J. Chem. Soc. (B), 1967

Elimination–Addition. Part XI.¹ Electronic Effects upon the Reactivity of Aryl Vinyl Sulphones towards Amines

By S. T. McDowell and C. J. M. Stirling,* The Queen's University, Belfast

Rates of addition of t-butylamine to a series of nuclear-substituted aryl vinyl sulphones have been measured for reactions in ethanol at 25°. The results are well correlated by the Hammett σ_p relationship, the value of p = +1.59 being obtained with substituents possessing σ constants in the range -0.268 to +0.778. The reaction is compared with others which proceed via a carbanionic transition state.

THE rates of reaction of amines with p-tolyl vinyl sulphone are sensitive to the nature of the solvent, an acceleration in more polar solvents indicating a transition state more polar than the reactants;¹ the rate with any particular amine, while insensitive to its proton basicity, was very sensitive to adverse nonbonded interactions between nucleophile and substrate.¹

We now report the effects of substituents in the aromatic nucleus of aryl vinyl sulphones upon their reactivities in addition reactions with t-butylamine (equation 1). Our object was to determine the nature

$$Ar \cdot SO_2 \cdot CH : CH_2 + Me_3 C \cdot NH_2 \longrightarrow$$

$$Ar \cdot SO_2 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CMe_3$$
 (1)

of the polarity of the transition state, and by measurement of the sensitivity of the reaction to substituent effects, to estimate the degree of polarity and hence, by comparison with other systems, the extent of bond formation in the transition state.

Substituent effects in nucleophilic additions to olefins have been examined by several workers and, in two cases, the results are well correlated by the Hammett $\sigma\rho$ relationship. Addition of barbiturate anion to β nitrostyrenes gives ${}^2 \rho = +0.74$. In this reaction, it is at the carbon atom adjacent to the nitro-group that an increase in electron density in the transition state is to be expected, and the rather low sensitivity to substituent effects (expressed by the low value of ρ) is not unexpected. For addition of methoxide ion to *trans*-dibenzoylethylenes bearing substituents in both nuclei, the results ³ suggest a value of $\rho = 1$ for the aroyl substituent β to the site of addition.

A number of reports dealing with the electronic effects of substituents on reactivity and equilibria of sulphonyl

^{*} Present address: Department of Chemistry, King's College, London W.C.2.

 $^{^{1}}$ Part X, S. T. McDowell and C. J. M. Stirling, preceding Paper.

² M. J. Kamlet and D. J. Glover, *J. Amer. Chem. Soc.*, 1956, **78**, 4556.

³ T. I. Crowell, G. C. Helsley, R. E. Lutz, and W. L. Scott, *J. Amer. Chem. Soc.*, 1963, **85**, 443.

349

compounds have appeared. Hogeveen ⁴ derived $\rho =$ +0.33 from the dissociation constants of trans- β -arylsulphonylacrylic acids, and the value for arylsulphonylacetic acids 5 (+0.25) may be compared with that (+0.24) for β -arylpropionic acids.⁶ Deuterium-hydrogen exchange in a series of 3-arylsulphonylbicyclo-[2,2,1]hept-5-ene-2-carboxylic acids under basic conditions has been studied 7 and a value of $\rho = +2.8$ has been obtained for the reaction. The authors consider⁸ that a large degree of carbanionic character is developed at the carbon atom adjacent to the arylsulphonyl group in the transition state, and the generally rather



Hammett plot for the addition of t-butylamine to aryl vinyl sulphones

low values of ρ suggest that interpolation of a sulphonyl group between the nucleus and the reaction centre results in a considerable attenuation of the electronic effects of substituents. Cremonini and Maioli have 9 discussed the relationship between inductive and resonance effects in sulphonyl compounds.

In the present work, seven aryl vinyl sulphones have been allowed to react with t-butylamine in ethanol at 25°. Rates of reaction were measured as previously described;¹ t-butylamine was chosen so as to give a conveniently measurable rate of reaction over the entire series of sulphones; adverse steric effects in this amine considerably reduce its reactivity. In all cases, high yields of 1: 1-adducts between amine and sulphone were obtained (Table 4). Rate constants for the series are given in Table 1 and the Hammett plot is shown in the Figure.

Treatment of the results by the least-squares procedure gives a value of $\rho = +1.58$ (r = 0.99, s = 0.10) and confirms that the transition state is anionic. The p value can be compared with that for deuterium-

⁵ D. J. Pasto, D. McMillan, and T. Murphy, *J. Org. Chem.*, 1965, **30**, 2688.

⁶ P. R. Wells, *Chem. Rev.*, 1963, **63**, 171. ⁷ H. Hogeveen, G. Maccagnani, F. Montanari, and F. Taddei, J. Chem. Soc., 1964, 4101.

