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KINETICS AND MECHANISM OF THE AMINOLYSIS OF CYCLOALKYLMETHYL ARENESULFONATES

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Nucleophilic substitution reactions of cycloalkylmethyl arenesulfonates ($C_mH_{2n-1}CH_2OSO_2C_6H_4Z$) with anilines ($XC_6H_4NH_2$) in methanol at 65.0 °C were studied. The reactivity order ($n=4>6>7>5$) reflects largely the order of steric effect of the ring size (*SEs* term) except for $n=5$, which exhibits the least reactivity. This reversal of the order for $n=5$ is considered to result from large rate retardation due to polar effect of the $\rho^*\sigma^*$ term. Application of the Taft equation to the rate data for $n=5$ and 6 gives $\rho^*=17{\cdot}4$ and $S=2{\cdot}3$ with correlation coefficient of 0·90. The σ^* values for $n=4$ and 7 are estimated to be $-0{\cdot}23$ and $-0{\cdot}11$, respectively. The positive ρ_{XZ} values of *ca* 0·3 are consistent with previous results for the reactions at primary reaction centers. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

It has been shown that a Taylor series expansion of log k_{xz} for dually substituted reaction systems leads to a simple second-order expression

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

$$\rho_{XZ}=\frac{\partial^2 \log k}{\partial\sigma_X\partial\sigma_Z}=\frac{\partial\rho_Z}{\partial\sigma_X}=\frac{\partial\rho_X}{\partial\sigma_Z} \quad (1b)$$

upon neglect of pure second-order (ρ_{XX} and ρ_{ZZ}) and higher order (ρ_{XXZ}, etc.) terms.[1] The magnitude of the cross-interaction constant ρ_{XZ} between two substituents on the nuclophile (X) and leaving group (Z) in S_N2 processes is a measure of the transition-state (TS) tightness;[1, 2] the greater is $|\rho_{XZ}|$, the tighter is the TS. An interesting aspect of the TS tightness for S_N2 processes is that the TS is tight ($|\rho_{XZ}|$ is large) or loose ($|\rho_{XZ}|$ is small) depending on whether the reaction center carbon is primary ($\rho_{XZ}\approx 0{\cdot}3$),[3] secondary ($\rho_{XZ}\approx 0{\cdot}1$)[4] or tertiary ($\rho_{XZ}\approx -0{\cdot}04$),[5] but the TS tightness varies very little with regard to the group attached to the reaction center. For nucleophilic substitution reactions of cycloalkyl arenesulfonates ($C_nH_{2n-1}OSO_2C_6H_4Z$, which react at secondary carbon centers) with anilines ($NH_2C_6H_4X$) in acetonitrile at 65·0 °C, the ρ_{XZ} values were uniformly 0·11 for all the compounds investigated ($n=4$–7) irrespective of the ring size;[6] the magnitude (0·11) is *ca* one third of the ρ_{XZ} values observed for primary carbon centers ($\rho_{XZ}\approx 0{\cdot}3$).[3, 4]

In this work, we carried out similar kinetic studies of the aminolysis of cycloalkyl compounds with primary carbon reaction centers, cycloalkylmethyl arenesulfonates

$$2XC_6H_4NH_2+C_nH_{2n-1}CH_2OSO_2C_6H_4Z \xrightarrow[65{\cdot}0\ ^\circ C]{MeOH}$$

$$C_nH_{2n-1}CH_2NHC_6H_4X+XC_6H_4NH_3^+ + {}^-OSO_2C_6H_4Z \quad (2)$$

$n=4$–7; X = *p*-OMe, *p*-Me, H or *p*-Cl; Z = *p*-Me, H, *p*-Cl or *p*-NO_2

in order to examine the effects of the ring size on the rate and on the TS tightness (or the magnitude of ρ_{XZ}) in the nucleophilic displacement reactions at primary carbon centers.

