# Reactivity of Vinyl Sulphonic Esters. Part VI.[1] $S_N1$-Type Reactivity of 1,2-Diphenyl-2-phenylthiovinyl and Triphenylvinyl Derivatives: Anchimeric Assistance due to the β-Sulphur Atom.[2]

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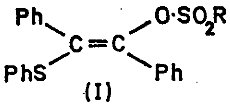
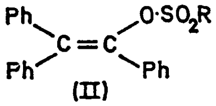
The kinetic responses of *trans*-1,2-diphenyl-2-phenylthiovinyl sulphonates (I) and of the analogous triphenylvinyl derivatives (II) in $S_N1$ processes are directly compared and anchimeric assistance effects in the case of the former esters are evaluated. Rate factors, $k_{(I)}/k_{(II)}$, ranging between 16 and 33 are observed in a variety of conditions and estimated as the lower limits of rate enhancements due to β-sulphur anchimeric assistance. The rather small kinetic effect due to β-sulphur assistance in, as well as the absence of β-aryl assistance from, $S_N1$-type reactions of derivatives (I) and (II) are probably due to the ' levelling ' effect of the α-aryl residue but other factors, such as the inherent difficulty of an intramolecular nucleophilic attack in the plane of the ethylenic system, may be involved.

THIS paper compares the kinetics of reactions of *trans*-1,2-diphenyl-2-phenylthiovinyl sulphonic esters (I) and their triphenylvinyl analogues (II) with the aim of defining the extent, if any, of anchimeric assistance due to the sulphur atom of the β-phenylthio-group in $S_N1$ processes.



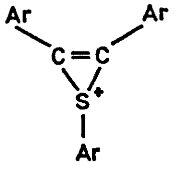
(I)



(II)

(a, R = 2,4,6-trinitrophenyl; b, R = tolyl; c, R = *p*-bromophenyl)

The unimolecular reactivity of ester (Ia) and substituted derivatives in solvolytic as well as in inert solvents has been reported.[1,3] The stereochemical course of the solvolysis (' retention ' of configuration) and the rearrangements due to β-arylthio-migration across the double bond observed in the final reaction products, led us to the conclusion that β-sulphur participation is involved at some stage. We also suggested[4] that the structure of the intermediate cation is that of a thiirenium ion (III) or close to that.



(III)

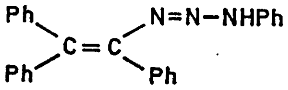
The kinetic determination of the effects of substituents on the various aryl residues of the esters (Ia) showed that electron-donating substituents on the β-phenylthio-ring are rather effective ($\rho = -1{\cdot}45$, nitromethane at 25 °C) and, in particular, more effective than those on the β-phenyl ring ($\rho = -1{\cdot}25$) in promoting the reaction rate. On the basis of this and other arguments, we suggested[3a] a quasi-cyclic transition-state geometry in which a filled orbital of the β-sulphur partially overlaps with the developing empty *p*-orbital at the α-vinylic carbon atom. This picture demands that rate enhancement for (I) relative to a structurally analogous unassisted system be verified.

Model compounds (II) are apparently adequate in this respect. Extensive work by Rappoport and his co-workers[5] has recently excluded any β-aryl anchimeric assistance effect in unimolecular solvolyses of triarylvinyl derivatives.

## RESULTS

Esters (I) were prepared by addition of benzenesulphenyl sulphonate to diarylacetylenes.[6]

Esters (II) were synthesized by decomposition[7,8] of 1-(triphenylvinyl)-3-phenyltriazene (IV) in the presence of the appropriate sulphonic acid.



