Solvolysis Mechanism of Indan-2-yl Arenesulfonates

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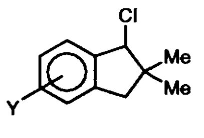
The solvolysis rates of 5-(Y)-substituted indan-2-yl (Z)-benzenesulfonates were determined in a variety of protic solvents at 45.0, 55.0 and 65.0 °C. Application of an extended Grunwald–Winstein equation indicates that kinetic responses to both solvent ionizing power, Y_{OTs}, and solvent nucleophilicity, N_{OTs}, are relatively low but increase in parallel with increasing leaving ability, m = 0.39–0.46 and l = 0.32–0.41 for Z = p-Me ~ p-NO$_2$. The magnitude of cross-interaction constant, ρ_{YZ}, is also relatively small (0.16–0.32), which is, however, much more dependent on the nucleophilicity rather than the ionizing power of the solvent. These are consistent with the typical S$_N$2 mechanism proceeding through a transition state in which solvent participates in both bond-making and -breaking processes.

The solvolysis of the indanyl system exhibits interesting mechanistic varieties. It has been shown that 1,1-dimethylindan-1-yl chlorides, **1**, solvolyze by a typical S$_N$1 (k_c) mechanism,[1]



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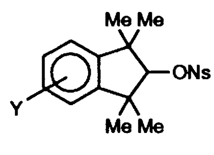

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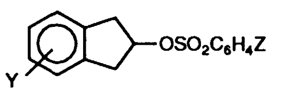

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whereas the solvolysis of 1,1,3,3-tetramethylindan-2-yl nitrobenzene-m-sulfonates, **2**, proceeds with aryl participation $(k_\Delta)^2$. These two derivatives have bulky methyl groups around the reaction centre, in common, which obstruct the approach of solvent nucleophiles preventing nucleophilic attack. However, the solvolysis of indan-2-yl systems, **3**, being free from such hindering groups, are known to proceed by a radically different mechanism involving nucleophilic solvent assistance (k_s).[2]

In a series of studies[3] on the application of cross-interaction constants, ρ_{ij} in eqn. (1), where i, j = X, Y or Z, as a measure of

$$\log (k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \qquad (1)$$

the transition state (TS) structure, the magnitude of ρ_{ij} is related to the tightness of TS structure and their variations with substituents in the nucleophile X, substrate Y, or leaving group (LG), Z. For example, the magnitude of ρ_{YZ}, eqn. (2), has been shown to be proportional to the degree of bond breaking in the TS.[4]

$$\rho_{YZ} = \frac{\partial^2 \log k_{YZ}}{\partial \sigma_Y \times \partial \sigma_Z} = \frac{\partial \rho_Z}{\partial \sigma_Y} = \frac{\partial \rho_Y}{\partial \sigma_Z} \qquad (2)$$

In this work, we report on the solvolysis of 5-(Y)-indan-2-yl (Z)-benzenesulfonates, **3** with Y = H, Br and NO$_2$ and Z = p-Me, H, p-Cl and p-NO$_2$, in various protic solvents at three temperatures, 45.0, 55.0 and 65.0 °C. Specifically, we are interested in the effects of solvent ionizing power, Y_{OTs}, and solvent nucleophilicity, N_{OTs}, and temperature on the degree of bond cleavage in the TS of a typical S$_N$2 reaction.

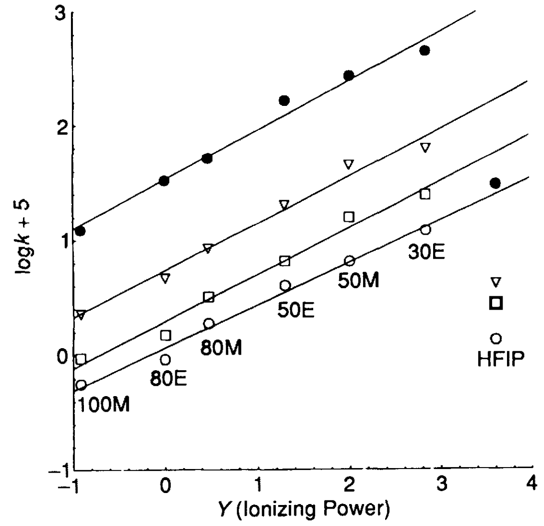

Fig. 1 Plots of log k_1 *vs.* Y(2-AdOTs)-value for the solvolysis of indan-2-yl arenesulfonates: (●) Z = NO$_2$; (▽) Z = Cl; (□) Z = H and (○) Z = Me.

