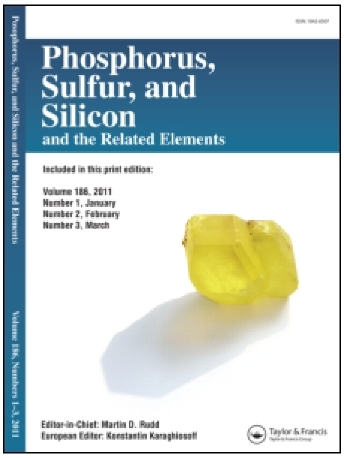

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DIPOLAR APROTIC SOLVENT EFFECTS IN THE HYDROLYSIS OF PHENYLMETHANESULFONATES AND PHENYLSULFONYLACETATES

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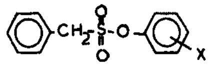
The hydrolytic behaviour under alkaline conditions of a group of sulfur compounds containing an active methylene group, in aqueous solvent mixtures with dimethylsulfoxide as the co-solvent has been investigated. The substrates studied are substituted phenyl phenylmethanesulfonates (A), substituted phenyl *p*-nitrophenylmethanesulfonates (B) and substituted phenylsulfonylacetates (C). It is known that methylenes adjacent to the sulfonyl group are acidic and evidences are available for the formation of the corresponding anions in alkaline solutions. Structure-reactivity correlations strongly suggest that these react not by the conventional addition–elimination mechanism ($B_{AC}2$), but by an elimination–addition mechanism (ElcB) involving a slow decomposition of the corresponding anions. The rate of hydrolysis of (A) increases with increasing percentage of dimethylsulfoxide in the solvent mixtures, whereas, the reverse is the case with (B) and (C). The results are analysed on the basis of a spectrum of pathways in the ElcB mechanism, and on the basis of the relative solvation of ground and transition states of the reaction.

The elimination–addition mechanism of alkaline hydrolysis of esters has received much attention in recent years. An excellent review on the various facets of this mechanism is now available.[1] Independent works[2,3] on the basic hydrolysis of esters of α-phenylmethanesulfonic acid clearly indicate the occurrence of such a mechanism in this instance. We now report the influence of dipolar–aprotic solvents, particularly dimethylsulfoxide (DMSO) on the rate of hydrolysis of substituted phenyl esters of α-phenylmethanesulfonic acid and α-*p*-nitrophenylmethane sulfonic acid. A recent investigation[4] on the hydrolysis of phenylsulfonylacetates also indicates an elimination–addition pathway for the alkaline hydrolysis of these esters. The influence of DMSO on the alkaline hydrolysis of ethyl esters of substituted phenylsulfonylacetates also forms a part of the present investigation.

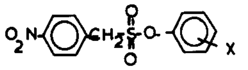
EXPERIMENTAL

Substituted phenyl α-phenylmethanesulfonates (A) were prepared according to procedure available in literature.[3] Substituted phenyl α-*p*-nitrophenylmethanesulfonates (B) were prepared by a similar procedure and the melting points of these esters are collected in Table I. The purity of these compounds were checked by comparing the uv spectrum of phenoxide produced after completion of reaction with that of the corresponding phenoxides. The purity, in many cases exceeded 95%.



(A)

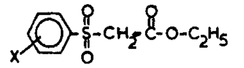
(Aa-*p*-NO$_2$; Ab: *m*-NO$_2$; Ac: *p*-Cl
Ad–*p*-COOEt; Ae–*p*COCH$_3$
Af–H)



(B)

(BA–*m*-NO$_2$; Bb–*p*-Cl;
Bc–*p*-COOMe; Bd–H)

Ethyl-α-substituted phenylsulfonylacetates (C) were extrapure materials from Parish Chemical Company.



(Ca–H; Cb–*p*Methyl; Cc–*p*-Cl; Cd–*p*-OMe)

Dimethylsulfoxide (DMSO) was purified under reduced pressure in an all-glass apparatus over calcium hydride (b.pt: 95–96°C; 31 mm) and stored in air tight bottles. 100% pure ethanol was prepared by the procedure of Vogel.[5] Carbonate free sodium hydroxide was prepared by the method of Vogel.[6]

The rates of alkaline hydrolysis of the various esters employed in the present investigation were followed spectrophotometrically using a Carl-Zeiss VSU2-P model spectrophotometer. In the case of hydrolysis of phenylmethanesulfonates (A), the release of phenoxide was followed at suitable

