Reactivity of Vinyl Sulphonic Esters. Part XIII.[1] Pronounced Anchimeric Assistance in the Solvolysis of Dialkyl-β-alkyl(or aryl)thiovinyl Sulphonates

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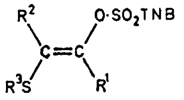
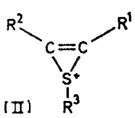
trans-1,2-Dimethyl-2-methylthiovinyl 2,4,6-trinitrobenzenesulphonate reacts *ca.* 4 × 10^4 times faster than trimethylvinyl 2,4,6-trinitrobenzenesulphonate in 9 : 1 nitromethane–methanol at 25°. These and other kinetic data on the solvolysis of a number of 1,2-dimethyl- and 1,2-di-n-propyl-β-alkyl(or aryl)thiovinyl sulphonates are taken as evidence of effective anchimeric assistance by the β-sulphur atom and of the intermediacy of thiirenium ions.

PREVIOUS papers[2] reported evidence of anchimeric assistance by the β-sulphur atom in the S_N1-type reactions of β-alkyl(or aryl)thiovinyl sulphonates (I; R^1 = Ar). The estimated rate enhancements (factors ranging from 1 to 33) were rather small and discussed in terms of a comparable stability of the two geometric structures of the intermediate vinyl cation; the bridged (thiirenium ion) (II) and the open linear one (III). However, it was not clear whether the small kinetic effects of anchimeric assistance were due to (*a*) the inherent inability of β-groups in vinylic systems to cause substantial rate enhancements such as those observed in the solvolysis of saturated systems or (*b*) to the ' levelling ' effect[3] of the α-aryl group (R^1 = Ar) capable of delocalizing the positive charge developing at the α-carbon atom and, hence diminishing the need for intramolecular aid. In order to single out the arguments under (*b*) we have undertaken the study of β-alkyl(or aryl)thiovinyl esters (I) bearing an α-alkyl group which is much less effective in stabilizing the adjacent positive charge than the aryl group and should destabilize the open cation (III) more than the bridged one (II). A stability difference in the absence of stabilizing α-functions is supported by the results[4] of non-empirical SCF-MO calculations on the ion $C_2H_3S^+$ which indicate that the bridged structure (II; $R^1 = R^2 = R^3$ = H) is *ca.* 66 kcal mol^{-1} more stable than the corresponding linear structure (III).


(I)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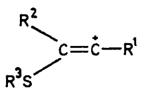
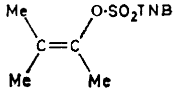

(III)

	R^1	R^2	R^3		R^1	R^2	R^3
a;	Me	Me	Me	f;	Pr^n	Pr^n	*p*-$MeOC_6H_4$
b;	Me	Me	Ph	g;	Pr^n	Pr^n	*p*-MeC_6H_4
c;	Me	Me	*p*-ClC_6H_4	h;	Pr^n	Pr^n	*m*-MeC_6H_4
d;	Pr^n	Pr^n	Me	i;	Pr^n	Pr^n	*p*-ClC_6H_4
e;	Pr^n	Pr^n	Ph	j;	Pr^n	Pr^n	*m*-ClC_6H_4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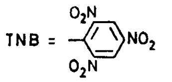

We present here the kinetic study[5] of the solvolysis of 1,2-dialkyl-2-alkyl(or aryl)thiovinyl 2,4,6-trinitrobenzenesulphonates (Ia—j) and of that of the trimethylvinyl 2,4,6-trinitrobenzenesulphonate (IV) chosen as a model compound for unassisted solvolytic reactivity.[6]

RESULTS

Esters (Ia—j) were prepared by addition of arene- or methane-sulphenyl trinitrobenzenesulphonate to the appropriate alkynes following the method of ref. 7. Ester (IV) was synthesized by the procedure of Jones and Maness[8] slightly modified according to the Scheme:

$$Me_2C{:}C(Me)Br \xrightarrow{i} Me_2C{:}C(Me)Li \xrightarrow{ii}$$

$$Me_2C{:}C(Me)N{:}N{\cdot}NHPh \xrightarrow{iii} Me_2C{:}C(Me)O{\cdot}SO_2TNB$$

SCHEME

Reagents: i, lithium; ii, phenyl azide; iii, 2,4,6-trinitrobenzenesulphonic acid.