(IV)

*Kinetics*.—Esters (I) and (II) react, under the conditions listed in Tables 1 and 2, by first-order kinetics up to at least 70%. The rates were measured by means of conductometry or spectrophotometry in the case of trinitrobenzenesulphonates and by a titrimetric method in the case of toluene-*p*-sulphonates and *p*-bromobenzenesulphonates. The estimated errors in the rate constants in the last case were rather high (±5%) since, owing to the low solubility, material for every kinetic point was weighted independently. Kinetic experiments carried out in 4 : 1 ethanol–water and in acetic acid in the case of esters (Ib), (Ic), and (IIb) showed that addition of base affects only very little the rate of solvolysis. The rate constants for the acetolysis of esters

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[1] Part V, G. Modena and U. Tonellato, *J. Chem. Soc.* (*B*), 1971, 381.

[2] Presented, in part: G. Modena and U. Tonellato, *Boll. Sci. Fac. Chim. Ind. Bologna*, 1969, **27**, 373.

[3] (*a*) Part IV, G. Modena and U. Tonellato, *J. Chem. Soc.* (*B*), 1971, 374; (*b*) Part III, G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc.* (*C*), 1970, 2625.

[4] G. Capozzi, G. Melloni, G. Modena, and U. Tonellato, *Chem. Comm.*, 1969, 1520.

[5] (*a*) Z. Rappoport and A. Gal, *J. Amer. Chem. Soc.*, 1969, **91**, 5246; (*b*) Z. Rappoport and J. Kaspi, *ibid.*, 1970, **92**, 3220; (*c*) Z. Rappoport and Y. Apeloig, *Tetrahedron Letters*, 1970, 1817.

[6] Part I, G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc.* (*C*), 1970, 2617.

[7] (*a*) W. M. Jones and D. D. Maness, *J. Amer. Chem. Soc.*, 1969, **91**, 4134; (*b*) W. M. Jones and D. D. Maness, *ibid.*, 1970, **92**, 5427.

[8] W. M. Jones and F. M. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 1960.

(IIb) are in good agreement with those reported by Jones and Maness.[7]

A direct comparison of the reactivity of esters (I) and (II) in several solvents and conditions shows that β-thiovinyl esters (I) are in each case more reactive than vinyl esters (II) (see the last column of Table 1 for relative rates). Table 1 also shows that *p*-bromobenzenesulphonate (Ic) reacts more rapidly than toluene-*p*-sulphonate (Ib) by a factor of 3·4 in acetic acid at 151 °C and of 4·5 in 4 : 1 ethanol–water at 130·5 °C.

Table 2 shows that electron-donating substituents in both α- and β-phenyl rings of ester (Ic) enhance the rate of acetolysis: the 1,2-dianisyl derivative reacts about 150 times more rapidly than the 1,2-diphenyl analogue. As expected, the effect on rate is greater for substituents on the α-phenyl ring (Y) than for those in the β-phenyl (Z). Although the range of substituents considered is limited, rate data for the terms with substituents on the α-phenyl ring fit the Hammett relationship with use of σ+ values and ρ is −2·3 (correlation coefficient = 0·9992). When temperature difference is allowed for, this value is comparable with that found for substituted esters (Ia) (−2·85 in nitromethane at 25 °C).

TABLE 1

Rate coefficients [a] ($10^5k$/s$^{-1}$) and activation parameters for esters (I) and (II)

| Ester | Solvent [b] | 15 °C | 25 °C | 35 °C | 45 °C | $E_a$ [c] kcal mol$^{-1}$ | $\Delta S^{\ddagger}$ [d] cal mol$^{-1}$ K$^{-1}$ | $k_{(I)}/k_{(II)}$ at 25 °C |
|---|---|---|---|---|---|---|---|---|
| (Ia) | N | 7·12 | 34·4 | 101·2 | | 23·4 | +2 | |
| | N–M 19 : 1 | | 38·3 | | | | | |
| | M | | 13·8 | 39·4 | 153 | 22·6 | −2·5 | |
| | AcOH | | 4·68 | 16·6 | 61·5 | 24·4 | +1·3 | |
| (IIa) | N | | 1·54 | 4·83 | | 22·0 | −11·0 | 22·3 |
| | N–M 19 : 1 | | 1·83 | | | | | 21 |
| | M | | 0·68 | | | | | 20·1 |
| | AcOH | | 0·14 | 0·508 | 1·91 | 24·7 | −4·7 | 33·4 |
| | | 130·5 °C | 140 °C | 151 °C | 160 °C | | | at 151 °C |
| (Ib) | AcOH | 13·4 | 30·3 | 78·5 [e] | | 29·3 | −6 | |
| | E–W 4 : 1 | 16·1 [f] | | | | | | |
| (IIb) | AcOH | | 2·30 | 5·01 [g] | 11·2 | 26·9 | −16 [h] | 15·6 |
| (Ic) | AcOH | 44·4 | 100·5 | 265·0 [i] | | 29·6 | −3·2 | |
| | E–W 4 : 1 | 73·7 [j] | | | | 25·8 | −11 [k] | |