Results and Discussion

Solvolysis rates of 5-(Y)-indan-2-yl (Z)-benzenesulfonates, **3**, in various protic solvents at 45.0 °C, and in MeOH at 45.0, 55.0 and 65.0 °C are summarized in Tables 1 and 2, respectively. The rate is faster with a more electron withdrawing group in the LG (*e.g.* Z = p-NO$_2$) and slower with a more electron withdrawing group in the substrate (*e.g.* Y = NO$_2$). The latter implies that positive charge is developed in the TS at the reaction centre. The rate is also accelerated by a greater ionizing power of the solvent, *i.e.* by a solvent with a greater Y_{OTs} value[5] (based on the solvolysis of adamant-2-yl toluene-p-sulfonates. This suggests that in the solvolysis of **3** bond breaking is important in the TS since the ionizing power has a major influence on bond cleavage.[6,7] A typical mY plot using eqn. (3) is presented in Fig.

$$\log (k/k_0) = mY_{OTs} \qquad (3)$$

1. In general, good straight line plots are obtained with m values ranging from 0.33 to 0.43 listed in Table 3. The large negative deviations of hexafluoroisopropanol (HFIP) in the mY plots and the relatively small m values (relative to $m \cong 1.0$)[7] suggest

Table 1 Rate constants[a] ($k_1 \times 10^5$ s^{-1}) for the solvolyses of 5-Y-indan-2-yl Z-benzenesulfonates at 45.0 °C

		Z[c]			
Solvent[b] (v/v)	Y[d]	*p*-Me	H	*p*-Cl	*p*-NO$_2$
80% EtOH	H	0.920	1.50	4.71	33.1
(0.00, 0.00)	Br	0.491	0.857	2.38	18.1
	NO$_2$	0.366	0.539	1.41	8.12
50% EtOH	H	3.96	6.52	20.5	162.6
(1.29, −0.09)	Br	2.36	3.33	9.80	69.4
	NO$_2$	1.13	1.88	5.50	30.6
30% EtOH	H	12.0	24.7	63.3	437.3
(2.84, −0.35)	Br	7.52	12.1	30.2	231.9
	NO$_2$	2.97	5.85	14.8	84.0
MeOH	H	0.568	0.949	2.30	12.3
(−0.92, −0.04)	Br	0.408	0.620	1.29	6.20
	NO$_2$	0.186	0.265	0.568	2.30
80% MeOH	H	1.89	3.19	8.57	51.9
(0.47, −0.05)	Br	1.00	1.60	4.44	26.4
	NO$_2$	0.586	0.816	2.04	10.7
50% MeOH	H	6.46	15.7	45.3	266.1
(2.00, −0.19)	Br	4.72	7.20	24.4	123.9
	NO$_2$	2.10	3.34	9.39	48.3
HFIP	H	1.35	2.76	4.25	30.2
(3.61, −4.27)	Br	—	—	—	—
	NO$_2$	—	—	—	—

[a] Rate coefficients were reproducible to within ±3%. [b] The Y_{OTs} values are followed by the N_{OTs} values in parentheses. [c] σ_Z values used are $\sigma_{p\text{-Me}} = -0.170$, $\sigma_{p\text{-Cl}} = 0.227$ and $\sigma_{p\text{-NO}_2} = 0.778$. [d] Since the 5-Y position corresponds to either *meta* and *para* positions relative to the leaving group, $(\sigma_m + \sigma_p)/2$ values are used;[13] $\sigma_{m\text{-Br}} = 0.390$, $\sigma_{p\text{-Br}} = 0.230$, $\sigma_{m\text{-NO}_2} = 0.710$ and $\sigma_{p\text{-NO}_2} = 0.778$.