Esters (Ia—j) react at a measurable rate at room temperature in nitromethane–methanol with first-order kinetics up at least 80% (followed by conductimetry). The first-order rate constant of ester (Ia) and, to a lesser extent, of esters (Ib) and (Ic), in nitromethane at 25°, decreases during a run. Such a decrease, probably due to a mass-law effect,[9] is entirely suppressed in 19 : 1 and 9 : 1 nitromethane–methanol. On the other hand, ester (IV) reacts at a temperature of 80 °C or higher. At these temperatures the reaction rate in nitromethane and 19 : 1 nitromethane–methanol could not be followed by conductimetry or spectrophotometry because of the decomposition of the trinitrobenzenesulphonic acid. Decomposition in 9 : 1 nitromethane–methanol is, instead, slow enough to be neglected and the kinetics were therefore followed for this solvent.

Table 1 shows first-order rate coefficients measured in nitromethane and in nitromethane–methanol for esters (IV) and (Ia—j). In nitromethane at 25°, the rate constants for the 2-arylthio-1,2-di-n-propylvinyl esters (Ie—j)

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[1] Part XII, G. Melloni and G. Modena, *J.C.S. Perkin I*, 1972, 1355.

[2] (*a*) G. Modena and U. Tonellato, *J. Chem. Soc.* (*B*), 1971, 1969; (*b*) G. Capozzi, G. Modena, and U. Tonellato, *ibid.*, p. 1700.

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

[4] A. S. Denes, J. G. Csizmadia, and G. Modena, *Chem. Comm.*, 1972, 8.

[5] Preliminary report, A. Burighel, G. Modena, and U. Tonellato, *Chem. Comm.*, 1971, 1325.

[6] M. A. Imhoff, R. H. Summerville, P. v. R. Schleyer, A. G. Martinez, M. Hanack, T. E. Dueber, and P. J. Stang, *J. Amer. Chem. Soc.*, 1970, **92**, 3802.

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

[8] W. M. Jones and D. D. Maness, *J. Amer. Chem. Soc.*, 1969, **91**, 4134; 1970, **92**, 5427.

[9] G. Modena and U. Tonellato, *J. Chem. Soc.* (*B*), 1971, 374.

TABLE 1

Rate coefficients[a] ($10^4\ k/s^{-1}$) and activation parameters for esters (I) and (IV) in nitromethane (N) and nitromethane–methanol (M)

					9 : 1 N–M				
Ester	15°	25°	35°	80°	90°	100°	110°	E_a[b]	$\Delta S^{\ddagger}$[c]
(IV)		($1{\cdot}1 \times 10^{-4}$)[d]		0·093	0·217	0·55	1·38	25·3	−12
(Ia)	1·09	4·07	13·4			(7560)[e]		22·3	−1

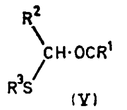
	N					19 : 1 N–M					9 : 1 N–M
	15°	25°	35°	E_a[b]	$\Delta S^{\ddagger}$[c]	19·4°	25°	33·8°	E_a[b]	$\Delta S^{\ddagger}$[c]	25°
(Ib)		0·39					0·43				0·47
(Ic)		0·17									
(Id)		59·7					65·3				
(Ie)	1·41	4·91	16·5	21·7	−3	2·97	6·32	17·3	21·9	−2	
(If)		14·2									
(Ig)		8·33									
(Ih)		6·24									
(Ii)		1·88									
(Ij)		1·15									

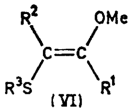
[a] Average of two or more kinetic runs. [b] kcal mol^{-1}; estimated error: ±0·8 kcal mol^{-1}. [c] cal mol^{-1} K^{-1} at 25°; estimated error: ±2 cal mol^{-1} K^{-1}. [d] Extrapolated from higher temperature measurements. [e] Extrapolated from lower temperature measurements.

fit the Hammett equation and ρ is −1·71 [r 0·9982 (ref. 10)]; a ρ value of −1·6 (two points only) can be calculated from the rates of the corresponding 1,2-dimethyl derivatives (Ib and c).