[a] Average of two or more kinetic runs. [Ester] = 1—6 × 10$^{-3}$M. [b] N = nitromethane, M = methanol, E = ethanol, W = water, AcOH = acetic acid. [c] Estimated errors: ±0·7 kcal mol$^{-1}$ for esters (Ia) and (IIa) and ±1 kcal mol$^{-1}$ for esters (Ib), (IIb), and (IIc). [d] At 25 °C for esters (Ia) and (IIa); estimated error: ±2 cal mol$^{-1}$ K$^{-1}$. At 151 °C ester (Ib) and (IIb); estimated error: ±3·5 cal mol$^{-1}$ K$^{-1}$. [e] 81·3 with added NaOAc (0·049M). [f] 17·2 with added NaOH (0·048). [g] 5·12 with added NaOAc (0·049M); 5·18 according to ref. 7. [h] 20·5 according to ref. 7*b*. [i] 279 with added NaOAc (0·049M). [j] 2·0 at 90 °C and 12·9 at 110 °C. [k] At 130·5 °C.

TABLE 2

Substituent effects on the rate of acetolysis of substituted esters (Ic), $Z{-}C_6H_4(PhS)C{:}C(O{\cdot}SO_2{\cdot}C_6H_4Br\text{-}p)C_6H_4{-}Y$, at 110 °C

| Y | H | *p*-Me | *p*-Me | *p*-MeO | *p*-MeO |
|---|---|---|---|---|---|
| Z | H | H | *p*-Me | H | *p*-MeO |
| $10^4k$/s$^{-1}$ [a] | 0·65 | 3·1 | 5·1 | 39·0 | 95·0 |

[a] Average of two or more kinetic runs.

*Reaction Products*.—The products of solvolysis of ester (Ia) in a variety of media have been investigated by us [3a] and those of acetolysis of ester (IIb) at 150·9 °C by Jones and Maness.[7]

The reaction products of the other compounds studied in this work have not been investigated in much detail. The products identified, reported in the Experimental section, are consistent with the hypothesis of a unimolecular reaction mechanism. In fact, in nucleophilic solvents, esters (I) and (II) yield mainly ketones (V) and (VI) respectively

Ph(PhS)CH·COPh
(V)

$Ph_2CH{\cdot}COPh$
(VI)

together with (or instead of) the expected substitution products. In anhydrous solvolytic media, ketones (V) and (VI) are likely to be formed by acid-catalysed decomposition [1,5a] of the primary solvolysis products as shown in the case of ketone (VI). On the other hand, in an inert solvent like nitromethane, the vinyl cation from ester (IIa) cannot be quenched by nucleophiles and a wide spectrum of compounds is formed.

## DISCUSSION

*Reaction Mechanism*.—The unimolecular mechanism by which esters (I) and (II) react in inert and solvolytic solvents has been discussed by us [3] for esters (Ia) and by others [5,7] for ester (IIb) and related compounds.

For esters (I) and (II) not previously investigated, consideration of the nature of the reaction products and of the kinetic effects due to structural variations, solvent properties, and addition of base, following criteria generally used and discussed,[3,5,7,9,10] leaves little doubt on the generality of the unimolecular mechanism already suggested.