RESULTS AND DISCUSSION

The reactions of cycloalkylmethyl arenesulfonates with anilines in methanol at 65·0 °C obey clean second-order kinetics:

$$k_{obs}=k_s+k_2\,[\text{aniline}] \quad (3)$$

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where k_s is the methanolysis rate constant. The solvolysis rates, k_s, are much slower (Table 1) than the corresponding aminolysis rates, k_2, summarized in Table 2. As expected from a typical S_N2 process, the rate is faster with a stronger nucleophile ($\delta\sigma_X<0$) and nucleofuge ($\delta\sigma_Z>0$). In contrast to the cycloalkyl derivatives for which the rate for $n=5$ ($C_5H_9OSO_2C_6H_4Z$) was the fastest,[6] the reactivity for both k_s and k_2 increases for n in the order $5<7<6<4$, with the lowest reactivity for $n=5$ ($C_5H_9CH_2OSO_2C_6H_4Z$). Obviously, the effects of ring size on the rate are expected to be twofold: steric (*Es*) and polar (σ^*). The two substituent constants, *Es* and σ^*, for ring sizes of $n=4$–7 are given in Table 3.

A literature survey showed that the σ^* values for $n=4$ and 7 are lacking. Application of the Taft equation:

$$\log (k/k_0)=\rho^*\sigma^*+SEs \qquad (4)$$

to the rate data (the k_2 values in Table 2 for X=*p*-OMe, *p*-Me, H and *p*-Cl with Z=H) for $n=5$ and 6 gave $\rho^*=17{\cdot}4$ and $S=2{\cdot}3$ with a correlation coefficient of 0·90. The σ^* values for $n=4$ ($-0{\cdot}23$) and $n=7$ ($-0{\cdot}11$) were then estimated using these ρ^* and S values based on the rate data for $n=5$ and 6.

The signs of ρ^* and S are both positive and hence the rates are retarded by both steric ($Es<0$) and electron-donating polar ($\sigma^*<0$) effects of the cycloalkyl rings. The rate-retarding effect of the electron donating polar effect ($\sigma^*<0$) suggests that the reaction center carbon becomes more negatively charged on going from the initial to transition state. This is in line with the relatively tight TS expected for an S_N2 process at a primary carbon center. The extremely large magnitude of ρ^* (17·4), which is about eight times of that for S (2·3), shows the importance of the polar effect relative to the steric effect on the rate retardation. This is why the rate order is reversed with the least reactivity for $n=5$. For other compounds the steric effect seems to dominate the reactivity order, $n=4>6>7$.

The Hammett and Brønsted coefficients are summarized

Table 1. Methanolysis rate constant ($k_s\times10^6\ s^{-1}$) of cycloalkylmethyl arenesulfonates at 65·0 °C

	Z			
	p-Me	H	*p*-Cl	*p*-NO_2
Cyclobutyl	1·29±0·08[a]	2·75±0·05	5·96±0·07	19·3±0·13
Cyclopentyl	0·171±0·008	0·608±0·001	0·690±0·008	2·59±0·05
Cyclohexyl	0·334±0·002	0·892±0·004	1·05±0·06	3·68±0·08
Cycloheptyl	0·186±0·003	0·771±0·006	0·880±0·007	2·82±0·01

[a] Standard deviations

Table 2. Second-order rate-constants ($k_2\times10^4\ dm^{-1}\ s^{-1}$) for the reactions of cycloalkylmethyl arenesulfonates with anilines in methanol at 65·0 °C

		Z			
	X	*p*-Me	H	*p*-Cl	*p*-NO_2
Cyclobutyl	*p*-OMe	0·970±0·007[a]	1·58±0·05	2·63±0·07	9·47±0·07
	p-Me	0·601±0·004	1·13±0·03	1·82±0·04	6·54±0·05
	H	0·380±0·006	0·650±0·013	1·02±0·06	4·40±0·05
	p-Cl	0·153±0·010	0·290±0·001	0·569±0·011	2·18±0·06
Cyclopentyl	*p*-OMe	0·364±0·014	0·527±0·003	0·900±0·009	3·24±0·04
	p-Me	0·243±0·005	0·366±0·003	0·630±0·003	2·30±0·04
	H	0·142±0·001	0·213±0·008	0·419±0·002	1·51±0·05
	p1-Cl	0·0580±0·002	0·0950±0·002	0·182±0·003	0·725±0·003
Cyclohexyl	*p*-OMe	0·820±0·013	1·26±0·05	1·97±0·06	7·53±0·02
	p-Me	0·520±0·005	0·906±0·011	1·49±0·03	5·46±0·01
	H	0·326±0·012	0·546±0·002	0·811±0·002	3·54±0·03
	p-Cl	0·129±0·003	0·299±0·001	0·448±0·011	1·71±0·02
Cycloheptyl	*p*-OMe	0·612±0·004	1·03±0·05	1·78±0·05	7·34±0·05
	p-Me	0·420±0·002	0·686±0·004	1·20±0·05	5·18±0·05
	H	0·218±0·012	0·384±0·003	0·676±0·06	3·19±0·06
	p-Cl	0·0920±0·010	0·177±0·003	0·321±0·01	1·53±0·01

[a] Standard deviations.