As observed[2,9] in the case of esters (I) previously investigated, the rate constants in nitromethane is only slightly smaller than in 19 : 1 or 9 : 1 nitromethane–methanol.

The product distribution also resembles that observed[2] in the case of the esters (I; R^1 = Ar, R^2 = H or Me). In nitromethane a variety of products is formed. Ketones (V) and disulphides ($R^3S{\cdot}SR^3$) were isolated and identified. In nitromethane–methanol the main products from the esters (I) were the ketones (V) (60—70%) presumably


(V)


(VI)

derived from the primary substitution products (VI) which are very labile in acidic media.[2] Variable, though small, amounts of benzo[*b*]thiophen derivatives were also detected among the products of solvolysis of 1,2-dimethyl- and 1,2-di-n-propyl-2-phenylthiovinyl esters in nitromethane–methanol. However (see Experimental section), they are probably formed by cyclization of ketones (V; R^3 = Ph) rather than occurring as primary products.[11]

Trimethylvinyl trifluoromethanesulphonate was recently reported[6] to solvolyse in a variety of solvents to give 3-methylbutan-2-one and 1,1-dimethylallene. Therefore, we did not investigate in detail the products from the trimethylvinyl ester (IV). In one experiment (9 : 1 nitromethane–methanol at 100°) we found evidence for the formation of 3-methylbutan-2-one identified as its phenylhydrazone.

DISCUSSION

The assumption that esters (Ia—j) and (IV) react by an S_N1-type pathway is supported by the close similarity of the kinetic features and product distribution observed for these esters and other esters previously investigated[2,6,9] for which a unimolecular mechanism[12] was established.

The main result from Table 1 is that ester (Ia) reacts *ca.* 4 × 10^4 times faster than ester (IV) in 9 : 1 nitromethane–methanol at 25°. Since polar effects due to the substitution of a β-methylthio for a β-methyl group are predictably[13] quite small and probably act to reduce the rate and steric effects can play but a minor role,[2,12] the observed difference in rate can only be explained in terms of anchimeric assistance. The change in rate is almost equally due to enthalpy and entropy factors; the less negative activation entropy in the case of ester (Ia), is in line with the trend generally observed[14] for assisted relative to unassisted processes.

Data on the enhanced reactivity of ester (Ia) are largely confirmed by those for all other 1,2-dialkyl esters (I). The magnitude of anchimeric assistance is better illustrated by Table 2 which also reports significant data for other vinyl sulphonates previously investigated.

The nucleophilic intervention of sulphur in the transition state is reflected by the large effect of groups bound to the β-sulphur atom. The ten-fold increase in rate on going from β-phenylthio- to β-methylthio-derivatives, (Ib)–(Ia); (Id)–(Ie), and the ρ value of −1·7 for substituents on the phenyl ring of β-phenylthio-derivatives clearly indicate that some positive charge resides on the sulphur atom in the transition state. The ρ value, −1·7, is of the order of the largest

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[10] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[11] G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc.* (*C*), 1970, 2621.

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[13] W. A. Pryor, ' Mechanisms of Sulphur Reactions,' McGraw-Hill, New York, 1962, pp. 31—33; J. E. Leffler and E. Grunwald, ' Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963, p. 173.

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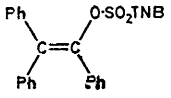
(−1·4 to −1·8) observed[15] in assisted solvolyses of β-arylthioethyl derivatives and is the largest observed in the series of β-phenylthiovinyl derivatives (see Table 2).