Further support for this hypothesis is given by the reactivity ratio of (Ic) to (Ib), corresponding to positive ρ values [5b] for substituents on the leaving group, which

[9] See, for a review: (*a*) M. Hanack, *Accounts Chem. Res.*, 1970, **2**, 209; see also (*b*) Z. Rappoport, T. Bässler, and M. Hanack, *J. Amer. Chem. Soc.*, 1970, **92**, 4985.

[10] (*a*) C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell Univ. Press, Ithaca, New York, 2nd edn., 1969; (*b*) C. A. Bunton, 'Nucleophilic Substitution at a Saturated Carbon,' Elsevier, London 1963, vol. I, p. 118.

rules out the electrophilic addition–elimination mechanism[11] recently advocated as an alternative to unimolecular heterolysis. The leaving-group effect is particularly pronounced on going from esters (Ib) and (IIb) to (Ia) and (IIa). The relative rates at 25 °C for toluene-*p*-sulphonate, trinitrobenzenesulphonate, and trifluoromethanesulphonate of type (II) are 1, 26,000, and 81,000 (data of ref. 7*b* and Table 1). Clearly the trinitrobenzenesulphonic group has leaving-group properties comparable with those of the exceedingly reactive trifluoromethanesulphonic group which has become fashionable in the study of vinyl cations.[12]

*Anchimeric Assistance.*—The simple approach to a quantitative definition of anchimeric assistance due to the β-sulphur, by comparing rate data of 1,2-diphenyl-2-phenylthiovinyl sulphonates with those of the corresponding triphenyl vinyl esters, faces the figures reported in Table 1. The 'raw' rate enhancements are certainly not spectacular (factors of 20 to 33 for trinitrobenzenesulphonates at 25 °C and of 16 for toluene-*p*-sulphonates at 151 °C) and one may wonder whether the 'true' values, when corrected for inductive and steric effects, are meaningfully large enough to define any anchimeric assistance at all.

Before trying to evaluate these corrections, we first discuss qualitative evidence of anchimeric assistance provided by the present study and complementing those anticipated in a previous paper.[3a] The substituent effects on the rate of acetolysis at 110 °C of *p*-bromobenzenesulphonates (Ia) show that electron-donating substituents in the α-phenyl ring are very effective in promoting the rate of solvolysis ($\rho = -2{\cdot}3$). The effect is, however, not as large as that found for the analogous triarylvinyl sulphonates. Rappoport and Kaspi[5b] reported that triphenylvinyl toluene-*p*-sulphonate is 830-fold less reactive than 1-anisyl-2,2-diphenylvinyl toluene-*p*-sulphonate (7 : 3 acetone–water at 120 °C). Such a rate difference would give a ρ value of $-3{\cdot}7$ ($\sigma^+$). On the other hand, the effect of substituents on the β-phenyl ring of esters (Ia) is greater than that observed in solvolyses of triarylvinyl sulphonates[5b] and halides.[5a] These arguments support the hypothesis of a quasi-cyclic transition state geometry in which the positive charge developing at the α-carbon is more delocalized in the rest of the molecule than in the transition state leading to the linear[13] triarylvinyl cations.

Activation entropies are less negative in the case of esters (I) than esters (II) in consonance with the observed trend for assisted and unassisted processes.[14] Apparently, the degree of anchimeric assistance (Table 1) is larger for acetolysis than for methanolysis and, in general, the rate of reaction of assisted esters (I) (see Table 1) is insensitive to the nucleophilic properties of the solvent, as expected.[15]

With the support of the above arguments, a more quantitative analysis of the kinetic data requires an evaluation of inductive and steric effect.

Inductive effects due to changes around the β-carbon atom in the two systems cannot alone be responsible for the 'raw' rate enhancements observed. First, the effect of changes at the β-carbon atom in unassisted $S_N1$ vinylic processes is usually very small.[5a,16,17] Secondly and more important, the phenylthio-group is, slightly more electron-attracting than the phenyl group as indicated by the available positive σ(PhS) values[18] being higher than those reported[19] for the phenyl. As a consequence of the predictable inductive effect alone, a small retardation instead of the observed rate increases should be measured in the case of β-phenylthiovinyl derivatives.