that the solvolysis proceeds by the nucleophilic solvent attack (S_N2 mechanism) on the indan-2-yl derivatives with a small degree of bond cleavage in the TS.[2] We note in Table 3 that the *m* value tends to decrease with a more electron-withdrawing group (Y) in the substrate as expected from a decrease in bond cleavage in the S_N2 process in which bond cleavage is ahead of bond formation. The relatively small *m* values observed may be partially ascribed to the delocalization of developing negative charge on the LG in the TS.[8] Close examination of Fig. 1, however, reveals systematic curvatures in the plots. Application of the extended Grunwald–Winstein equation (4), gives slightly

$$\log(k/k_o) = mY_{OTs} + lN_{OTs} \qquad (4)$$

improved linearities with similar *m* values as those from the plots of eqn (3). On the other hand the kinetic response, *l*, to the solvent nucleophilicity, N_{OTs}, also has a similar magnitude with parallel increase in the magnitudes as the leaving ability gets stronger with a more electron-withdrawing group, Z, (Table 4). The *m* values are slightly greater than the corresponding *l* values. The low *m* and *l* values suggest that the kinetic responses to Y_{OTs} and N_{OTs} are relatively weak with possibility of push–pull solvent participation in the TS.

The Hammett reaction constants, ρ_Y and ρ_Z, obtained with substituent variation of σ_Y and σ_Z, respectively, are collected in Table 5 and the cross-interaction constants ρ_{YZ} in Table 6.

In agreement with our previous notion that bond cleavage precedes bond formation in the TS, ρ_Y values are negative indicating that the reaction centre becomes more positive (or less negative) in the TS. The ρ_Z value decreases, consistent with the decrease in *m* observed above (Table 3), with a stronger electron-withdrawing (Y) substituent. The significant increase in the magnitude of ρ_Y (a more negative value) with a more electron-withdrawing group (Z) in the LG implies a greater degree of bond cleavage with a better LG. This is, however, in contrast with a relatively small increase in *m* with a better LG, due most probably to a greater degree of negative charge delocalization with a more electron-withdrawing Z group.[8]

The magnitudes of ρ_{YZ} in Table 6 are relatively small ($|\rho_{YZ}| = 0.16$–0.32) compared to those of the S_N1 processes of α-*tert*-butylbenzyl arenesulfonates involving extensive bond cleavage ($|\rho_{YZ}| = 0.6$–1.1).[17]

Variations of ρ_Z and ρ_Y with either solvent ionizing power, Y_{OTs}, or solvent nucleophilicity, N_{OTs}, were very small and correlations were not satisfactory. The susceptibility of ρ_{YZ} to variation of solvent nucleophilicity was, however, found to be much greater than that to variation of Y_{OTs}, albeit the correlation was only fair; the value of $\partial|\rho_{YZ}|/\partial N_{OTs}$ was $+0.36$ with the correlation coefficient of 0.80 compared to $\partial|\rho_{YZ}|/\partial Y_{OTs}$ of -0.03 with a less satisfactory correlation ($r = 0.76$). It appears, therefore, that the TS structure, especially the degree of bond cleavage ($|\rho_{YZ}|$) in the TS, is dependent on the solvent nucleophilicity. This means that in the solvolysis of indan-2-yl benzenesulfonates, the nucleophilic attack of solvent *i.e.*, 'push', is as much important as the electrophilic 'pull' of the LG by solvent in the bond breaking step. The low charge density due to delocalization of negative charge on the LG may contribute to the weak response of the bond cleavage process to the solvent ionizing power.

Numerical values of all first derivative parameters (*e.g.* ρ_Y and ρ_Z) invariably decrease as the reaction temperature, *T*, is raised.[8,9] This is indeed observed in Table 2. This decrease in the magnitude of ρ_Y and ρ_Z may easily be misleadingly associated with a decrease in the degree of bond cleavage, with the increase in temperature. However, this cannot be true since as the temperature rises the stretching mode of vibration is excited so that the bond length of the cleaving bond is stretched,[10] *i.e.*, the degree of bond breaking should increase. This is correctly reflected in the observed increase in the numerical values of ρ_{YZ} with the increase in temperature, albeit the actual increment per degree is very small. We note that $|\rho_Y|$ decreases by 0.21 (for Z = H) whereas $|\rho_{YZ}|$ increases by 0.05 for a 20 °C rise in temperature. This increase of 0.05 for the latter is small, reflecting that it is a third derivative parameter, in contrast to the former, a second derivative parameter, eqns. (5a) and (5b). Normally the temperature effect on ρ_{YZ} or any other

