113/REACTIVITY OF VINYL SULPHONIC ESTERS. XVII. THE SOLVOLYTIC BEHAVIOUR OF β-ARYLOXYVINYL SULPHONATES (+)

UMBERTO TONELLATO (°) and GIUSEPPE VERSINI
Centro Meccanismi di Reazioni Organiche del CNR;
Istituto di Chimica Organica dell'Università, Padova

Summary. — The solvolysis of β-aryloxyvinyl sulphonates [V] in dry ethanol gives mainly benzil, phenol, and sulphinic acid derivatives. The kinetic study shows that substituent effects on rate and activation parameters are quite different from those observed in the S_N1-type solvolysis of the analogous β-thio- and β-aminovinyl sulphonates thus suggesting the presence of a different, perhaps homolytic, reaction mechanism.

Riassunto. — I solfonati β-arilossivinilici [V] danno, per solvolisi in etanolo anidro, derivati del benzile, del fenolo e dell'acido solfinico, come prodotti più abbondanti. I dati cinetici indicano che sia gli effetti dei sostituenti, sia i parametri di attivazione sono nettamente diversi da quelli osservati nell'etanolisi di tipo S_N1 dei solfonati β-tio- e β-amminovinilici ad analoga struttura e suggeriscono l'insorgere di un diverso meccanismo di reazione, probabilmente di carattere omolitico.

Previous studies (1) showed that the solvolytic reactivity of vinyl sulphonic esters of general structure [I] may be strongly influenced by the nature of β-substituents *Y*. Thus on the one hand, when *Y* = SR, S*Ar*, I, and (to a minor extent) Br, anchimeric assistance effects (2-4) promote a remarkable rate acceleration in the heterolytic fission of the carbon-oxygen bond leading to the formation of a vinyl cation and sulphonate anion [II]; on the other hand, when *Y* = N(*Me*)*Ar*, electronic conjugative assistance (5)

(°) To whom correspondence should be addressed: Istituto di Chimica Organica, Via Marzolo 1, 35100 Padova.

(+) For Part XVI, see P. Bassi, U. Tonellato, *J. Chem. Soc. Perkin II*, 1283 (1974).

(1) G. Modena, U. Tonellato, *Adv. Phys. Org. Chem.*, **9**, 185 (1971); *Chimica e Industria*, **56**, 207 (1974).

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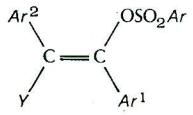
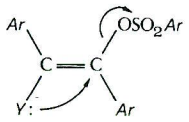
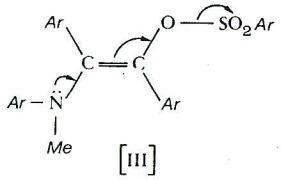
by the nitrogen atom favours, at least in dry ethanol, oxygen-sulphur heterolysis to give a sulphinate anion [III]:



[I]



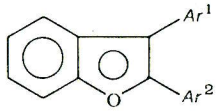
[II]



[III]

We present the results of an investigation on the solvolytic behaviour of β-aryloxyvinyl sulphonate [I] ($Y = OAr$) aimed at comparing the effect of oxygen to that of nitrogen and sulphur atoms.

In a previous work (6), β-aryloxyvinyl esters were found to react, in inert solvents in the presence of boron trifluoride, to give benzo[*b*]furans [IV] in a cyclisation reaction similar to that observed for the β-arylthio- and β-arylaminovinyl (7) esters presumably occurring *via* a vinyl cation intermediate. However, evidence was reported against any significant participation of the ether oxygen in this process.

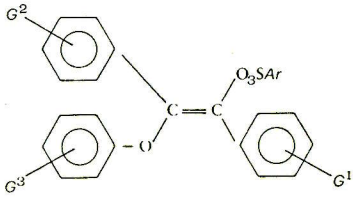


[IV]

Ethanol was chosen in the present study as the solvent where a "sulphonate" type mechanism [II] followed by the β-thiovinyl esters and a "sulphinate" type mechanism [III] followed by the β-amino analogues could be clearly discriminated (5).

RESULTS AND DISCUSSION

Esters [V] of table 1 were synthesized following a described method (6). The *trans* geometry was assigned to the major isomeric product of the synthesis; minor amounts of the *cis* isomer were also obtained and in one case this has been isolated.

