–C); δ_H($CDCl_3$) 0.9 [$C(CH_3)_3$, 9 H, s], 3.6 (CH_2, 2 H, s) and 7.3 ~ 7.7 (Ph, 5 H, m) (Found: C, 67.3; H, 8.3; O, 24.5. Calc. for $C_{11}H_{16}O_3$: C, 67.4; H, 8.2; O, 24.5%). Neopentyl *p*-methylarenesulfonate; m.p. 41–42 °C; ν_{max}(KBr)/cm^{-1} 1360, 1195 (SO_2), 1030, 1192 (SO_2), 1022 (SO) and 813 (S–O–C); δ_H($CDCl_3$) 0.8 [$C(CH_3)_3$, 9 H, s], 3.7 (CH_2, 2 H, s) and 7.2 ~ 7.8 (Ar, 4 H, m) (Found: C, 68.7; H, 8.6; O, 30.0. Calc. for $C_{12}H_{18}O_3$: C, 68.6; H, 8.6; O, 22.9%). Neopentyl *p*-chloroarenesulfonate; m.p. 62–63 °C; ν_{max}(KBr)/cm^{-1} 1362, 1192 (SO_2), 1020 (SO) and 812 (S–O–C); δ_H($CDCl_3$) 0.9 [$C(CH_3)_3$, 9 H, s], 3.7 (CH_2, 2 H, s) and 7.3 ~ 7.6 (Ar, 4 H, m) (Found: C, 67.8; H, 7.6; O, 24.7. Calc. for $C_{11}H_{15}O_3$: C, 67.7; H, 7.7; O, 24.6%). Neopentyl *p*-nitroarenesulfonate; m.p. 98–99 °C; ν_{max}(KBr)/cm^{-1} 1360, 1190 (SO_2), 1020 (SO) and 812 (S–O–C); δ_H($CDCl_3$) 0.9 [$C(CH_3)_3$, 9 H, s], 3.7 (CH_2, 2 H, s) and 7.8 ~ 8.4 (Ar, 4 H, m) (Found: C, 58.1; H, 6.6; O, 35.3. Calc. for $C_{11}H_{15}O_5$: C, 58.2; H, 6.6; O, 35.2%).

Kinetic Procedures.—Rates were measured conductimetrically at 55.0 ± 0.05 °C in methanol. The conductivity bridge used in this work was a self-made computer interface automatic A/D converter conductivity bridge. Substrates were injected with a syringe. Pseudo-first order rate constants, k_{obs}, were determined by the Guggenheim method[27] with a large excess of aniline: [neopentyl arenesulfonate] = 10^{-3} mol dm^{-3} and [aniline] = 0.05 ~ 0.50 mol dm^{-3}. Second-order rate constants, k_2, are obtained from the slope of a plot of k_{obs} *vs.* [aniline] with more than four concentrations of aniline.

Product Analysis.—Neopentyl arenesulfonate was reacted with excess aniline with stirring for more than 13 half-lives at 55.0 °C in methanol, and the products were isolated by evaporating the solvent under reduced pressure. The TLC analysis of the product mixture gave three spots (silica gel, glass plate, 10% ethyl acetate–hexane). R_f values: 0.39 [$(CH_3)_3CCH_2NHPh$], 0.22 [$(CH_3)_3CCH_2OSO_2Ph$], 0.20 ($PhNH_2$). The product mixture was treated with column chromatography (silica gel, 10% ethyl acetate–hexane). Analysis of the products, $(CH_3)_3CCH_2NHPh$ and $PhOSO_2{}^-NH_3{}^+Ph$, gave the following results. $(CH_3)_3CCH_2NHPh$: $\delta_H(CDCl_3)$ 0.9 [$C(CH_3)_3$, 9 H, s], 3.5 (CH_2, 2 H, s), 3.0 (NH, 1 H, br) and 7.3 ~ 7.7 (Ph, 5 H, m). $PhOSO_2{}^-NH_3{}^+Ph$: $\delta_H(CDCl_3)$ 4.8 ($NH_3{}^+$, 3 H, br) and 7.1 ~ 7.7 (Ph, 10 H, m).

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