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The spin-delocalization substituent parameter $\sigma^{\bullet}_{JJ}$. 9. Cyclodimerization rates of *para*-methylsulfinyl and *para*-methylsulfonyl α,β,β-trifluorostyrenes

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Abstract

^{19}F NMR data and rate constants for the thermal cyclodimerization of *para*-methylsulfinyl α,β,β-trifluorostyrene (**1**) and *para*-methylsulfonyl α,β,β-trifluorostyrene (**2**) have been measured. On the basis of these data, the σ_{mb} and $\sigma^{\bullet}_{JJ}$ values for p-MeSO and p-MeSO$_2$ groups have been evaluated. Three methods for the calculation of the $\sigma^{\bullet}_{JJ}$ scale yielded the same set of $\sigma^{\bullet}_{JJ}$ constants.

Introduction

Very recently, we have reported a self-consistent and thoroughly cross-checked scale of spin-delocalization substituent constants, $\sigma^{\bullet}_{JJ}$, which is based on the ^{19}F NMR data for Y-substituted α,β,β-trifluorostyrenes (Y-TFSs) and the rate constants for their thermal cyclodimerization reactions. [1] The $\sigma^{\bullet}$ value of a substituent should only reflect the ability of this substituent to delocalize the spin. We consider that it would be desirable to obtain reliable $\sigma^{\bullet}$ values for sulfur-containing groups. Although the methylthio group is already known to possess an exceptionally high ability to delocalize spin [2], the spin-stabilizing ability of sulfur in its oxidized forms (e.g. in sulfoxides and sulfones) is not known with certainty. On the one hand, Arnold's $\sigma^{\bullet}_{\alpha}$ values [3] suggest that MeSO ($\sigma^{\bullet}_{\alpha}=0.018$) is much more capable of stabilizing spin than MeSO$_2$ ($\sigma^{\bullet}_{\alpha}=0.005$). On the other hand, Creary's $\sigma^{\bullet}_{C}$ values for these two groups are almost the same [4]. Therefore, with the objective of tackling this problem by our approach, we synthesized *para*-methylsulfinyl and *para*-methylsulfonyl α,β,β-trifluorostyrenes (**1** and **2**), obtained their ^{19}F NMR and σ_{mb} values, measured their rates of thermal cyclodimerization and thereby evaluated their $\sigma^{\bullet}_{JJ}$ values. In this paper, the results of three methods of calculating the $\sigma^{\bullet}_{JJ}$ values are also presented.

Results and discussion

In Y-TFSs, the chemical shifts of F^1 and F^2, as well as the difference between the chemical shifts of F^3 and F^1 (δ_{3-1}), or F^3 and F^2 (δ_{3-2}), reflect the degree of polarization of the double bond in Y-TFSs [5]. Thus, the effects of polar substituent on the π-bonds of Y-TFSs can be evaluated by eqn. (1)

$$\sigma_{mb}=0.16\Delta\delta_{3-1}-0.09 \qquad (1)$$

where $\Delta\delta_{3-1}=(\delta_{3-1})_Y-(\delta_{3-1})_H$. The tailor-made polar substituent parameter σ_{mb} reflects the ability of a given substituent Y to polarize the π-bond of the corresponding Y-TFS in the ground state.

We have used a dual parameter [eqn. (2)] in our approach to the $\sigma^{\bullet}_{JJ}$ scale.

$$\log(k/k_H)=\rho_{mb}\sigma_{mb}+\rho^{\bullet}\sigma^{\bullet}_{JJ} \qquad (2)$$

In eqn. (2), the kinetic rate constants (k values) are measured for the thermal dimerization of Y-TFSs at five different temperatures. The value of $\rho^{\bullet}$ is arbitrarily taken as unity. In the initial development stage of our $\sigma^{\bullet}_{JJ}$ approach [6], an operable or 'reasonable' value of ρ_{mb} had to be found. We therefore made a tentative assumption that the spin-delocalizing effect of a *meta*-methyl group on the transition state of a benzylic radical is negligible, i.e. the $\sigma^{\bullet}_{JJ}$ value of m-Me is virtually zero. With this assumption, eqn. (2) becomes eqn. (3):

$$\rho_{mb}=\log(k_{m-\mathrm{Me}}/k_H)/\sigma_{mb\ \mathrm{for}\ m-\mathrm{Me}} \qquad (3)$$

which yields the ρ_{mb} values for the different temperatures (see Table 1) if the corresponding $k_{m-\mathrm{Me}}$, k_H and σ_{mb} values are substituted into eqn. (3). By using five ρ_{mb} values for the five temperatures, all the $\sigma^{\bullet}_{JJ}$ values can be calculated via eqn. (4) if the k_Y values of the Y-TFSs and the σ_{mb} values of the Ys have been accurately

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TABLE 1. The ρ_{mb} values at different temperatures

	Temperature (°C)					
	110	120	140	150	160	Average
ρ_{mb}(*m*-Me)	−0.38	−0.40	−0.30	−0.37	−0.30	−0.35 ± 0.04
ρ_{mb}(*m*-NO_2)[a]	−0.31	−0.24	−0.23	−0.21	−0.21	

[a]The ρ_{mb}(*m*-NO_2) values were calculated on the basis of the tentative assumption that the σ_m value for the *m*-NO_2 group was essentially zero.

measured. This method of calculation is designated Method A, which also yields the averaged $\sigma_{JJ}^{\bullet}$ values recommended for general use in the second to last column of Table 2.