Evaluation of steric effects in unimolecular vinylic reactions, on the basis of the data at disposal, is not easy. Kelsey and Bergman[20] suggested that the different rates of silver-catalysed acetolysis of *cis*- and *trans*-cyclopropyl-1-iodo-1-propene ($k_{cis}/k_{trans} = 9{\cdot}5$) is due to relief of steric strain between the α-cyclopropyl and the β-methyl residue as the cation approaches linearity. Similar arguments have been more recently advanced by Rappoport and Atidia[21] to rationalize the relative reactivity of the isomeric 1,2-dianisylvinyl bromides ($k_{cis}/k_{trans} = ca.\ 20$) in acetic acid. On the other hand, very small rate differences (factors of less than 2) have been observed on going from β-unsubstituted to the more crowded ββ'-diaryl-[5a,b] or ββ'-dimethyl-vinyl systems[22] bearing a large α-substituent and the changes in reactivity are those expected on the basis of inductive rather than steric effects. In the present case, the bulkiness of sulphur and phenyl should be compared. Although an exact evaluation is difficult, it seems unlikely that the different steric requirements of the two groups are sufficiently large to determine sizable rate difference between esters (I) and (II).

We conclude that (*a*) the rate enhancements observed are due to anchimeric assistance by the sulphur atom of the phenylthio-group and (*b*) the 'true' rate enhancements are *at least* as great as the 'raw' values, because of unfavourable inductive effects.

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[11] P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, 1968, **90**, 6515; W. M. Schubert and G. W. Barfknecht, *ibid.*, 1970, **92**, 207.

[12] P. J. Stang and R. H. Summerville, *J. Amer. Chem. Soc.*, 1969, **91**, 4600; M. A. Inhoff, R. H. Summerville, P. v. R. Schleyer A. G. Martinez, M. Hanack, T. E. Deuber, and P. J. Stang, *ibid.*, 1970, **92**, 3802.

[13] Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, 1969, **91**, 6734.

[14] See, *e.g.*, S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, 1956, **78**, 4801; D. J. Cram and L. A. Singer, *ibid.*, 1963, **85**, 1075; C. J. Lancelot and P. v. R. Schleyer, *ibid.*, 1969, **91**, 4291.

[15] S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 1953, **75**, 147.

[16] L. L. Miller and G. A. Kaufman, *J. Amer. Chem. Soc.*, 1968, **80**, 7282.

[17] C. A. Grob and G. Cseh, *Helv. Chim. Acta*, 1964, **47**, 194.

[18] H. Szmant and G. Suld, *J. Amer. Chem. Soc.*, 1956, **78**, 3400; C. Y. Meyers, *Gazzetta*, 1963, **93**, 1206; H. Hogeveen, *Rec. Trav. chim.*, 1964, **83**, 813.

[19] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' John Wiley and Sons, New York, 1963.

[20] D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, 1970, **92**, 228.

[21] Z. Rappoport and M. Atidia, *Tetrahedron Letters*, 1970, 1817.

[22] C. A. Grob and R. S. Spaar, *Tetrahedron Letters*, 1969, 1439.

Rate changes due to β-sulphur participation are small when compared with those reported for saturated systems [23] (factors of $10^3$ for the β-arylthioethyl halides). Moreover, anchimeric assistance by the β-aryl group is totally absent from the case of triarylvinyl compounds whereas large kinetic effects have been observed in the solvolysis of ββ'-diphenylethyl and neophyl derivatives.[5a, 23]

The absence of effective neighbouring-group assistance on the rate of solvolysis of α-arylvinyl derivatives may well be due to the effect of the adjacent aromatic nucleus which can effectively supply electrons to the reaction centre and hence diminish the demand of intramolecular nucleophilic assistance. The large ' levelling ' effect of an α-aryl residue in saturated systems has been recently demonstrated.[24]