Table 3. Taft steric (*Es*) and polar (σ^*) substituent constants for alkyl rings, C_nH_{2n-1}[a]

	n			
	4	5	6	7
Es	−0·06	−0·51	−0·79	−1·10
σ^*	−0·23[b]	−0·20	−0·15	−0·11[b]

[a] Taken from Ref. 7.
[b] Estimated values in this work.

in Table 4. The data show that the magnitude of ρ_X ($\delta|\rho_X|<0$) and ρ_Z ($\delta\rho_Z<0$) is smaller and hence the TS is earlier for a stronger nucleophile ($\delta\sigma_x<0$) and nucleofuge ($\delta\sigma_z>0$). This is in line with the positive ρ_{XZ} values observed in accordance with equation (1b)[1] (see below). There is a barely noticeable trend that the magnitude of ρ_X (β_X) and ρ_Z (β_Z) is the greatest for the most sterically hindered compound, $n=7$. This is suggestive of the latest TS along the reaction coordinate for $n=7$ among the compounds studied ($n=4$–7), which is consistent with our previous results for cycloalkyl compounds with secondary carbon centers;[6] the greater the ring size, the later was the TS. We interpreted the results as a manifestation of the Bell–Evans–Polanyi (BEP) principle,[8] which asserts that the greater the endothermicity (owing to instability of the more hindered product) of the reaction, the later is the TS and the higher is the activation barrier.

The cross-interaction constants, ρ_{XZ} (and β_{XZ}), obtained by subjecting the rate data in Table 2 to multiple regression analysis using equation (1a) [and using a similar expression based on pK_a(X) and pK_a(Z) instead of σ_X and σ_Z) are shown in Table 5. Strikingly, the magnitudes of ρ_{XZ} (*ca* 0·3) and β_{XZ} (*ca* 0·2) *are similar to those for other reactions at primary carbon centers*, $\rho_{xz}\approx0.3$ ($\beta_{XZ}\approx0.2$).[1c, 3] The present results confirm our previous conclusion that the TS is tight or loose depending on whether the reaction center carbon is

Table 4. Hammett (ρ_X and ρ_Z)[a] and Brønsted (β_X[b] and β_Z[c]) coefficients for reactions of Z-substituted cycloalkylmethyl arenesulfonates with X-substituted anilines

	Z	ρ_X	β_X	X	ρ_Z	β_Z
Cyclobutyl	*p*-Me	−1·57	0·56	*p*-OMe	1·03	−0·28
	H	−1·48	0·53	*p*-Me	1·06	−0·28
	p-Cl	−1·34	0·48	H	1·10	−0·30
	p-NO_2	−1·26	0·45	*p*-Cl	1·19	−0·32
Cyclopentyl	*p*-Me	−1·59	0·57	*p*-OMe	1·01	−0·27
	H	−1·48	0·54	*p*-Me	1·03	−0·28
	p-Cl	−1·37	0·49	H	1·09	−0·30
	p-NO_2	−1·29	0·46	*p*-Cl	1·15	−0·31
Cyclohexyl	*p*-Me	−1·58	0·57	*p*-OMe	1·01	−0·27
	H	−1·48	0·54	*p*-Me	1·05	−0·28
	p-Cl	−1·32	0·48	H	1·08	−0·29
	p-NO_2	−1·28	0·45	*p*-Cl	1·15	−0·32
Cycloheptyl	*p*-Me	−1·66	0·60	*p*-OMe	1·13	−0·30
	H	−1·53	0·55	*p*-Me	1·14	−0·31
	p-Cl	−1·49	0·54	H	1·21	−0·33
	p-NO_2	−1·36	0·49	*p*-Cl	1·26	−0·34

[a] The σ values were taken from Ref. 11. Correlation coefficients >0·998.
[b] The pK_a values were taken from Ref. 12. Correlation coefficients >0·998.
[c] The pK_a values are for methyl transfer.[13] Correlation coefficients >0·995.