The trimethylvinyl ester (IV) reacts 2×10^3 times slower than the triphenylvinyl analogue (VII). The change in reactivity is the result of structural variations both at the α- and the β-carbon atoms. However the effect of β-substituents in unassisted solvolyses is a minor one as compared with that of α-substituents. Rappoport and Gal[16] observed a five-fold increase in the rate of solvolysis of α-*p*-methoxyphenylvinyl bromides in 4 : 1 ethanol–water at 120° on going from the β,β′-diphenyl to the β,β-′dimethyl derivative. Therefore, the large difference in rate between the esters (IV) and (VII) is the lower limit of rate enhancement due to the substitution of a methyl for a phenyl group at the α-carbon atom.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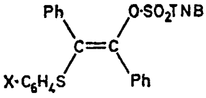
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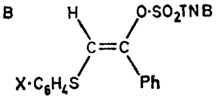
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TABLE 2

Relative rates of solvolysis of various vinyl trinitrobenzenesulphonates at 25°

	(IV)	(Ia)	(Ib)	(Id)	(Ie–j)	(VII) [d]	(VIII) [e]	(IX) [f]
k_{rel} [a]	1	$3{\cdot}8 \times 10^4$	$3{\cdot}5 \times 10^3$	$6{\cdot}2 \times 10^5$	$6{\cdot}1 \times 10^4$	$2{\cdot}1 \times 10^3$	$4{\cdot}4 \times 10^4$	$(1{\cdot}3 \times 10^3)$ [g]
k_{rel} [b]		1		16			1·1	
ρ(X) [c]					−1·7		−1·45	−0·88

[a] Relative to ester (IV); X = H; 9 : 1 nitromethane–methanol. [b] Relative to ester (Ia); X = H; 9 : 1 nitromethane–methanol. [c] In nitromethane. [d] From ref. 2a. [e] From ref. 9. [f] From ref. 2b. [g] Evaluated from data for 19 : 1 nitromethane–methanol.

A similar change in the series of β-alkyl (or aryl) thiovinyl esters, from (Ia) to (VIII; X = H) (see Table 2), does not affect the reactivity. Clearly the loss in relative stability in the transition state due to the absence of conjugative delocalization of the positive charge into the α-phenyl ring is compensated by intramolecular aid by the β-sulphur atom. Therefore, in the case of 1,2-dialkylvinyl esters (I), the bridged cation (II) must be considerably preferred to the linear one (III).

We conclude that β-groups can effectively assist solvolytic processes of vinyl compounds and large kinetic effects may also be expected in these cases. The only peculiarity so far observed is that not all of the atoms capable of β-participation in saturated systems[17] are effective in vinyl systems (*e.g.*, oxygen[18a] and nitrogen[18b]) although the number of cases investigated is still too limited to allow any definite conclusion on the subject.

The greater (by a factor of *ca.* 15, see Table 2) rate of 1,2-di-n-propyl derivatives as compared with that of the corresponding 1,2-dimethyl esters (I) is difficult to explain. It was argued[2b] that the stability of the thiirenium ion as a function of substituents at the carbon atoms may follow the same order of substituent effects observed for the cyclopropenium ion, H ⋘ Ph < Me. However such an argument cannot be invoked for a possible greater stability of the di-n-propyl (II; $R^1 = R^2 = Pr^n$) than that of the dimethyl (II; $R^1 = R^2 = Me$) thiirenium ions since recent work by Ciabattoni and Nathan[19] has established that the trimethylcyclopropenium ion is slightly more stable than the tri-n-propyl analogue. In the absence of further experimental support, relief of steric strain on going from the ground to the transition state in the case of the di-n-propyl esters may be tentatively suggested as one of the factors responsible for the observed rate difference.

EXPERIMENTAL

M.p.s are uncorrected. Chemical shifts are relative to tetramethylsilane. Solvents used in the kinetic experiments were purified as described. But-2-yne and oct-4-yne were commercial products used without purification. The synthesis of β-thiovinyl esters (Ia—j) by addition of arene- or methane-sulphenyl trinitrobenzenesulphonate was carried out as described.[7] Table 3 shows physical and analytical data for the new esters (I). All compounds display i.r. absorption bands at 1400—1420 and 1175—1200 cm^{-1} characteristic of the covalent sulphonate groups. Some of the esters listed in Table 3, in particular (If, g, and h) decompose readily in the solid state and poor analyses could be obtained in these cases. 1,2-Dimethylpropenyl bromide, b.p. 121—123 °C (lit.,[20] b.p. 120—121°) and phenyl azide, b.p. 30 °C at 1 mmHg (lit.,[21] b.p. 30° at 1 mmHg) were prepared by literature methods.