Professor F. Montanari, personal communication. C. Y. Meyers, B. Cremonini, and L. Maioli, J. Amer. Chem. Soc., 1964, 86, 2944.

hydrogen exchange⁷ on carbon adjacent to an arylsulphonyl group, a reaction centre very similar to that under discussion. We consider that our value of p indicates that considerable anionic character is developed

TABLE 1

Rate constants, k_2 (l. mole⁻¹ sec.⁻¹) for additions of t-butylamine to aryl vinyl sulphones

Substituent	$10^{3}k_{2}$	Substituent	$10^{3}k_{2}$					
p-NO2	$22 \cdot 4 \pm 0 \cdot 1$	None	1.58 ± 0.01					
<i>m</i> -MeSO ₂	$16\cdot 1 \pm 0\cdot 3$	p-Me •	0.86 ± 0.01					
<i>p</i> -Cl	3.78 ± 0.09	<i>p</i> -MeO	0.53 ± 0.01					
<i>m</i> -MeO	1.65 ± 0.03							
^a Experimental details in Part X. ¹								

at the carbon atom adjacent to the arylsulphonyl group. This has the corollary that, for a concerted reaction, the degree of β -C-N bond formation at the transition state is considerable, and the great sensitivity of the reaction to the steric requirements of both amine¹ and olefin 10 is accountable on this basis. Further, the entropies of activation for the reaction are very negative¹⁰ as expected for well advanced adduct formation between nucleophile and substrate.

EXPERIMENTAL

For general directions see Part X.¹

Preparation of Aryl Vinyl Sulphones.-The sequence: arenethiol \longrightarrow aryl 2-hydroxyethyl sulphide \longrightarrow aryl 2-chloroethyl sulphone —> aryl vinyl sulphone was used. A typical procedure is given for each step and the compounds prepared are tabulated.

(a) Thiols. p-Methoxybenzenethiol had b. p. 98-102°/ 12 mm., $n_{\rm p}^{19}$ 1.5812 (lit.,¹¹ b. p. 89-90°/5 mm., $n_{\rm p}^{19}$ 1.5801); m-methoxybenzenethiol, b. p. 126°/15 mm. (lit.,¹² b. p. 74.5°/2 mm.). *m*-Methylsulphonylbenzenethiol,¹³ obtained (62%) by reduction of the sulphonyl chloride 14 with lithium aluminium hydride had b. p. 145°/ 0.05 mm.

(b) Aryl 2-hydroxyethyl sulphides. m-Methoxybenzenethiol (0.1 mole) was added to sodium ethoxide (0.1 mole)in ethanol (150 ml.). 2-Chloroethanol (0.11 mole) was then added to the solution with stirring and the mixture was refluxed for 1 hr. The mixture was diluted with water (400 ml.), acidified, and extracted with dichloromethane. The extracts were washed with saturated aqueous sodium hydrogen carbonate, dried, and evaporated. Distillation of the residue gave the hydroxy-sulphide (66%), b. p. 117°/0.01 mm. (Found: C, 58.7; H, 6.7. C₉H₁₂O₂S requires C, 58.7; H, 6.55%).

Similarly prepared were the p-methoxy-derivative (63%), b. p. 106°/0·01 mm., $n_{\rm D}^{20}$ 1·5843, m. p. 40·5—41° (from diisopropyl ether) (Found: C, 58.7; H, 6.6. Calc. for $C_{9}H_{12}O_{2}S$: C, 58.7; H, 6.6%) (lit.,¹⁵ m. p. 42-43°); the

- S. T. McDowell and C. J. M. Stirling, following Paper.
 C. M. Suter and H. L. Hansen, J. Amer. Chem. Soc., 1932,
- 54, 4100. ¹² H. C. Godt and R. E. Wann, J. Org. Chem., 1961, 28, 4047. ¹³ H. C. Godt and R. E. Wann, J. Andersen J. Amer. Chem. Soc.,
- ¹³ F. G. Bordwell and H. M. Andersen, J. Amer. Chem. Soc., 1953, 75, 6019.
- ¹⁴ R. F. Twist and S. Smiles, J. Chem. Soc., 1925, 127, 1248.

¹⁵ D. J. Drain, J. G. B. Howes, R. Lazare, A. M. Salaman, R. Shadbolt, and H. W. R. Williams, J. Medicin. Pharmaceut. Chem., 1963, 6, 63.

⁴ H. Hogeveen, Rec. Trav. chim., 1964, 83, 813.

p-chloro-derivative ¹⁶ (88%), b. p. 158-159°/11 mm., $n_{\rm p}$ 1.6020;¹⁷ the *p*-nitro-derivative (91%), m. p. 58-59° (lit.,¹⁸ m. p. 62°).

(c) Aryl 2-chloroethyl sulphones. The hydroxy-sulphide (0.05 mole) was suspended in 5N-hydrochloric acid (120 ml.) and to the vigorously stirred mixture was added 10% aqueous sodium hypochlorite (0.1 mole) at such a rate that the temperature did not exceed 10°. After addition was acid, saturated aqueous sodium hydrogen carbonate, and dried. Evaporation of the solution yielded the vinyl sulphone. Details are given in Table 3.