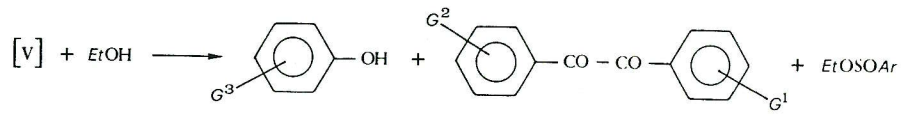


[V]

Esters [V] react in dry ethanol only well above 120 °C. The products isolated and identified after five half-lives from *p*-bromobenzenesulphona-

(6) G. Capozzi, G. Modena, *J. Chem. Soc. Perkin I*, 216 (1972).
(7) G. Capozzi, G. Modena, L. Ronzini, *J. Chem. Soc. Perkin I*, 1136 (1972).

tes [V] ($G^1=G^2=G^3=H$) and [V] ($G^1=G^3=p-Me$; $G^2=H$) at 140 °C account for *ca.* 60% of the reacted ester as in eq. [1]:



[1]

Small amounts (3–5%) of the *cis* isomer and sulphonic acid were also present, among other products. Free sulphinic acid was absent but blank experiments proved that it is unstable in these reaction conditions. Benzo-[*b*]furan and benzoin derivatives ([5]) were not detected. The product distribution was not affected by the presence of air.

There is a definite analogy between the products of the ethanolysis of [V] and those obtained ([5]) from the β-arylamino analogues in the same solvent, *i.e.* benzil, aniline and sulphinic acid derivatives. These products would suggest that a " sulphinate " type heterolytic mechanism operates also in the case of esters [V]. Kinetic data are however quite different.

The first order rate law was obeyed up to at least 70% reaction and data shown in table 1 are reproducible within the estimated error (±5–6%). Air, base (*Et*ONa) up to 3×10^{-4} *M*, benzoyl peroxide and hydroquinone do not appreciably affect the rate.

TABLE 1. – RATE COEFFICIENTS FOR THE ETHANOLYSIS OF ESTERS [V] AT 140.6 °C

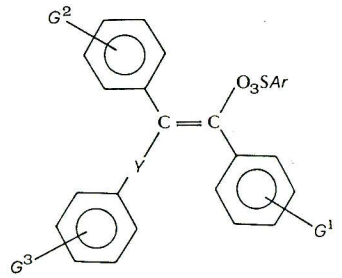
O_3SAr ([a])	G^1	G^2	G^3	$k\times10^5$, sec^{-1}
BS	H	H	H	2.15 ([b]) ([c])
TS	H	H	H	2.3
BS	*p-Me*	H	H	2.2
TS	*p-Me*	H	H	2.53
BS	*p*-Cl	H	H	2.15
BS	H	*p-Me*	H	3.6
BS	H	*m*-Cl	H	1.3
BS	H	H	*p-Me*	2.75
BS	H	H	*p*-Cl	1.4
BS	H	H	*m*-Cl	1.1

([a]) BS = *p*-bromobenzenesulphonate; TS = *p*-toluensulphonate. ([b]) 0.92 at 133.3 °C; 7.40 at 152 °C. ([c]) 0.45 for the *cis* isomer.

As shown in table 2, the effects of structural changes, in particular that at the sulphonate residue, on the rate and the activation parameters observed for the solvolysis of β-aryloxyvinyl sulphonates are substantially different from those obtained for the β-arylamino and β-arylthio analogues. On the whole, the reaction rate is only slightly enhanced by electron donation from β-substituents but the magnitude of the effects, as indicated by the appro-

ximate ρ values of table 2, is too small to support a polar transition state for any type of ionic mechanism ([1,8]), including addition-elimination processes ([9]).

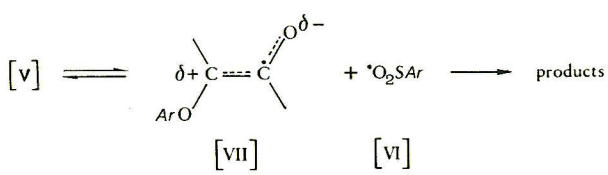
TABLE 2. – SUBSTITUENT EFFECTS AND ACTIVATION PARAMETERS (APPROXIMATE VALUES) FOR THE SOLVOLYSIS OF SULPHONATE ESTERS OF STRUCTURE