$$\frac{\partial \rho_Y}{\partial T} = \frac{\partial^2 \log k}{\partial \sigma_Y \times \partial T} \qquad (5a)$$

$$\frac{\partial \rho_{YZ}}{\partial T} = \frac{\partial^3 \log k}{\partial \sigma_Y \times \partial \sigma_Z \times \partial T} \qquad (5b)$$

second derivative parameter, ρ_{ij}, is very small and almost insignificant. For example ($\partial|\rho_{YZ}|/\partial T$) for the reactions of (Y)-benzyl (Z)-benzenesulfonates with anilines in acetonitrile at 35.0, 45.0 and 55.0 °C was found to be of similar magnitude, *ca.* +0.04 per 20 °C rise in temperature.[11] How can we then account for the increase in $|\rho_{YZ}|$ in contrast to the decrease in ρ_Z with temperature observed? The normalized degree of bond cleavage, a_{fission}, is defined by eqn. (6),[12] where ρ_e is the

$$a_{\text{fission}} = \frac{\rho_Z}{\rho_e} \qquad (6)$$

Hammett coefficient for the equilibrium constant of the reaction concerned. The temperature effect on the degree of bond cleavage is then given by eqn. (7). This shows that a_{fission} can

Table 2 Rate Constants[a] ($k_1 \times 10^5$ s^{-1}) for the solvolysis of 5-Y-indan-2-yl Z-benzenesulfonate in MeOH at 65.0, 55.0 and 45.0 °C and ρ_Y, ρ_Z and ρ_{YZ} values

		Z[c]				
T/°C	Y[d]	p-Me	H	p-Cl	p-NO$_2$	ρ_Z (r)
65.0	H	6.84	9.91	22.0	104	1.27 ± 0.02[f] (0.999)[b]
	Br	4.69	6.20	14.8	52.3	1.13 ± 0.04 (0.994)
	NO$_2$	2.80	3.78	7.13	23.6	0.99 ± 0.02 (0.999)
	ρ_Y	−0.52 ±0.01[f] (1.00)	−0.56 ±0.01 (0.997)	−0.66 ±0.01 (0.997)	−0.86 ±0.01 (0.999)	$\rho_{YZ} = -0.37$ (0.998)[e]
55.0	H	2.14	3.26	7.52	35.8	1.31 ± 0.02 (0.999)
	Br	1.27	2.26	4.11	18.2	1.25 ± 0.02 (1.00)
	NO$_2$	0.753	1.06	2.08	7.23	1.05 ± 0.02 (0.999)
	ρ_Y	−0.60 ±0.02 (0.996)	−0.66 ±0.02 (0.995)	−0.75 ±0.01 (0.998)	−0.93 ±0.01 (1.00)	$\rho_{YZ} = -0.35$ (1.00)[e]
45.0	H	0.568	0.949	2.30	12.3	1.42 ± 0.02 (0.999)
	Br	0.408	0.620	1.29	6.20	1.26 ± 0.01 (1.00)
	NO$_2$	0.186	0.265	0.568	2.30	1.17 ± 0.02 (0.998)
	ρ_Y	−0.66 ±0.03 (0.991)	−0.75 ±0.02 (0.996)	−0.82 ±0.01 (1.00)	−0.98 ±0.01 (1.00)	$\rho_{YZ} = -0.32$ (0.999)[e]

[a] Rate constant are reproducible to within ±3%. [b] Correlation coefficients (r) are shown in parentheses. [c,d] σ values used are given as footnotes in Table 1. [e] Correlation coefficients with 99% confidence level: S. Wold and M. Sjostrom, *Correlation Analysis in Chemistry*, eds., N. B. Chapman and J. Shorter, Plenum, New York, 1978, ch. 1. [f] Errors shown are standard errors of estimate.