Table 5. Cross-interaction constants (ρ_{XZ} and β_{XZ}) for nucleophilic substitution reactions

Reaction	Solvent	ρ_{XZ}[a]	β_{XZ}[a]
$XC_6H_4NH_2+c\text{-}C_4H_7CH_2OSO_2C_6H_4Z$	MeOH	0·30 (0·998)	0·17 (0·987)
$XC_6H_4NH_2+c\text{-}C_5H_9CH_2OSO_2C_6H_4Z$	MeOH	0·30 (0·999)	0·18 (0·993)
$XC_6H_4NH_2+c\text{-}C_6H_{11}CH_2OSO_2C_6H_4Z$	MeOH	0·29 (0·999)	0·17 (0·990)
$XC_6H_4NH_2+c\text{-}C_7H_{13}CH_2OSO_2C_6H_4Z$	MeOH	0·29 (0·999)	0·18 (0·990)

[a] Values in parentheses are correlation coefficients.

Table 6. Kinetic isotope effects observed for the reactions of *p*-nitro(Z)-substituted cycloalkylcarbinyl benzenesulfonates with *p*-methoxy(X)-substituted *N*-deuteriated aniline nucleophile in MeOD at 65·0 °C

Substrate	$k_H \times 10^4$ ($M^{-1}s^{-1}$)[a]	$k_D \times 10^4$ ($M^{-1}s^{-1}$)	k_H/k_D
Cyclobutyl	9·47±0·07	10·4±0·4	0·910±0·006[b]
Cyclopentyl	3·24±0·04	3·56±0·03	0·910±0·005
Cyclohexyl	7·53±0·02	8·37±0·03	0·900±0·006
Cycloheptyl	7·34±0·05	8·16±0·02	0·900±0·005

[a] Standard deviations.
[b] Standard errors.

primary, secondary or tertiary, but the TS tightness varies very little with regard to the group attached to the reaction center carbon.

We determined secondary kinetic isotope effects involving deuterated aniline nucleophiles as shown in Table 6. The k_H/k_D values are less than unity (*ca*. 0.9), reflecting an increase in the N–D vibrational frequency due to steric crowding in the TS.[1c] However, the effects seem to be weak compared with those for the other reactions at primary carbon centers ($k_H/k_D \approx 0.8–0.9$).[9] This could be an indication of an earlier TS with a lower degree of bond making (and also of bond cleavage) compared with those for other reactions at primary carbon centers, even though the overall tightness is similar. Such speculation is supported by the generally smaller magnitude of ρ_X (β_X) and ρ_Z (β_Z) in Table 4 compared with those for other similar reactions.[6]

EXPERIMENTAL

Materials

Analytical-grade methanol (Merck) was used without further purification. The aniline nucleophiles were Aldrich GR products and were redistilled or recrystallized before use. The preparation of deuteriated anilines was performed as described previously.[9] The analysis (NMR spectroscopy) of the deuteriated nucleophiles showed >99% deuterium content, so no corrections to kinetic isotope effects for incomplete deuteration were made. Cyclobutylmethyl benzenesulfonate was prepared by adding anhydrous methylene chloride to cyclobutylmethanol followed by ethylenediamine. Benzenesulfonyl chloride was added and reacted at 0 °C. After 2 h, the mixture was extracted with diethylether and the extract was washed with 1 N sodium thiosulfate and then dried over $MgSO_4$. After filtration and removal of the solvent under reduced pressure, the final product was obtained by column chromatography. The substrates synthesized were confirmed by spectral analyses as follows.

Cyclobutylmethyl benzenesulfonate. Liquid; δ_H ($CDCl_3$) 1·66–1·92 (6H, m, cyclic ring), 1·97–2·04 (1H, M, *t*-H), 4·10 (2H, d, —CH_2—O, *J*=6·59 Hz), 7·64 (2H, t, *m*-H, *J*=8.06 Hz), 7·66 (1H, t, *p*-H, *J*=7·32 Hz), 7·91 (2H, d, *o*-H, *J*=7.33 Hz); IR (cm^{-1}) 1448, 1511 (phenyl), 1360, 1183 (ν_{SO-O}), 834(ν_{S-O}).