However, other factors may be important in the case of vinyl substrates. Intramolecular nucleophilic attack by the neighbouring group at the reaction centre, necessarily in the plane of the ethylenic system, may not occur (as in the case of intermolecular displacements [25]) before the valence state arrangement of the α-carbon is sufficiently changed from $sp^2$ to $sp$, whereas intramolecular as well as intermolecular nucleophilic displacements in saturated systems can occur at an $sp^3$-hybridized carbon. Moreover, overlap of available occupied orbitals of the β-group with the new empty *p*-orbital of the α-carbon atom requires a more severe bond-angle distortion than in the saturated analogues. As a result, the neighbouring-group intervention may be quite late in the reaction co-ordinate and, in most cases, irrelevant in the transition state of the reaction. As the reaction proceeds and the empty *p*-orbital at the α-carbon develops, then interaction may occur and lead to stereochemical and migratory effects.

TABLE 3

Physical and analytical data of esters (I), $Z{\cdot}C_6H_4(C_6H_5S)C{:}C(O_3SR\text{-}p)C_6H_4{\cdot}Y$

| Ester | | | | Found % | | | | | Required % | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Z | Y | R | M.p./°C | C | H | Br | S | Formula | C | H | Br | S |
| H | H | $Me{\cdot}C_6H_4$ | 139—140 | 70·95 | 4·95 | — | 14·15 | $C_{27}H_{22}O_3S_2$ | 70·7 | 4·85 | — | 14·0 |
| H | Me | $Br{\cdot}C_6H_4$ [a] | 158—159 | 60·5 | 4·2 | 14·7 | 11·8 | $C_{27}H_{21}BrO_3S_2$ | 60·35 | 3·95 | 14·9 | 11·95 |
| Me | Me | $Br{\cdot}C_6H_4$ [b] | 129 | 61·05 | 4·3 | 14·6 | 11·7 | $C_{28}H_{23}BrO_3S_2$ | 61·0 | 4·2 | 14·5 | 11·65 |
| H | OMe | $Br{\cdot}C_6H_4$ [c] | 129—131 | 58·45 | 3·85 | 14·65 | 11·4 | $C_{27}H_{21}BrO_4S_2$ | 58·6 | 3·8 | 14·45 | 11·6 |
| OMe | OMe | $Br{\cdot}C_6H_4$ [d] | 124—125 | 57·7 | 4·1 | 14·0 | 11·15 | $C_{28}H_{23}BrO_5S_2$ | 57·65 | 3·95 | 13·7 | 11·0 |

$^1$H n.m.r. bands in $CDCl_3$: [a] 2·5—3·1 (m, 18 H) and 7·65 (s, 3 H); [b] 2·5—3·1 (m, 17 H), 7·63 (s, 3 H), and 7·77 (s, 3 H); [c] 2·4—3·1 (m, 18 H) and 6·22 (s, 3 H); [d] 2·4—3·2 (m, 17 H), 6·20 (s, 3 H), and 6·29 (s, 3 H).

## EXPERIMENTAL

M.p.s are uncorrected. The $^1$H n.m.r. positions are given for carbon disulphide solutions (unless otherwise specified) on the τ scale relative to tetramethylsilane. The solvents used in the kinetic runs were purified as described elsewhere.[3a] Substituted diphenylacetylenes were prepared by literature methods.[1, 26, 27]

The synthesis of the trinitrobenzenesulphonate (I) and *p*-bromobenzenesulphonate (I) has been described.[6] By the same general method the new *esters*, (Ib) and substituted (Ic), reported in Table 3 were obtained. The overall yield, after two or more crystallizations from ethanol, ranged between 30 and 52%.

Triazene (IV) was synthesized by reaction of the corresponding vinyl Grignard reagent with phenyl azide [28] following the method outlined by Jones and Maness.[8] Virtually by the same procedure,[7b] the triazene was obtained from triphenylvinyl bromide [29] in 62% overall yield. It had m.p. 105—106 °C (lit.,[7b] m.p. 102—103 °C); the $^1$H n.m.r. spectrum shows a broad singlet at 0·81 (1 H) and four distinct signals (5 H each) at 2·77, 2·85, 3·01, and 3·10.