Table 3 Derived values of the Grunwald–Winstein parameter, m, for the solvolysis of 5-Y-indan-2-yl Z-benzenesulfonates from eqn. (3)

Z[b]	Y[c]	m	r[a]
p-Me	H	0.37	0.993
	Br	0.37	0.983
	NO$_2$	0.33	0.995
H	H	0.40	0.991
	Br	0.35	0.987
	NO$_2$	0.37	0.998
p-Cl	H	0.41	0.992
	Br	0.38	0.981
	NO$_2$	0.39	0.993
p-NO$_2$	H	0.43	0.991
	Br	0.42	0.996
	NO$_2$	0.41	0.989

[a] Correlation coefficients. [b,c] σ values used are given as footnotes in Table 1.

Table 4 Derived values of m and l for the solvolysis of 5-Y-indan-2-yl Z-benzenesulfonates (Z = H) from eqn. (4)

Z[b]	m	l	r[a]
p-Me	0.39	0.32	0.993
H	0.43	0.33	0.990
p-Cl	0.44	0.40	0.994
p-NO$_2$	0.46	0.41	0.995

[a] Correlation coefficients. [b] σ values used are given as footnotes in Table 1.

Table 5 Hammett coefficients, ρ_Y and ρ_Z, for the solvolysis of 5-Y-indan-2-yl Z-benzenesulfonates at 45.0 °C[a]

Solvent (v/v)	Y[b]	ρ_Z	Z[c]	ρ_Y
80% EtOH	H	1.67	p-Me	−0.52
	Br	1.67	H	−0.59
	NO$_2$	1.45	p-Cl	−0.69
			p-NO$_2$	−0.82
50% EtOH	H	1.73	p-Me	−0.73
	Br	1.60	H	−0.72
	NO$_2$	1.53	p-Cl	−0.76
			p-NO$_2$	−0.97
30% EtOH	H	1.64	p-Me	−0.82
	Br	1.59	H	−0.83
	NO$_2$	1.52	p-Cl	−0.84
			p-NO$_2$	−0.97
MeOH	H	1.42	p-Me	−0.66
	Br	1.26	H	−0.75
	NO$_2$	1.17	p-Cl	−0.82
			p-NO$_2$	−0.98
80% MeOH	H	1.53	p-Me	−0.67
	Br	1.52	H	−0.78
	NO$_2$	1.36	p-Cl	−0.83
			p-NO$_2$	−0.92
50% MeOH	H	1.67	p-Me	−0.67
	Br	1.53	H	−0.89
	NO$_2$	1.46	p-Cl	−0.92
			pNO^2	−0.99

[a] Correlation coefficients are better than 0.985. [b,c] σ values used are given as footnotes in Table 1.

$$\frac{\partial \alpha_{\text{fission}}}{\partial T} = \left[\left(\frac{\partial \rho_Z}{\partial T}\right)\rho_e - \left(\frac{\partial \rho_e}{\partial T}\right)\rho_Z\right]\rho_e^{-2} \qquad (7)$$

increase with temperature *i.e.*, bond cleavage can be greater, as the increase in $|\rho_{YZ}|$ suggested, if the quantity in square brackets is positive, *i.e.*, $(\partial\rho_Z/\partial T)\rho_e > (\partial\rho_e/\partial T)\rho_Z$ or $|\partial\rho_Z/\partial T|\rho_e < |\partial\rho_e/\partial T|\rho_Z$ since the temperature coefficient of the first derivative parameters are negative. We therefore conclude that a decrease in ρ_Z with temperature does not necessarily indicate a

Table 6 Cross-interaction constants, ρ_{YZ}, for the solvolysis of 5-Y-indan-2-yl Z-benzenesulfonates at 45 °C calculated using eqn. (1)

Solvent (v/v)	$\rho_Y{}^H$	$\rho_Z{}^H$	ρ_{YZ}	r[a]
80% EtOH	−0.59	1.71	−0.31	0.997
50% EtOH	−0.74	1.71	−0.27	0.997
30% EtOH	−0.83	1.65	−0.16	0.999
MeOH	−0.73	1.40	−0.32	0.999
80% MeOH	−0.76	1.56	−0.23	0.998
50% MeOH	−0.81	1.65	−0.28	0.995

[a] Correlation coefficients with 99% confidence level: (footnote *e* in Table 2).