Y	ρ ([a])			k_{BS}/k_{TS}	*Ea* (kcal mole^{-1})	$\Delta S^{\neq}$ (cal mole^{-1} °K^{-1})
	G^1	G^2	G^3			
S ([b])	—2.3 ([c])	—1.2	—1	3.1	26	—10
N*Me* ([d])	0	—0.6	—2.2	2.9	27	— 4
O ([e])	0	—0.6	—0.7	1.0	38	+ 9.5

([a]) Hammett's reaction constant. ([b]) In acetic acid at 110 °C ([3]); unpublished data in ethanol accord with those obtained in acetic acid. ([c]) By the use of σ^+ constants. ([d]) At 90 °C in ethanol ([5]). ([e]) At 140.6 °C in ethanol.

The products and kinetic data not exclude the presence of a fragmentation reaction proceeding *via* the homolytic fission of the oxygen-sulphur bond, to give a sulphonyl [VI] and an enol radical [VII], of the type proposed by Frydman and Mazur ([10]) for the thermal rearrangement of vinyl sulphonates [VIII] to β-ketosulphones [IX]. However, the latter reaction proceeds *via* a free radical chain mechanism (eq. [2]) which cannot be invoked in our case. According to the above authors, the chain reaction is no longer possible when the β-carbon of the vinyl sulphonate possesses substituents



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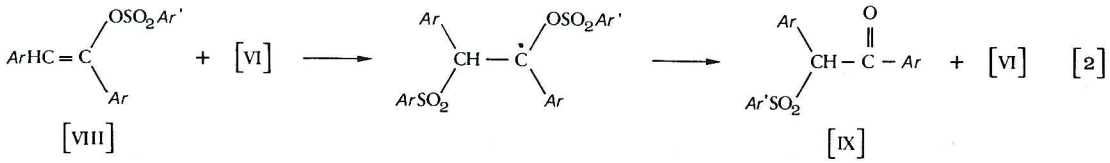
([9]) P. E. Peterson, J. M. Indelicato, *J. Amer. Chem. Soc.*, **90**, 6515 (1968).

([10]) N. Frydman, Y. Mazur, *J. Amer. Chem. Soc.*, **92**, 3203 (1970).



[VIII] [IX]

bulkier than hydrogen, due to the stereochemical inaccessibility to an attack by the sulphonyl radical [VI]. The exact nature of the reaction mechanism followed by esters [V] is of interest and will be the object of further study.

The facts to date quite clearly indicate that the β-aryloxy substituent retards any type of S_N1 mechanism because of its electron-withdrawing effect ([11]). This is not compensated for by anchimeric or conjugative assistance due to the oxygen atom, at variance with what has been observed in the case of sulphur, nitrogen and heavy halogens and, at least under the conditions chosen, a different mechanism prevails. These facts once again point to the variety of the reaction paths available to vinyl sulphonic esters.

EXPERIMENTAL

The synthesis of esters [V] by sulphonylation of the corresponding 2-aryl-2--aryloxyacetophenones in the presence of sodium hydride has been described ([6]).

The aryloxyketones were prepared following a published procedure ([12]) in 67–75% yield. The new products (all $C_{20}H_{15}O_2Cl$) were: *2-m-chlorophenyl-2-phenyloxyacetophenone*, m.p. = 73–5 °C; elemental analysis, found % (calcd for $C_{20}H_{15}O_2Cl$): C 74.15 (74.42); H 4.65 (4.68); Cl 11.15 (10.98). *2-m-Chlorophenyloxy-2-phenylacetophenone*, m.p. = 61–2 °C; elemental analysis, found %: C 74.1; H 4.75; Cl 10.95. *2-p-Chlorophenyloxy-2-phenylacetophenone*, m.p. = 91–2 °C; elemental analysis, found %: C 74.05; H 4.95; Cl 11.05.

The sulphonates [V] not described were obtained in moderately low yield (10–30%). The products were obtained in one geometric form by means of chromatography of the crystallised ester on a silica gel column, using mixtures of pentane and CH_2Cl_2 or *Me*OH as eluant and further crystallisation from *Me*OH. Analytical data are in table 3.