*Triphenylvinyl* 2,4,6-*Trinitrobenzenesulphonate*.—The triazene (IV) (3·5 g) in dichloromethane (50 ml) was added slowly to a suspension of anhydrous trinitrobenzenesulphonic acid (3·1 g) in dichloromethane (50 ml) with stirring under nitrogen. The temperature was kept at −50 °C during the addition, then maintained at −10 °C for 3 h. During the addition, the solution became deep orange and a fine residue was precipitated. The mixture was filtered, pentane (300 ml) was added, and a yellow-orange product crystallized. This was recrystallized from dichloromethane–pentane and washed on the filter with pentane containing a few drops of methanol and then pentane. The *product* (3·1 g, 61%) had m.p. 140 °C (decomp.) (Found: C, 57·05; H, 3·15; N, 7·5; S, 6·0. $C_{26}H_{17}N_3O_9S$ requires C, 57·05; H, 3·15; N, 7·65; S, 5·85%). The i.r. spectrum (solid, KBr) shows bands at 3070, 1560vs, 1390s, 1350vs, 1195s, 910, 803, and 693 cm$^{-1}$. Triphenylvinyl p-toluenesulphonate was obtained by the same procedure from triazene (IV) (1·5 g) and dry toluene-*p*-sulphonic acid (1·38 g), and was crystallized from ethanol. The colourless product (0·63 g, 41%), had m.p. 166—167 °C (lit.,[7b] m.p. 169 °C).

*Product Analysis*.—The procedure described [3a] for the products from trinitrobenzenesulphonate (I) in nitromethane and in 19 : 1 nitromethane–methanol was used in the cases below. Experiments at high temperatures were carried out in sealed glass vials containing a weighed amount of ester and solvent (150 ml).

*Ester* (Ia) *in acetic acid at* 25 °C. From the ester (0·435 g)

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[23] See, *e.g.*, A. Streitwieser, jun., ' Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962, pp. 108–110.

[24] P. G. Gassman and A. F. Fentiman, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 1545; 1970, **92**, 2549.

[25] Z. Rappoport, in ' Advances in Physical Organic Chemistry,' ed. V. Gold, vol. 7, Academic Press, London, 1970.

[26] A. Orekhoff and M. Tiffenau, *Bull. Soc. chim. France*, 1925, **37**, 1416.

[27] W. Schlenk and E. Bergmann, *Annalen*, 1928, **463**, 82.

[28] O. Dimroth, *Ber.*, 1902, **35**, 1032.

[29] C. F. Koelsch, *J. Amer. Chem. Soc.*, 1932, **54**, 2054.

the only product identified was one geometric isomer of 1,2-*diphenyl-2-phenylthiovinyl acetate* (0·192 g, 66%), crystallized from ethanol (Found: C, 76·4; H, 5·35; S, 9·4. $C_{22}H_{18}O_2S$ requires C, 76·25; H, 5·25; S, 9·25%), $^1$H n.m.r. bands at 2·5—3·0 (m, 15 H) and 8·23 (3 H), m.p. 86 °C.

*Ester* (Ib) *in acetic acid at* 150 °C. From the ester (0·460 g) the products isolated were 1,2-diphenyl-2-phenylthiovinyl acetate, (0·190 g, 54·8%) and 2-phenyl-2-phenylthioacetophenone (0·092 g, 30%), by comparison of its i.r. spectrum with that of an authentic sample.[3b]

*Ester* (Ic).—(a) *In acetic acid at* 150 °C. From the ester (0·525 g) the following products were isolated and identified: 1,2-diphenyl-2-phenylthiovinyl acetate (0·210 g, 60·5%) and 2-phenyl-2-phenylthioacetophenone, m.p. 82—83° (0·096 g, 31·5%), as above.