TABLE I

p-NO$_2$–C$_6$H$_4$CH$_2$SO$_2$–OC$_6$H$_4$X	m.pt (°C)
(X–)	
m-NO$_2$	147–149
p-Cl	134–135
H	133–135
p-COOCH$_3$	121–124

TABLE II

Temp.: 27°C

	% Organic solvent–% H_2O (v/v)	k_2 lit mol^{-1} sec^{-1}		
		EtOH–H_2O	DMSO–H_2O	Acetone–H_2O
Aa	40–60	28.6		19.4
	50–50	17.7		51.6
	60–40	17.3		—
	70–30	26.9		—
	80–20	15.0		—
Ab	40–60	0.257	1.85	0.329
	50–50	0.357	4.24	0.506
	60–40	0.439	11.0	1.10
	70–30	0.263	—	1.69
	80–20	0.122	—	6.19
Ac[a]	40–60	6.05	50.6	
	50–50	5.78	122	
	60–40	10.4	369	
	70–30	13.3	1590	
	80–20	178	15,000	
Ad	40–60	0.101	1.00	
	50–50	0.102	4.47	
	60–40	0.104	14.1	
	70–30	0.178	—	
	80–20	0.316	—	
Ae	40–60	0.360	2.46	
	50–50	0.349	6.61	
	60–40	0.415	14.3	
	60–40	0.497	—	
	80–20	0.552	—	
Af[a]	40–60	1.78	8.06	
	50–50	1.07	9.69	
	60–40	3.16	40.3	
	70–30	7.94	52.8	
	80–20	39.8	186	

[a] $10^4 k_2$

wavelengths. The disappearance of the anions of *p*-nitrophenylmethanesulfonates (B) and phenylsulfonylacetates (C) was followed at 480 nm and 285 nm or 310 nm respectively. Pseudo first order rate constants for the hydrolysis were calculated from the slopes of plots of log $(A_\infty - A_t)$ *vs.* time or log $(A_t - A_\infty)$ *vs.* time. The method of least square was employed and the slopes and correlation coefficients were determined using a Micro 2200 programmable computer (Hindustan Computers). The alkaline hydrolysis of *p*-nitrophenylmethanesulfonates has also been measured in nitrogen atmosphere and the aerial oxidation was found to be negligible.

RESULTS

The alkaline hydrolysis of substituted phenyl-α-phenylmethane sulfonates have been studied in aqueous ethanol and aqueous DMSO. The reaction obeys good first order rate expression for the release of phenoxide. The reaction also exhibits a first order dependence on the initial concentrations of sodium hydroxide. The second order rate constants for the various esters in both these solvent media and for different compositions are presented in Table II.

A solvent deuterium oxide isotope effect of 1.20 and 1.25 has been observed for the *m*-nitrophenyl ester (Ab) in 40% EtOH and 30% DMSO respectively (Table III).

The bimolecular rate constants obey a good Hammett correlation only when σ^- constants are used for *p*-nitro, *p*-acetyl and *p*-carbethoxy sub-

TABLE III

[Ab]: 5 × 10^{-4} M [NaOH(D)]: 7.6 × 10^{-3} M Temp.: 27°C

Solvent composition	k_2 lit/mol/sec	k_{OD}/k_{OH}
40% EtOH–60% H_2O (v/v)	0.257	1.20
40% EtOH–60% D_2O (v/v)	0.308	
30% DMSO–70% H_2O (v/v)	0.906	1.25
30% DMSO–70% D_2O (v/v)	1.13	

TABLE IV
Temp.: 27°C

% Organic solvent–% H_2O	ρ	
	EtOH–H_2O	DMSO–H_2O
40–60	4.31	5.00
50–50	4.33	5.53
60–40	3.95	5.28
70–30	3.80	—
80–20	2.78	—

stituents. The Hammett reaction constants are large for these hydrolytic reactions (ρ = 2.78–5.53) (Table IV, Figures 1 and 2).

A different kinetic picture has been noticed in the case of the esters of *p*-nitrophenylmethanesulfonic acid (B) when hydrolysed under alkaline conditions in these solvent media viz., ethanol–water and DMSO–water. The anions of these esters are readily produced with a large excess of NaOH and the disappearance of these anions has been followed spectrophotometrically.[7] Consequently, these hydrolytic reactions have no dependence on the initial concentration of OH^- in the region employed for the present investigation. The pseudo first order rate constants for the disappearance of the anions are collected in Table V.