Trimethylvinyl 2,4,6-*trinitrobenzenesulphonate* (IV).—Freshly distilled 1,2-dimethylpropenyl bromide (17 g) was added to finely sliced lithium (1·7 g) in dry ether (350 ml) and the mixture was stirred under reflux for 4 h. To the green-gray solution of trimethylvinyl lithium[20] thus obtained, phenyl azide (12·6 g in 15 ml of ether) was added dropwise. After stirring at room temperature for 1 h, the mixture was poured into 100 ml of ammonium chloride–ammonia solution (20 g of ammonium chloride, 8 ml of conc. ammonium hydroxide, made up to 100 ml with water). The ether layer was dried (Na_2SO_4) and evaporated. The resulting dark oil (20 ml) could not be

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[15] H. L. Goering and K. L. Howe, *J. Amer. Chem. Soc.*, 1957, **79**, 6542; D. R. Hogg, *Quart. Reports Sulphur Chem.*, 1967, **2**, 339 and references therein.

[16] Z. Rappoport and A. Gal, unpublished results.

[17] *E.g.*, A. Streitwieser, jun., 'Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962.

[18] (*a*) G. Capozzi and G. Modena, *J.C.S. Perkin I*, 1972, 216; (*b*) G. Capozzi, G. Modena, and L. Ronzini, *ibid.*, p. 1136.

[19] J. Ciabattoni and E. C. Nathan, tert., *Tetrahedron Letters*, 1969, 4997.

[20] E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 1955, 3331.

[21] O. Dimroth, *Chem. Ber.*, 1902, **35**, 1032.

TABLE 3

Physical and analytical data of esters (I)

	M.p. (°C)	Colour	Found (%)					Calc. (%)				
			C	H	N	S	Cl	C	H	N	S	Cl
(Ia) [a]	85 [c]	Orange-red	33·4	2·6	10·65	16·2		33·6	2·8	10·65	16·3	
(Ib)	103—104	Orange-red	42·4	3·05	9·1	14·35		42·2	2·9	9·2	14·1	
(Ic)	95—96	Yellow	39·4	2·5	8·75	13·3	7·15	39·25	2·45	8·55	13·1	7·25
(Id)	79 [c]	Orange	40·4	4·2	9·5	14·5		40·1	4·25	9·35	14·25	
(Ie)	92—93	Yellow	46·7	4·35	8·2	12·6		46·95	4·15	8·2	12·55	
(If)	84 [c]	Orange	46·1	4·05	8·1	12·0		46·55	4·3	7·75	11·85	
(Ig) [b]	91—92 [c]	Orange-red	47·75	4·35	7·8	12·0		48·0	4·4	8·0	12·2	
(Ih)	86 [c]	Yellow	46·9	4·1	7·9	12·2		48·0	4·4	8·0	12·2	
(Ii)	93—94	Orange	43·9	3·6	7·5	11·7	6·75	44·0	3·7	7·7	11·75	6·5
(Ij)	101·5	Yellow	43·8	3·7	7·6	11·75	6·5	44·0	3·7	7·7	11·75	6·5

[a] τ 1·36 (s, 2H), 7·76 (s, 3H), 7·82 (q, 3H), and 8·03 (q, 3H). [b] τ 1·35 (s, 2H), 2·84 (m, 4H), 7·25 (t, 2H), 7·71 (s, 3H), 7·87 (t, 2H), 8·5 (m, 4H), 9·10 (t, 3H), and 9·26 (3H). [c] Decomp.

crystallized; it decomposed readily, with nitrogen evolution, in acidic solutions. Vacuum distillation and column chromatography resulted in extensive decomposition of the material which was used in the subsequent step without purification. A solution of the oil (2·6 g) in anhydrous methylene chloride (20 ml) was added dropwise to a well stirred, ice-cooled suspension of 2,4,6-trinitrobenzenesulphonic acid (4·0 g) in methylene chloride (50 ml). During addition the mixture turned a deep orange colour; it was stirred for 30 min at room temperature and filtered. The solution was passed through a short silica gel column and the solvent was evaporated. The residue was crystallized from methylene chloride–pentane. The *product*, bright yellow needles (1·0 g, 21·5%), had m.p. 137° (Found: C, 36·55; H, 3·15; N, 11·7; S, 8·85. $C_{11}H_{11}N_3O_9S$ requires C, 36·5; H, 3·05; N, 11·6; S, 8·85%), $\nu_{max.}$ (KBr) 3000, 2850, 1500, 1370, 1350, 1200, and 900 cm^{-1}, τ ($CDCl_3$) 1·37 (2H), 7·98 (3H), and 8·26 (6H).