(b) *In* 4 : 1 *ethanol–water at* 130·5 °C. From ester (0·450 g) the crude product showed, besides aromatic proton $^1$H n.m.r. signals, one singlet at 4·30, two equivalent quartets around 6·4, and two equivalent triplets around 8·9. The products isolated and identified were a mixture of 1 : 1 cis- and trans-1,2-*diphenyl-2-phenylthiovinyl ethyl ether*, oil (0·110 g, 38·5%) (Found: C, 79·8; H, 6·3; S, 9·5. $C_{22}H_{20}OS$ requires C, 79·5; H, 6·05; S, 9·65%); $^1$H n.m.r. signals at 2·5—3·0 (m, 15 H), two equivalent quartets (2 H each) centred at 6·38 and 6·46 and two equivalent triplets (3 H each) at 8·85 and 8·93; and 2-phenyl-2-phenylthioacetophenone (0·109 g, 41·5%) as above.

*Ester* (IIa).—(a) *In nitromethane.* From the ester (0·501 g) nine products were detected by t.l.c. and seven isolated. Only small amounts (0·015 g, 6%) of αα-diphenylacetophenone were identified by the i.r. spectrum identical with that of an authentic sample.

(b) *In* 19 : 1 *nitromethane–methanol at* 25 °C. From the ester (0·423 g), αα-diphenylacetophenone (0·109 g, 52%), was isolated. It had m.p. 134—135 °C (lit.,[30] m.p. 135—136 °C) and showed $^1$H n.m.r. bands at 2·12 (2 H), 2·6—2·9 (m, 13 H), 4·13 (s, 1 H).

(c) *In* 4 : 1 *acetone–methanol at* 25 °C. From the ester (0·894 g) the following products were isolated and identified: 1,2,2-triphenyl-1-methoxyethylene 0·116 g, 25%), m.p. 109 °C (lit.,[31] m.p. 108·4—109·2 °C); $^1$H n.m.r. bands at 2·8—3·1 (m, 10 H) and 6·62 (s, 3 H); and αα-diphenylacetophenone (0·216 g, 48%), as above.

(d) *In acetic acid at* 25 °C. From the ester (0·582 g) the only product isolated and identified was triphenylvinyl acetate, (0·261 g, 78%), m.p. 103—104 (lit.,[32] m.p. 104—105·5°).

1,2,2-Triphenyl-1-methoxyethylene obtained under (c) (0·08 g), dissolved in 10 ml methanol containing two drops on conc. sulphuric acid, after five days at room temperature was completely converted into αα-diphenylacetophenone (by $^1$H n.m.r. analysis).

*Kinetic Procedures.*—The conductometric and spectrophotometric methods have been described.[3a] In the case of trinitrobenzenesulphonate (II) in acetic acid and methanol the rates were followed spectrophotometrically both at 420 and 410 nm. The rate constants of methanolysis thus obtained were in agreement, within experimental error, with those obtained by the conductometric technique.

The rates of toluene-*p*-sulphonates (I) and (II) in acetic acid and of *p*-bromobenzenesulphonates (I) in 4 : 1 ethanol–water and acetic acid were followed by a titrimetric method, as follows. The ester was weighed individually (20—30 mg) into each of 6—9 glass ampoules. Solvent (10 ml) was added and the ampoules were sealed. These were heated at the desired temperature in a thermostatted oil-bath of ±0·2 °C temperature accuracy and vigorously shaken until all the substrate was dissolved. The ampoules were taken out at appropriate intervals after thermal equilibrium was achieved (1·5—2 min). The samples in 4 : 1 ethanol–water were titrated against sodium hydroxide (bromothymol blue). When experiments were carried out in the presence of added sodium hydroxide, the excess of base was titrated against hydrochloric acid. On the other hand, the samples in acetic acid were titrated against sodium acetate in acetic acid (bromophenol blue) according to a described method.[33] When acetolysis was carried out in the presence of sodium acetate, the samples were titrated against perchloric acid in acetic acid. Infinity kinetic points were in good agreement (within 3%) with the calculated values.

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