Table 7 Activation parameters, $\Delta H^\ddagger$ (kcal mol^{-1}) and $\Delta S^\ddagger$ (cal deg^{-1} mol^{-1}) for solvolysis of 5-Y-indan-2-yl Z-benzenesulfonates in MeOH

	Z							
	p-Me		H		*p*-Cl		*p*-NO$_2$	
Y	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
H	26.0	−1.0	24.4	−4.8	23.5	−0.60	22.2	−7.0
Br	25.4	−3.7	24.0	−6.9	25.4	−1.4	22.1	−8.4
NO$_2$	28.4	4.2	27.8	3.0	26.4	0.3	24.2	−3.9

decrease in the degree of bond cleavage. In contrast an increase in $|\rho_{YZ}|$ with temperature correctly reflects an increase in the degree of bond fission with a temperature increase.

Activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, are summarized in Table 7. Examination of this Table reveals that the $\Delta H^\ddagger$ values (22–28 kcal mol^{-1} †) are relatively high and the $\Delta S^\ddagger$ values are low (−7–4 e.u.‡). These values are rather unusual for an S_N2 reaction and actually similar to those for the limiting S_N1 processes.[18] The anomalously low $\Delta S^\ddagger$ values may be ascribed to a relatively strained structure of the reaction centre carbon within a five-membered ring in the reactant, which is relaxed partially by the bond cleavage, with little solvent reorganization in the TS; hindered approach of the nucleophile or solvent due to the out-of-plane hydrogens in the adjacent carbons and relatively low degree of bond cleavage with delocalized negative charge in the LG should lead to the low degree of solvent reorganization. The steric crowding in the TS keeps the nucleophile or solvent molecules from close approach to the reaction centre carbon, which in turn leads to a lesser degree of bond cleavage due to a lesser degree of charge transfer to the lowest unoccupied MO (LUMO) of the cleaving bond, σ^*_{C-O}. This could be the reason why the magnitude of ρ_{YZ}, *i.e.* the degree of bond cleavage in the TS, is more dependent on the solvent nucleophilicity, N_{OTs}, than on the solvent ionizing power, Y_{OTs}, as noted above. Moreover, in the leaving group, arenesulfonate, the developing negative charge is efficiently delocalized and hence the effect of the solvent ionizing power on the solvent reorganization in the TS should be small. The steric hindrance to the nucleophilic attack may also contribute to the relatively high activation enthalpies observed, *i.e.* the bond-making is more endoergic as discussed above.

Experimental

Materials.—Merck G.R. grade methanol, ethanol and Aldrich G.R. grade hexafluoroisopropanol (HFIP) (99 + %) were used without further purification. In the preparation of 5-substituted indan-2-yl Z-benzenesulfonates, the Aldrich indan-2-ol was first acetylated, and then 5-NO$_2$ and 5-Br groups were introduced by well known methods.[13] These were reverted to indan-2-ols, which were then reacted with *p*-substituted benzenesulfonyl chloride by the Tipson method to benzenesulfonates.[14]

The substrates synthesized were confirmed by spectral and elementary analyses as follows.

Indan-2-yl benzenesulfonate. M.p. 90.2 °C; ν_{max}(KBr)/cm^{-1} 1600, 1460 (C=C arom), 1364, 1194 (SO$_2$) and 1171 (C–O); δ_H(60 MHz; CDCl$_3$) 3.1 (β-H, d, 4 H), 5.2 (α-H, q, 1 H) and 7.0–8.0 (Ph, m, 9 H) (Found: C, 65.8; H, 5.4; S, 11.8. $C_{15}H_{14}O_3S$ requires C, 65.68; H, 5.14; S, 11.69%).

*Indan-2-yl nitrobenzene-*p*-sulfonate.* M.p. 96.0 °C; ν_{max}(KBr)/cm^{-1} 1600, 1480 (C=C arom), 1531, 1335 (NO$_2$), 1364, 1194 (SO$_2$) and 1172 (C–O); δ_H(60 MHz; CDCl$_3$) 3.2 (β-H, d, 4 H), 5.3 (α-H, q, 1 H) and 7.0–8.5 (Ph, m, 8 H) (Found: C, 56.4; H, 4.3; S, 10.3; N, 4.4. $C_{15}H_{13}NO_5S$ requires C, 56.42; H, 4.10; S, 10.04; N, 4.39%).