Product Analysis.—The general procedure has been described.[9]

Vinyl ester (Ia). *In* 9 : 1 *nitromethane–methanol at* 25°. From ester (0·510 g) the only product isolated besides the sulphonic acid and tarry material was 3-methylthiobutan-2-one (0·09 g, 58%), oil (lit.,[22] b.p. 50—54° at 20 mmHg), τ ($CDCl_3$) 6·66 (q, 1H), 7·71 (s, 3H), 8·03 (s, 3H), 8·64 (d, 3H), $\nu_{max.}$ (CS_2) 1715 (C=O) cm^{-1}.

Ester (Ib). (a) *In nitromethane at* 25°. From ester (0·407 g), the following products were isolated and identified: diphenyl disulphide (21 mg; 10·7%) by its i.r. spectrum identical with that of an authentic sample; 3-phenylthiobutan-2-one (45 mg; 27·5%), oil (lit.,[23] b.p. 136°), τ ($CDCl_3$) 2·5—2·8 (m, 5H), 6·22 (q, 1H), 7·50 (s, 3H), and 8·60 (d, 3H). Tarry material was isolated but not identified.

(b) *In* 9 : 1 *nitromethane–methanol at* 25°. From ester (0·606) the products isolated and identified were: an oily residue (8—15 mg) showing the characteristic u.v. pattern[24] of the 2,3-dimethylbenzo[*b*]thiophen, $\lambda_{max.}$ (EtOH) 302, 291, 268, and 232 nm; 3-phenylthiobutan-2-one (0·191 g; 78%) as described above. In a separate experiment, pure 3-phenylthiobutan-2-one was allowed to react in 9 : 1 nitrimethane–methanol containing an equimolar amount of trinitrobenzenesulphonic acid at 25°. After the time for the decomposition of ester (Ia), 2,3-dimethylbenzo[*b*]thiophen (6%) was isolated from the mixture and identified by its u.v. spectrum.

Ester (Ic). (a) *In nitromethane at* 25°. From ester (0·48 g) the products isolated and identified were: diphenyl disulphide (14 mg; 7%); *5-phenylthio-octan-4-one* (0·123 g; 55%), oil (Found: C, 71·4; H, 8·8; S, 13·3. $C_{14}H_{20}OS$ requires: C, 71·15; H, 8·55; S, 13·55%), τ ($CDCl_3$) 2·8 (m, 5H), 6·51 (t, 1H), 7·53 (t, 2H), 8·2—8·8 (m, 6H), 9·11 (t, 3H), and 9·18 (t, 3H), $\nu_{max.}$ (CS_2) 1722 (C=O) cm^{-1}.

(b) *In* 19 : 1 *nitromethane–methanol at* 25°. From the ester (0·557 g) the products isolated and identified were: an oily residue (10 mg) showing the characteristic u.v. pattern[24,25] of benzo[*b*]thiophen derivatives, $\lambda_{max.}$ (MeOH) 298, 262, and 232 nm, presumably 2,3-di-n-propylbenzo[*b*]thiophen (4%); 5-phenylthio-octan-4-one (0·170 g; 67%. A separate experiment carried out as described for the decomposition of ester (Ia) in 9 : 1 nitromethane–methanol, showed that 2,3-di-n-propylbenzo[*b*]thiophen is formed (7—8%) by cyclization of 5-phenylthio-octan-4-one.

Kinetic Measurements. The experimental procedure and the methods of calculation have been reported.[9] The kinetic runs at high temperatures were carried out in sealed vials as described.[2a]

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