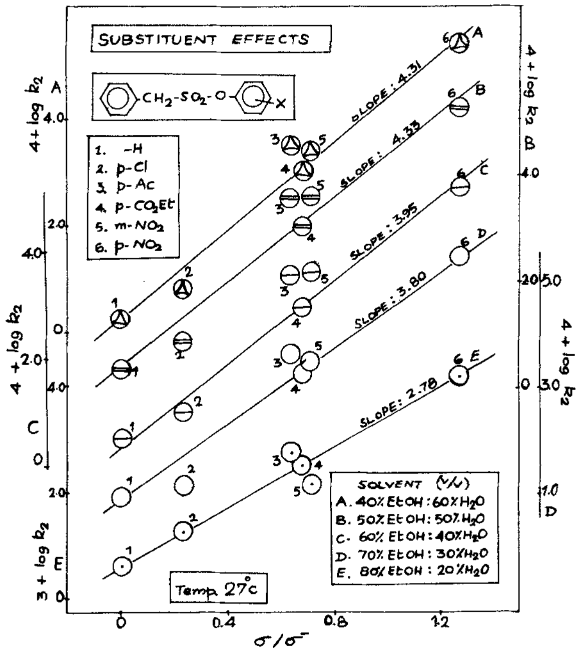


FIGURE 1

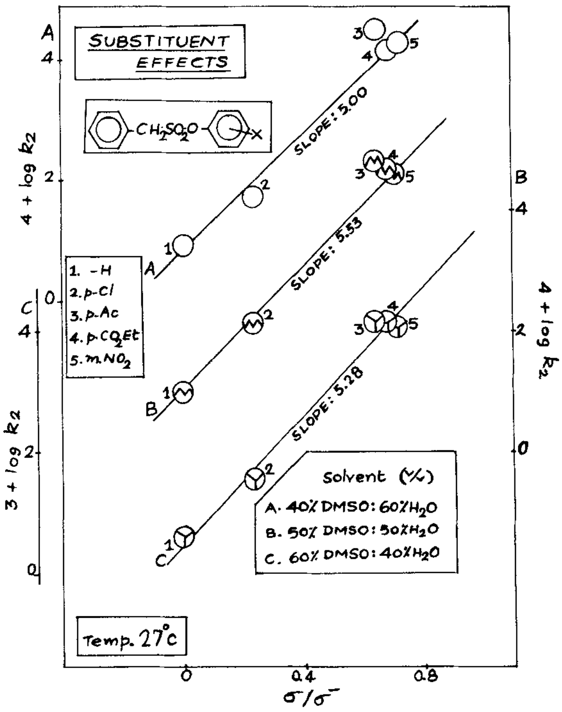


FIGURE 2

TABLE V
[NaOH]: 1.0 x 10^{-2} M Temp.: 27°C

	% Organic solvent–% H_2O (v/v)	$10^6\ k_1$ sec^{-1}	
		EtOH–H_2O	DMSO–H_2O
Ba	60–40	—	56,300
	70–30	—	22,700
	80–20	—	5280
Bb	60–40	8680	4000
	70–30	17,600	140
	80–20	19,900	41.3
Bc	60–40	—	26,900
	70–30	—	13,200
	80–20	—	3940
Bd	60–40	2180	634
	70–30	4000	11.9
	80–20	5030	2.02

TABLE VI
Temp.: 27°C

% DMSO–% H_2O (v/v)	ρ
60–40	2.75
70–30	4.25
80–20	5.00

The reaction series obeys a good Hammett correlation with σ^- values in the case of *p*-COOMe. The ρ values are large (Table VI, Figure 3).