*Indan-2-yl chlorobenzene-*p*-sulfonate.* M.p. 105.0 °C; ν_{max}(KBr)/cm^{-1} 1600, 1460 (C=C arom), 1357, 1190 (SO$_2$), 623 (C–Cl) and 1177 (C–O); δ_H(60 MHz; CDCl$_3$) 3.2 (β-H, d, 4 H), 5.2 (α-H, q, 1 H) and 7.0–7.9 (Ph, m, 8 H) (Found: C, 58.4; H, 4.4; S, 10.4. $C_{15}H_{13}ClO_3S$ requires C, 58.35; H, 4.24; S, 10.38%).

*Indan-2-yl toluene-*p*-sulfonate.* M.p. 118.0 °C; ν_{max}(KBr)/cm^{-1} 1600, 1430 (C=C arom), 1343, 1169 (SO$_2$), 815 (S–O–C) and 1100 (C–C); δ_H(60 MHz; CDCl$_3$) 2.4 (*p*-CH$_3$, s, 3 H), 3.1 (β-H, d, 4 H), 5.2 (α-H, q, 1 H) and 7.0–7.9 (Ph, m, 8 H) (Found: C, 66.3; H, 5.9; S, 11.1. $C_{16}H_{16}O_3S$ requires C, 66.65; H, 5.59; S, 11.12%).

5-*Bromoindan-2-yl benzenesulfonate.* M.p. 81.0 °C; ν_{max}(KBr)/cm^{-1} 1600, 1450 (C=C arom), 1368, 1190 (SO$_2$) and 1101 (C–O); δ_H(60 MHz; CDCl$_3$) 3.1 (β-H, d, 4 H), 5.3 (α-H, q, 1 H) and 6.8–8.0 (Ph, m, 8 H) (Found: C, 51.0; H, 3.9; S, 9.1. $C_{15}H_{13}BrO_3S$ requires C, 51.01; H, 3.71; S, 9.08%).

5-*Bromoindan-2-yl toluene-*p*-sulfonate.* M.p. 113.0 °C; ν_{max}(KBr)/cm^{-1} 1600, 1470 (C=C arom), 1360, 1174 (SO$_2$) and 1100 (C–O); δ_H(60 MHz; CDCl$_3$), 2.5 (*p*-CH$_3$, s, 3 H), 3.1 (β-H, d, 4 H), 5.3 (α-H, q, 1 H) and 7.0–8.0 (Ph, m, 7 H) (Found: C, 51.25; H, 4.3; S, 8.4. $C_{16}H_{15}BrO_3S$ requires C, 50.72; H, 4.26; S, 9.03%).

5-*Bromoindan-2-yl chlorobenzene-*p*-sulfonate.* M.p. 75.0 °C; ν_{max}(KBr)/cm^{-1} 1600, 1450 (C=C arom), 1356, 1175 (SO$_2$), 623 (C–Cl) and 1086 (C–O); δ_H(60 MHz; CDCl$_3$) 3.1 (β-H, d, 4 H), 5.3 (α-H, q, 1 H) and 7.0–8.0 (Ph, m, 7 H) (Found: C, 46.5; H, 3.2; S, 8.2. $C_{15}H_{12}BrClO_3S$ requires C, 46.47; H, 3.12; S, 8.27%).

5-*Bromoindan-2-yl nitrobenzene-*p*-sulfonate.* M.p. 112.0 °C; ν_{max}(KBr)/cm^{-1} 1600, 1478 (C=C arom), 1531, 1357 (NO$_2$), 1357, 1193 (SO$_2$) and 1096 (C–O); δ_H(60 MHz; CDCl$_3$) 3.1 (β-H, d, 4 H), 5.3 (α-H, q, 1 H) and 7.1–8.5 (Ph, m, 7 H) (Found: C, 44.7; H, 3.1; S, 7.8; N, 3.4. $C_{15}H_{12}BrNO_5S$ requires C, 45.24; H, 3.04; S, 8.05; N, 3.52%).