Cyclobutylmethyl tosylate. Liquid; δ_H ($CDCl_3$) 1·63–1·88 (6H, m, cyclic ring), 1·94–2·02 (1H, m, *t*-H), 2·54 (3H, s, CH_3), 3·95 (2H, d, —CH_2—O, *J*=6·59 Hz), 7·32 (2H, d, *m* − H, *J*=7·33 Hz), 7·76 (2H, d, *o*-H, *J*=8·06 Hz); IR (cm^{-1}) 1447, 1583 (phenyl), 1363, 1186 (ν_{SO-O}), 1090 (ν_{Cl}), 829 (ν_{S-O}).

Cyclobutylmethyl p-chlorobenzenesulfonate. Liquid: δ_H ($CDCl_3$) 1·59–1·99 (6H, m, cyclic ring), 2·01–2·07 (1H, m, *t*-H), 4·02 (2H, d, —CH_2—O, *J*=6·60 Hz), 7·54 (2H, d, *m*-H, *J*=8·79 Hz), 7·85 (2H, d, *o*-H, *J*=8·80 Hz); IR (cm^{-1}) 1541, 1665 (phenyl), 1363, 1181 (ν_{SO-O}), 849 (ν_{S-O}).

Cyclobutylmethyl p-nitrobenzenesulfonate. Liquid; δ_H ($CDCl_3$) 1·70–1·98 (6H, m, cyclic ring), 2·01–2·09 (1H, m, *t*-H), 4·11 (2H, d, —CH_2—O, *J*=6·59 Hz), 8·11 (2H, d, *m*-H, *J*=7·33 Hz), 8·41 (2H, d, *o* − H, *J*=7·33 Hz); IR (cm^{-1}) 1541, 1665 (phenyl), 1363, 1181 (ν_{SO-O}), 849 (ν_{S-O}).

Cyclopentylmethyl benzenesulfonate. Liquid; δ_H ($CDCl_3$) 1·15–1·58 (8H, m, cyclic ring), 1·71–1·74 (1H, m, *t*-H), 3·92 (2H, d, —CH_2—O, *J*=7·33 Hz), 7·56 (2H, t, *m*-H, *J*=8·06 Hz), 7·56 (1H, t, *p*-H, *J*=7-32 Hz), 7·92 (2H, d, *o*-H, *J*=6·59 Hz); IR (cm^{-1}) 1448, 1592 (phenyl), 1361, 1184 (ν_{SO-O}), 827 (ν_{S-O}).

Cyclopentylmethyl tosylate. Liquid; δ_H ($CDCl_3$) 1·15–1·70 (8H, m, cyclic ring), 1·72–1·74 (1H, m, *t*-H), 2·45 (3H, s, CH_3), 3·90 (2H, d, —CH_2—O, *J*=7·33 Hz), 7·34 (2H, d, *m*-H, *J*=8·06 Hz), 7·80 (2H, d, *o*-H, *J*=8·79 Hz); IR (cm^{-1}) 1445, 1599 (phenyl), 1360, 1179 (ν_{SO-O}), 818 (ν_{S-O}).

Cyclopentylmethyl p-chlorobenzenesulfonate. M.p. 50–52 °C; δ_H ($CDCl_3$) 1·15–1·67 (8H, m, cyclic ring), 1·70–1·75 (1H, m, *t*-H), 3·92 (2H, d, —CH_2—O, *J*=7·33 Hz), 7·52 (2H, d, *m*-H, *J*=6·59 Hz), 7·84 (2H, d, *o*-H, *J*=8·06 Hz); IR (cm^{-1}) 1458, 1589 (phenyl), 1367, 1181 (ν_{SO-O}), 1090 (ν_{Cl}), 818 (ν_{S-O}).

Cyclopentylmethyl p-nitrobenzenesulfonate. M.p. 106–108 °C; δ_H ($CDCl_3$) 1·16–1·57 (8H, m, cyclic ring), 1·72–1·75 (1H, m, *t*-H), 4·01 (2H, d, —CH_2—O, *J*=7·33 Hz), 8·10 (2H, d, *o*-H, *J*=8·79 Hz), 8·40 (2H, d, *m*-H, *J*=8·79 Hz); IR (cm^{-1}) 1470, 1541 (phenyl), 1363, 1181 (ν_{SO-O}), 852 (ν_{S-O}).