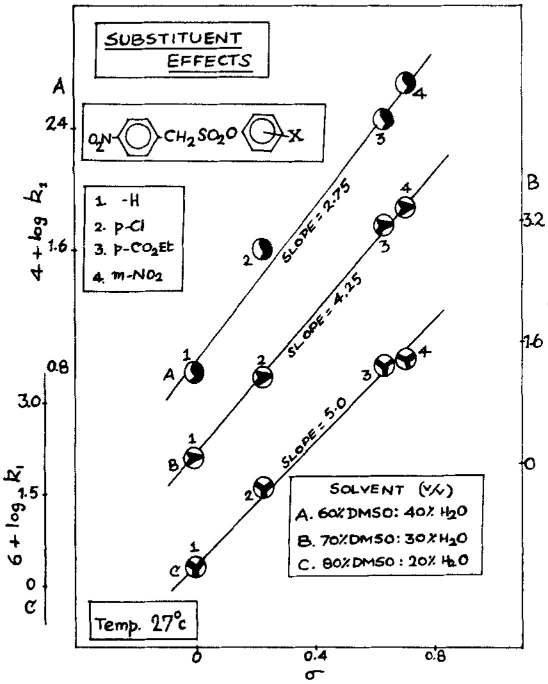


FIGURE 3

TABLE VII

Temp.: 30°C

% Organic solvent–% H_2O (v/v)		$10^2 k_1$ sec^{-1}	
		EtOH–H_2O	DMSO–H_2O
Ca	50–50	—	1.42
	60–40	—	0.287
	70–30	1.66	0.0654
	80–20	1.01	0.0160
	90–10	0.902	—
Cb	50–50	—	2.35
	60–40	—	0.749
	70–30	3.02	0.112
	80–20	2.19	0.0257
	90–10	1.66	—
Cc	50–50	—	0.770
	60–40	—	0.247
	70–30	1.35	0.0476
	80–20	0.795	0.0141
	90–10	0.726	—
Cd	50–50	—	7.59
	60–40	—	1.07
	70–30	7.59	0.259
	80–20	6.76	0.0354
	90–10	4.37	—

The phenylsulfonylacetates are, readily converted into anions in highly basic solution. The disappearance of the anion has been followed at suitable wavelengths (285 or 310 nm). The decomposition of the anion obeys a clean first order kinetics. The rate of the reaction has no dependence on $[OH^-]$ in the concentration region studied (0.005–0.01 M). Obviously this is a plateau region. The pseudo first order rate constants for the disappearance of anions are collected in Table VII.

Increasing percentage of organic solvent content decreases the rate of reaction in both the solvent

TABLE VIII

Temp.: 30°C

% Organic solvent–% H_2O	ρ	
	Ethanol	DMSO
50–50	—	−0.89
60–40	—	−0.96
70–30	−0.85	−0.81
80–20	−1.0	−0.50
90–10	−0.90	—