Solvolysis products

A solution of 0.50 g of *p*-bromobenzenesulphonate, [V] ($G^1=G^2=G^3=H$), in 200 ml of *Et*OH were sealed in a glass ampoule and heated at 140.6 °C for 56 h. Following a described procedure ([5]), from the reaction mixture the following products were isolated and identified: benzil (120 mg, 57%) by comparison of its IR spectrum with that of an authentic sample; ethyl *p*-bromobenzenesulphinate, [145 mg, 60%, oil ([13])], from its IR [CCl_4, ν(SO) = 1142 cm^{-1}] and ^1H-NMR spectrum [CCl_4, signals at τ: 2.4 (m, 4H), 5.83–6.34 (apparent quartet of quartets, *AB* part of an

([11]) G. Kohnstam, D. L. H. Williams in "The Chemistry of Ether Linkage", S. Patai Ed., Interscience, London, 1967, p. 81.

([12]) M. G. Richard, *Compt. Rend.*, **198**, 1242 (1934).

([13]) M. Kobayashi, M. Terao, A. Yamamoto, *Bull. Chem. Soc. Japan*, **39**, 802 (1966).

TABLE 3. – PHYSICAL AND ANALYTICAL DATA FOR NEW ESTERS [V]

G^1	G^2	G^3	O_3SAr	M.p. (°C)	Formula	Elemental analysis (a)				
						C	H	Br	Cl	S
H	H	H	BS (b)	165–166	$C_{26}H_{19}BrO_4S$	61.95 (61.54)	3.85 (3.73)	15.35 (15.75)		6.22 (6.32)
H	H	H	TS (c)	130–131	$C_{27}H_{22}O_4S$	73.05 (73.28)	5.9 (6.01)			7.05 (7.24)
p-*Me*	H	H	TS (d)	133–134	$C_{28}H_{24}O_4S$	73.35 (73.66)	5.50 (5.29)			6.92 (6.92)
p-Cl	H	H	BS	169–171	$C_{26}H_{18}BrClO_4S$	57.56 (57.63)	3.32 (3.35)		21.15 (21.28)	6.32 (5.92)
H	*m*-Cl	H	BS	142–144	$C_{26}H_{18}BrClO_4S$	57.3 (57.63)	3.45 (3.35)		21.25 (21.28)	6.0 (5.92)
H	H	*m*-Cl	BS	148–150	$C_{26}H_{18}BrClO_4S$	56.95 (57.63)	3.45 (3.35)		21.65 (21.28)	6.25 (5.92)
H	H	*p*-Cl	BS	135–136	$C_{26}H_{18}BrClO_4S$	56.85 (57.63)	3.35 (3.35)		21.3 (21.28)	6.3 (5.92)

(a) Calculated values in parentheses. (b) *cis* isomer. (c) ^{1}H-NMR signals (CS_2) at τ: 2.5–3.3 (m, 19H) and 7.95 (s, 3H) ppm.
(d) ^{1}H-NMR signals (CS_2) at τ: 2.7–3.2 (m, 18H), 7.91 (s, 3H) and 7.97 (s, 3H) ppm.

ABX_3 system, 2 diastereotopic H, $—CH_2—$) and at 8.72 (t, 3H)] analogous in the ethyl region to that of an authentic sample of ethyl *p*-toluensulphinate; phenol (48 mg, 38%); *p*-bromobenzenesulphonic acid (*ca.* 20%) and unreacted ester [V], mostly in the "*cis*" form, by IR (0.25 mg, 5%). At least three other products were detected but not identified.

From 0.510 g of *p*-bromobenzenesulphonate, [V] ($G^1=G^3=p—Me$; $G^2=H$), by the same procedure, the following products were isolated and identified: *p*-methylbenzil (125 mg, 63%) by comparison of its IR and ^{1}H-NMR spectrum with that of an authentic sample; *p*-ethyl-*p*-bromobenzenesulphinate (135 mg, 60%) as said above; *p*-cresol (51 mg, 53%); *p*-bromobenzenesulphonic acid (26%) and unreacted ester (30 mg, almost equivalent amounts of the two isomers).

KINETICS

Samples of a solution of the ester (*ca.* 8×10^{-5} *M*) in *Et*OH were sealed under a nitrogen atmosphere in carefully cleaned glass vials (5 ml). These were heated in a thermostatted oil bath of ±0.2 °C temperature accuracy and taken out at appropriate intervals. The disappearance of the substrate was followed by measuring, at 25 °C, the decrease of an absorption band in the range 275–295 nm, characteristic of each ester under study, by means of a "Gilford" 2400 spectrophotometer. Rate constants were calculated by applying the integrated first-order equation using a least-squares computer program.

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