Cyclohexylmethyl benzenesulfonate. Liquid; δ_H ($CDCl_3$) 1·09–1·24 (10H, m, cyclic ring), 1·66–1·70 (1H, m, *t* − H), 3·83 (2H, d, —CH_2—O, *J*=5·86 Hz), 7·56 (2H, t, *m*-H, *J*=8·06 Hz), 7·64 (H, t, *p*-H, *J*=7·32 Hz), 7·91 (2H, d, *o*-H, *J*=7·33 Hz); IR (cm^{-1}) 1448, 1596 (phenyl), 1360, 1182 (ν_{SO-O}), 828 (ν_{S-O}).

Cyclohexylmethyl tosylate. M.p. 33–35 °C; δ_H($CDCl_3$) 1·06–1·24 (10H, m, cyclic ring), 1·63 (1H, m, *t*-H), 2·45 (3H, s, CH_3), 3·80 (2H, d, —CH_2—O, *J*=6·59 Hz), 7·34 (2H, d, *m*-H, *J*=8·79 Hz), 7·78 (2H, d, *o*-H, *J*=8·06 Hz);

IR(cm^{-1}) 1450, 1596 (phenyl), 1395, 1179 (ν_{SO-O}), 818 (ν_{S-O}).

Cyclohexylmethyl p-chlorobenzenesulfonate. Liquid, δ_H($CDCl_3$) 1·09–1·25(10H, m, cyclic ring), 1·16–1·72(1H, m, *t*-H), 3·84 (2H, d, —CH_2—O, *J*=5·86 Hz), 7·53 (2H, d, *m*-H, *J*=8·79 Hz), 7·84(2H, d, *o*-H, *J*=8·79 Hz); IR (cm^{-1}) 1477, 1595 (phenyl), 1364, 1185 (ν_{SO-O}), 1091 (ν_{Cl}), 852 (ν_{S-O}).

Cyclohexylmethyl p-nitrobenzenesulfonate. M.p. 102–104 °C; δ_H ($CDCl_3$) 1·08–1·28 (10H, m, cyclic ring), 1·65–1·74 (1H, m, *t*-H), 3·92 (2H, d, —CH_2—O, *J*=5·87 Hz), 8·11 (2H, d, *m*-H, *J*=8·80 Hz), 8·41 (2H, d, *o* − H, *J*=8·79 Hz); IR (cm^{-1}) 1456, 1608 (phenyl), 1361, 1182 (ν_{SO-O}), 850 (ν_{S-O}).

Cycloheptylmethyl benzenesulfonate. Liquid; δ_H ($CDCl_3$) 1·10–1·69 (12H, m, cyclic ring), 1·83 (1H, m, *t*-H), 3·82 (2H, d, —CH_2—O, *J*=6·59 Hz), 7·56 (2H, t, *J*=7·32 Hz), 7·65 (H, t, *p*-H, *J*=8·06 Hz), 7·92 (2H, d, *o*-H, *J*=7·33 Hz); IR (cm^{-1}) 1441, 1633 (phenyl), 1366, 1180 (ν_{SO-O}), 811 (ν_{S-O}).

Cycloheptylmethyl tosylate. Liquid; δ_H($CDCl_3$) 1·09–1·68 (12H, m, cyclic ring), 1·81 (1H, m, *t*-H), 2·45 (3H, s, CH_3), 3·79 (2H, d, —CH_2—O, *J*=6·60 Hz), 7·34 (2H, d, *m*-H, *J*=8·06 Hz), 7·78 (2H, d, *o* − H, *J*=8·06 Hz); IR (cm^{-1}) 1459, 1652 (phenyl), 1378, 1184 (ν_{SO-O}), 816 (ν_{S-O}).

Cycloheptylmethyl *p*-chlorobenzenesulfonate. M.p. 51–53 °C; δ_H ($CDCl_3$) 1·13–1·69 (12H, m, cyclic ring), 1·83 (1H, m, *t*-H), 3·83 (2H, d, —CH_2—O, *J*=6·60 Hz), 7.54 (2H, d, *m*-H, *J*=7·89 Hz), 7.85 (2H, d, *o*-H, *J*=8·06 Hz); IR (cm^{-1}) 1461, 1650 (phenyl), 1363, 1181 (ν_{SO-O}), 1088 (ν_{Cl}), 816 (ν_{S-O}).