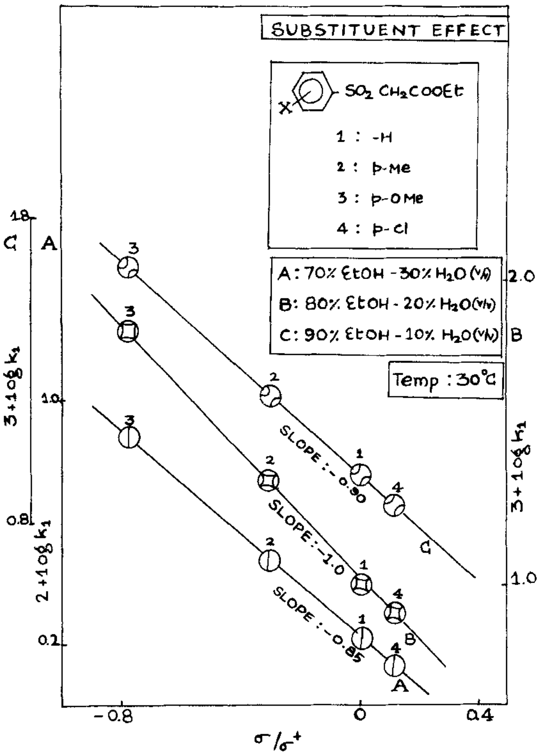


FIGURE 4

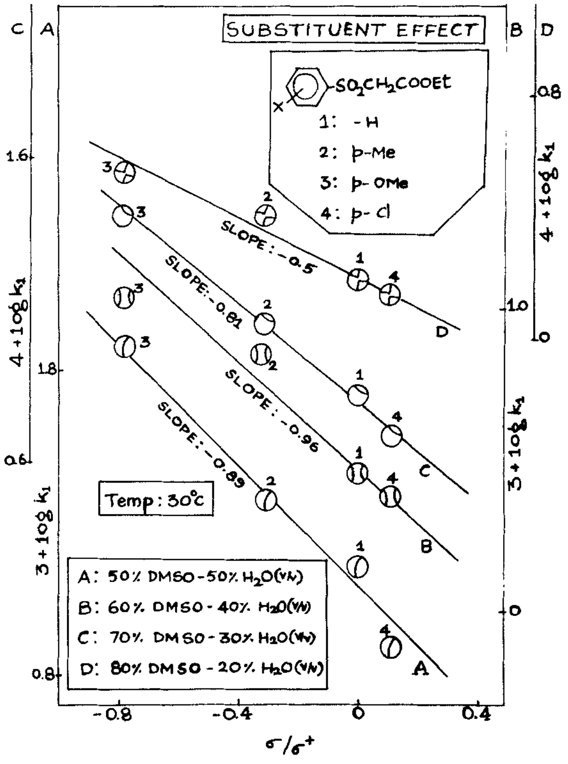


FIGURE 5

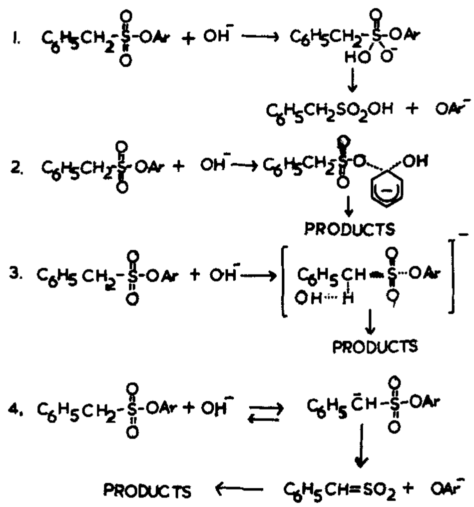
systems. The kinetic data for the substituted phenylsulfonylacetates fit into the Hammett equation when σ^+ values are employed for substituents like *p*-chloro, *p*-methoxy and *p*-methyl. The Hammett ρ's are collected in Table VIII (Figures 4 and 5).

DISCUSSION

Hydrolysis of Phenylmethanesulfonates

Recent investigations[2,3] on the hydrolysis of substituted phenyl-α-phenylmethanesulfonates have clearly indicated that these hydrolyse by an elimination–addition mechanism. Esters of weakly acidic phenols undergo hydrolysis by an ElcB pathway and that of acidic phenols follow an irreversible ElcB mechanism or an E_2 pathway. The present investigation concerning the solvent influences on the alkaline hydrolysis of the former type of esters has been undertaken to study the influence of DMSO on these reactions.

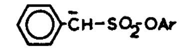
Four major types of pathway have been envisaged for the hydrolysis of phenylmethanesulfonates under alkaline conditions.[3] These may be depicted as follows:

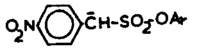


On the basis of the fact that the reactivity of the system correlates much better with σ^- of the substituent in the leaving group, indicating considerable charge on the oxygen of the aryloxy group in the transition state, Eq. (1) can be dropped. Benzene sulfonates which undergo hydrolysis by such an addition–elimination mechanism correlate with σ of the substituent in leaving aryloxy group and the Hammett reaction constants are of the order of 2,[3] whereas in the case of phenylmethanesulfonates these values range from 2.78–5.53 which are rather higher than those encountered in reactions by addition–elimination mechanism. O^{18} incorporation studies[3] on the hydrolysis of phenylmethanesulfonates have provided evidence against the pathway involving an aromatic nucleophilic substitution leading onto the ejection of the sulfonate group (Eq. 2). Equations 3 and 4 merit detailed consideration. Phenylmethanesulfonates are known for the marked lability of the hydrogen atoms α to the sulfonyl group. Many studies[2] of exchangeability with solvent deuterons have been made and the C—H pK_a in DMSO is for example 22.0.[3] Thus these esters are prone to react by an elimination–addition route via sulfenes (Eq. 4). An E_2 elimination (Eq. 3) is ruled out on the basis of solvent isotope effect (Table III), for such reactions exhibit an isotope effect of the order of 5.[8]

The operation of an ElcB rather than an E_2 pathway is exemplified in a more clearcut way with α-*p*-nitrophenylmethane sulfonates. In these substrates the introduction of a strongly electron withdrawing *p*-nitro function in the α-benzyl moiety boosts the acidity of the α-hydrogens to such an extent that carbanion formation is almost instantaneous.[7] There is not only a better correlation of the rate with σ^- but a limiting rate has already been reached in the concentration region of OH^- used in the present experiments. The "zero order" dependence on $[OH^-]$ is thus a direct indication of the formation of a carbanion. However, there seems to be a subtle variation in the influence of DMSO on the course of hydrolysis of these two systems. In the case of α-phenylmethane sulfonates increasing DMSO content in the solvent increases the rate, while increasing DMSO content decreases the rate in α-*p*-nitrophenylmethanesulfonates. This interesting divergence can be understood on the basis of solvation of ground and transition states of the reaction by DMSO.