5-*Nitroindan-2-yl benzenesulfonate.* M.p. 100.5 °C; ν_{max}(KBr)/cm^{-1} 1600, 1480 (C=C arom), 1519, 1362 (NO$_2$), 1345, 1179 (SO$_2$) and 1090 (C–O); δ_H(60 MHz; CDCl$_3$) 3.2 (β-H, d, 4 H), 5.3 (α-H, q, 1 H) and 7.0–8.1 (Ph, m, 8 H) (Found: C, 56.3; H, 4.2; S, 10.1; N, 4.4. $C_{15}H_{13}NO_5S$ requires C, 56.42; H, 4.10; S, 10.04; N, 4.39%).

5-*Nitroindan-2-yl toluene-*p*-sulfonate.* M.p. 135.0 °C; ν_{max}(KBr)/cm^{-1} 1600, 1460 (C=C arom), 1517, 1349 (NO$_2$), 1349, 1171 (SO$_2$) and 1043 (C–O); δ_H(60 MHz; CDCl$_3$) 2.5 (*p*-CH$_3$, s, 3 H), 3.2 (β-H, d, 4 H), 5.3 (α-H, q, 1 H) and 7.01–8.2 (Ph, m, 7 H) (Found: C, 57.3; H, 4.3; S, 9.6; N, 4.2. $C_{16}H_{15}NO_5S$ requires C, 57.65; H, 4.54; S, 9.62; N, 3.52%).

5-*Nitroindan-2-yl chlorobenzene-*p*-sulfonate.* M.p. 139.5 °C; ν_{max}(KBr)/cm^{-1} 1600, 1480 (C=C arom), 1513, 1357 (NO$_2$), 1347, 1174 (SO$_2$) and 1070 C–O); δ_H(60 MHz; CDCl$_3$) 3.2 (β-H, d, 4 H), 5.3 (α-H, q, 1 H) and 7.0–8.1 (Phenyl, m, 7 H) (Found:

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† 1 kcal mol^{-1} = 4.18 kJ mol^{-1}.

‡ 1 e.u. = 4.18 J K^{-1} mol^{-1}.

C, 51.2; H, 3.5; S, 9.3; N, 4.0. $C_{15}H_{12}ClNO_5S$ requires C, 50.78; H, 3.70; S, 9.04; N, 4.20%).

5-Nitroindan-2-yl nitrobenzene-p-*sulfonate*. M.p. 132.0 °C; ν_{max}(KBr)/cm^{-1} 1600, 1480 (C=C arom), 1517, 1371 (NO_2), 1351, 1178 (SO_2) and 1100 (C–O); δ_H(60 MHz; $CDCl_3$) 3.3 (β-H, d, 4 H), 5.5 (α-H, q, 1 H), 7.0–8.5 (Ph, m, 7 H) (Found: C, 49.2; H, 3.4; S, 9.0; N, 7.7. $C_{15}H_{12}N_2O_7S$ requires C, 49.46; H, 3.32; S, 8.80; N, 7.69%).

Rate Constants.—Rates were measured conductimetrically at 45 ± 0.05 °C and rate constants were determined as described previously.[15]

Product Analysis.—The identity of solvolysis products was confirmed by TLC and NMR analysis. TLC analysis (hexane–ethyl acetate, 80:20) of reaction mixtures showed three spots, corresponding to three products, nitrobenzene-*p*-sulfonic acid (*a*) and the main product, indan-2-yl methyl ether (*b*) and a trace amount of indene (*c*) from acid catalyzed mechanism similar to the dehydration of alcohols.[16] The three R_f values were (*a*), 0.0; (*b*), 0.50 and (*c*), 0.67. The NMR data for the major product (*a*) are δ_H(60MHz; $CDCl_3$), 3.0 (β-H, m, 4 H), 3.25 (OCH_3, s, 3 H), 4.5 (α-H, q, 1 H) and 7.05 (Ph, s, 4 H); and for the trace indene (*c*) are δ_H(60 MHz; $CDCl_3$) 2.9–3.3 (OCH_3, β-H, m), 4.3 (α-H, q), 6.55 (olefin, m) and 7.2 (Ph, m).

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