Cycloheptylmethyl p-nitrobenzenesulfonate. M.p. 100–102 °C; δ_H ($CDCl_3$) 1·14–1·58 (12H, m, cyclic ring), 1·66 (1H, m, *t*-H), 3·92 (2H, d, —CH_2—O, *J*=6·59 Hz), 8·11 (2H, d, *o*-H, *J*=7·33 Hz), 8·41 (2H, d, *m*-H, *J*=8·79 Hz); IR (cm^{-1}) 1456, 1608 (phenyl), 1361, 1182 (ν_{SO-O}), 850 (ν_{S-O}).

Kinetic procedure. Rates were measured conductimetrically at 65·0 °C in methanol. The k_2 values were determined [equation (3)] with at least four nucleophile (aniline) concentrations using the procedure described previously.[4–6, 10]

Product analysis

Solvolysis product. The TLC analysis of the reaction mixture showed spots corresponding to anilide, salt and unreacted substrate and nucleophile. The ether spot was confirmed by GC and was separated by chromatography. The NMR analytical data for the ethers are as follows.

Methyl cyclobutylmethyl ether. Liquid; δ_H ($CDCl_3$) 1·14–1·98 (7H, m, cyclic ring), 3·21 (2H, d, —CH_2—O, *J*=6·59 Hz), 3·34 (3H, s, OCH_3).

Methyl cyclopentylmethyl ether. Liquid; δ_H ($CDCl_3$) 1·17–1·99 (9H, m, cyclic ring), 3·20 (2H, d, —CH_2—O, *J*=7·33 Hz), 3·28 (3H, s, OCH_3).

Methyl cyclohexylmethyl ether. Liquid; δ_H ($CDCl_3$) 1·11–1·86 (11H, m, cyclic ring), 3·19 (2H, d, —CH_2—O, *J*=5·86 Hz), 3·33 (3H, s, OCH_3).

Methyl cycloheptylmethyl ether. Liquid; δ_H ($CDCl_3$) 1·10–1·78 (13H, m, cyclic ring), 3·15 (2H, d, —CH_2—O, *J*=6·60 Hz), 3·32 (3H, s, OCH_3).

Aminolysis product. Cyclobutylmethyl benzenesulfonate was reacted with excess aniline with stirring for more than 15 half-lives at 65·0 °C in methanol and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was subjected to column chromatography (silica gel, 5% ethyl acetate–*n*-hexane). Analysis of the product gave the following results.

Cyclobutylmethyl anilide. Liquid; δ_H ($CDCl_3$) 1·02–1·59 (6H, m, cyclic ring), 1·74–1·98 (1H, m, *t*-H), 3·16 (2H, d, —CH_2—N, *J*=7·32 Hz), 3·69 (1H, broad, NH), 6·63 (2H, t, *m*-H, *J*=8·86 Hz), 6·73 (1H, t, *p*-H, *J*=7·33 Hz), 7·21 (2H, d, *o*-H, *J*=8·79 Hz).

Cyclopentylmethyl anilide. Liquid; δ_H ($CDCl_3$) 1·24–1·63 (8H, m, cyclic ring), 1·80–1·81 (1H, M, *t*-H), 3·00 (2H, d, —CH_2—O, *J*=7·32 Hz), 6·58 (2H, d, *m*-H, *J*=8·06 Hz), 6·67 (1H, t, *p*-H, *J*=7·33 Hz), 7·15 (2H, t, *o*-H, *J*=7·32 Hz).

Cyclohexylmethyl anilide. Liquid, δ_H ($CDCl_3$) 1·01–1·80 (10H, m, cyclic ring), 1·81–1·87 (1H, m, *t*-H), 2·98 (2H, d, —CH_2—N, *J*=6·84 Hz), 3·73 (1H, broad, NH), 6·64 (2H, t, *m*-H, *J*=7·81 Hz), 6·72 (1H, t, *p*-H, *J*=7·32 Hz), 7·21 (2H, d, *p*-H, *J*=7·61 Hz).

Cycloheptylmethyl anilide. Liquid; δ_H ($CDCl_3$) 1·23–1·77 (12H, m, cyclic ring), 1·79–1·88 (1H, m, *t*-H), 2·96 (2H, d, —CH_2—O, *J*=6·59 Hz), 3·60–3·80 (1H, broad NH), 6·61 (2H, d, *m*-H, *J*=8·06 Hz), 6·71 (1H, t, *p*-H, *J*=7·33 Hz), 7·22 (2H, t, *o*-H, *J*=8·06 Hz).

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