The fact that both these systems fit into a good Hammett correlation only when σ^- values are employed in the case of electron withdrawing substituents in the leaving phenoxy group, clearly suggests a charge-dispersed transition state for the reaction. According to Parker[9] such negatively charged transition states are solvated to a greater extent by dipolar aprotic solvents than protic solvents. Therefore it is not unreasonable to assume that the two transition states are solvated more or less to the same extent by DMSO. Thus, the observed reactivity of these two systems in our opinion, could be traced to differences in the ability of the ground state to get solvated by DMSO.


(I)


(II)

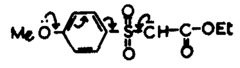
Of these two anions (ground state), (II) has a more charge delocalized structure than (I) on account of the severe mesomeric interaction of a *p*-nitro group with the carbanion centre. As a consequence of this, anion (II) would be solvated to a larger extent by DMSO than by H_2O or ethanol, whereas the reverse would be the case with anion (I). Our argument is supported by the fact that $C_6H_5CH_2Cl$ has a value of +0.1 for log MeOH γ DMF whereas the value for $4\text{-}NO_2C_6H_4CH_2Br$ is −1.2.[9] A similar type of behaviour can be extended to these anions. Thus, it is clearly evident that the behaviour of these two systems in DMSO is mainly due to the difference in the solvation of the ground state anions of the reaction.

Hydrolysis of Phenylsulfonylacetates

The kinetic data viz., a first order dependence on the substrate and an independence of rate on $[OH^-]$ in the concentration region studied are clear indications of the operation of an ElcB route. Other similar examples of the base induced hydrogen exchange of methylene hydrogens positioned α to a sulfonyl group have been reported and they have been explained on the basis of the formation of a carbanion stabilized by a strongly electron withdrawing inductive effect of the sulfonyl group and a 3d orbital resonance with adjacent sulfur atom.[10] It is thus clearly seen that the phenylsulfonylacetates undergo hydrolysis in the following way:

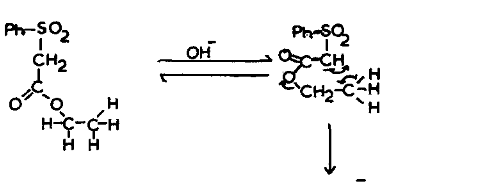
$$\begin{tikzcd}
C_6H_5SO_2CH_2COOEt \arrow[r, shift left, "OH^-"] & C_6H_5SO_2\bar{C}H\text{-}COOEt \arrow[l, shift left] \arrow[d] \\
C_6H_5SO_2CH_2COOH & C_6H_5SO_2CH{=}C{=}O + OEt^- \arrow[l, "H_2O"']
\end{tikzcd} \quad (5)$$

The formation of the carbanion in a fast equilibrium has been demonstrated, for this, in fact, forms the basis of measurement of rate of the reaction. The above mechanism is also consistent with the observed effect of substituents on the reaction rate. The reactivity of these compounds correlate with σ^+ for both *p*-OCH_3 and *p*-Cl underscoring the operation of the following type of resonance stabilization.



Consequently the Hammett ρ's for these reactions are also on the low side and are of the order −0.5 to −1.0 (Table VIII).

Sera and Maruyama[4] have considered yet another alternative route for the hydrolysis of 2-phenylethyl phenylsulfonylacetates. According to them the carbanionic centre formed can act intramolecularly as an attacking base against β hydrogen of the leaving alkyl group to promote an elimination reaction; that is, an intramolecular carbanionic elimination can take place to give an olefin. In their investigation styrene was obtained in addition to the corresponding alcohol. Applied to the present studies, this mechanism could be written thus (Eq. 6):


(6)

The above proposal commends itself for consideration because the carbanionic centre seems to act as a base to abstract the β-hydrogen through a six-membered transition state. The formation of ethylene, unfortunately, could not be confirmed under the experimental conditions.

The retarding influence of DMSO on the rate of hydrolysis of phenylsulfonylacetates can again be traced to the solvation of the ground state anion which decomposes in the slow step of the hydrolytic reaction. Such instances of ground state solvation leading to lowered reactivity in DMSO–Water mixtures containing high percentage of dipolar aprotic solvent content have been noticed in the case of acetoacetates,[11] benzoyl acetates[12] and indole-2-carboxylate.[13]

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