Addition of t-Butylamine to Aryl Vinyl Sulphones.---The vinyl sulphone (0.001 mole) and t-butylamine (0.005 mole) were kept in ethanol (25 ml.) for 4 hr. at 25°. Evaporation of the solvent gave the adduct which was crystallised or distilled. Details are given in Table 4.

TABLE 2

Aryl 2-chloroethyl sulphones

	Yield	Found (%)					Required (%)	
Substituent	(%)	М. р.	С	н	Formula	С	н	
<i>p</i> -MeO	70	$54 - 55^{\circ}$	46.2	4.6	C ₉ H ₁₁ ClO ₃ S	46 ·1	4.7	
<i>m</i> -MeO	86	158°/0·01 mm.«	46.3	4 ·6	C ₉ H ₁₁ ClO ₃ S	46.1	4.7	
None	85	54-55			(Lit., ¹⁶ m. p. 54-55°)			
p-Cl	90	92			(Lit., ¹⁴ m. p. 96°)			
m-MeSO ₂	89	130132°	38.2	$3 \cdot 8$	C ₉ H ₁₁ ClÔ ₄ S ₂	38.2	3.9	
p-NO2	94	127			(Lit., 16 m. p. 128°)			
		● B. p			,			

TABLE 3

Aryl vinyl sulphones

	Yield	Found (%)					Required (%)	
Substituent	(%)	М. р.	С	н	Formula	С	н	
<i>p</i> -MeO	99	73·5-74°	54.7	4.95	C ₉ H ₁₀ O ₃ S	54.5	$5 \cdot 1$	
<i>m</i> -MeO	78	120/0·01 mm. ^a	54.3	4 ·8	$C_9H_{10}O_3S$	54.5	$5 \cdot 1$	
None	87	6768			(Lit.,* m. p. 68-70°)			
<i>p</i> -Cl	99	b	47.5	3.6	C ₈ H ₇ ClO ₂ S	47.4	3.5	
m-MeSO ₂	89	107.5 - 110	43 ·6	4.4	$C_9H_{10}O_4S_2$	43 ·9	4.1	
<i>p</i> -NO ₂	98	111.5-112	44 ·9	$3 \cdot 1$	C ₈ H ₇ NO ₄ S •	$45 \cdot 1$	3.3	

^a B. p. ^b B. p. 106-107°/0.06 mm., np²² 1.5694. ^c Found: N, 6.4; read. 6.6%.

* J. Heyna and W. Reimenschneider, G.P. 932,488.

TABLE 4

Adducts obtained from aryl vinyl sulphones and t-butylamine

	Vield		Found (%)				Required (%)		
Substituent	(%)	М. р.	c	Н	N	Formula	Ċ	Н	N
p-OMe	96	169/0.2 °	51.0	7.3	4.7	C1.H.,CINO,S	50.7	7.2	4.55
<i>m</i> -OMe	95	142-145 "	50.5	7.4	4 ⋅8	C ₁ ,H ₂ ,CINO,S ^b	50.7	$7 \cdot 2$	4.55
<i>m</i> -MeSO ₂	99	9899	48 ·9	6.7		C, H, NO, S,	48.9	6.6	
<i>p</i> -Cl	93	6668	$52 \cdot 1$	6.3	4.9	C ₁₂ H ₁₈ CINO,S	52.3	6.7	$5 \cdot 1$
p-NO ₂	99	124 - 125	50.2	6.25	10.0	$C_{12}H_{18}N_2O_4S$	50.3	6.3	9 ∙8
None	92	130/0.04 a	60·0	8.05	6.0	$C_{12}H_{19}NO_{2}S$	59 ·7	7.9	5.8
		- D							

^a B. p. ^b For hydrochloride.

complete, the product was extracted with dichloromethane and the extracts were washed with aqueous sodium sulphite and dried. Removal of the solvent yielded the chlorosulphone. Details are given in Table 2.

(d) Aryl vinyl sulphones. The chloro-sulphone (0.025 mole) and triethylamine (Na dried) (0.03 mole) in dry benzene (100 ml.) were stirred for 16 hr. at 20°. The precipitated triethylamine hydrochloride was filtered off and washed with benzene. The combined filtrate and washings were successively washed with 2n-hydrochloric

Kinetics .-- Reactions were followed by use of the thioladdition method described 1 previously. Mean values of rate constants are given in Table 1. Initial concentrations of sulphone were ca. 0.01-0.05M and of amine ca. 0.02-0.15м.

[6/1225 Received, September 29th, 1966]

- G. Baddeley and G. M. Bennett, J. Chem. Soc., 1933, 46.
 J. Heyna and W. Reimenschneider, G.P. 887,505.
- ¹⁸ G. M. Bennett and W. A. Berry, J. Chem. Soc., 1927, 1666.