$$\sigma_{JJ\ \mathrm{for}\ Y}^{\bullet} = \log(k_Y/k_H) - \rho_{mb}\sigma_{mb\ \mathrm{for}\ Y} \qquad (4)$$

In order to cross-check the reliability of these $\sigma^{\bullet}$ values, we also tried two other approaches, designated as Method B and Method C, respectively. In Method B, only one ρ_{mb} value of −0.35 (the average of the five ρ_{mb} values listed in Table 1) was used for the calculation of the $\sigma^{\bullet}$ values listed in Table 3. In Method C, only one ρ_{mb} value of −0.30 (the value derived for 140 °C) was used to give the $\sigma^{\bullet}$ values listed in Table 4. Again, for each method we calculated five sets of $\sigma_{JJ}^{\bullet}$ constants for each of the five temperatures, as well as the average of these five sets (average $\sigma_{JJ}^{\bullet}$ values, cf. Tables 3 and 4). We tried these different methods of calculation (A, B and C) on the basis that only the relative magnitudes of the $\sigma_{JJ}^{\bullet}$ constants are of significance. Hence, the trustworthiness and reliability of our $\sigma_{JJ}^{\bullet}$ scale can be cross-checked and tested via the correlation between all the $3 \times 6 = 18$ sets of $\sigma_{JJ}^{\bullet}$ values.

As shown in all these tables, the standard deviations of the $\sigma_{JJ}^{\bullet}$ values for most of the substituents are less than 0.05 units. This indicated that the $\sigma_{JJ}^{\bullet}$ values are not much affected by temperature, and the precision (or repeatability) of the $\sigma_{JJ}^{\bullet}$ values is relatively good.

TABLE 2. Method A: $\sigma_{JJ}^{\bullet}$ values based on different ρ_{mb} values at different temperatures

Y	Temperature (°C)					
	110	120	140	150	160	Averaged $\sigma_{JJ}^{\bullet}$ values
H	0	0	0	0	0	0
p-NMe_2	1.15	1.07	1.00	0.89	0.91	1.00 ± 0.11
p-MeS	0.52	0.56	0.59	0.71	0.71	0.62 ± 0.09
p-COMe	0.59	0.55	0.50	0.59	0.49	0.54 ± 0.05
p-MeSO	0.53	0.47	0.47	0.48	0.54	0.50 ± 0.03
p-Ph	0.49	0.49	0.44	0.45	0.46	0.47 ± 0.02
p-CN	0.43	0.45	0.36	0.47	0.39	0.42 ± 0.04
p-$MeSO_2$	0.40	0.39	0.36	0.44	0.45	0.41 ± 0.04
p-COOH	0.44	0.42	0.34	0.34	0.37	0.38 ± 0.05
p-$CONH_2$	0.39	0.40	0.37	0.40	0.33	0.38 ± 0.03
p-NO_2	0.40	0.41	0.32	0.40	0.29	0.36 ± 0.06
p-COOMe	0.32	0.34	0.30	0.38	0.32	0.33 ± 0.03
p-$SiMe_3$	0.33	0.32	0.29	0.31	0.28	0.31 ± 0.02
p-Pr^c	0.37	0.30	0.27	0.25	0.25	0.29 ± 0.05
p-Bu^t	0.23	0.25	0.30	0.23	0.30	0.26 ± 0.04
p-OMe	0.28	0.24	0.23	0.21	0.20	0.23 ± 0.03
p-Br	0.24	0.23	0.21	0.25	0.24	0.23 ± 0.02
p-Cl	0.24	0.22	0.19	0.22	0.22	0.22 ± 0.02
p-Me	0.16	0.14	0.14	0.14	0.15	0.15 ± 0.01
p-Et	0.17	0.15	0.14	0.16	0.14	0.15 ± 0.01
p-CF_3	−0.004	−0.004	−0.03	−0.02	−0.003	−0.01 ± 0.01
p-F	0.02	−0.03	−0.04	−0.01	−0.05	−0.02 ± 0.03
m-Me	0	0	0	0	0	0
m-Br	0.16	0.17	0.07	0.10	0.08	0.12 ± 0.05
m-Bu^t	0.09	0.09	0.10	0.15	0.12	0.11 ± 0.03
m-CN	0.10	0.14	0.11	0.12	0.09	0.11 ± 0.02
m-OMe	0.11	0.09	0.09	0.11	0.08	0.10 ± 0.01
m-COOMe	0.10	0.05	0.12	0.10	0.12	0.10 ± 0.03
m-F	0.05	0.04	0.02	0.04	−0.001	0.03 ± 0.02
m-NO_2	−0.03	0.01	−0.01	0.03	0.003	0.001 ± 0.02
m-Cl	−0.04	−0.03	−0.09	−0.04	−0.06	−0.05 ± 0.02
m-CF_3	−0.05	−0.06	−0.10	−0.06	−0.08	−0.07 ± 0.02

TABLE 3. Method B: $\sigma^{\bullet}_{JJ}$ values at different temperatures based on an averaged ρ_{mb} value of -0.35

Y	Temperature (°C)					Averaged $\sigma^{\bullet}_{JJ}$ values
	110	120	140	150	160	
H	0	0	0	0	0	0
p-NMe$_2$	1.18	1.11	0.95	0.91	0.86	1.00±0.14
p-MeS	0.53	0.57	0.58	0.72	0.70	0.62±0.08
p-COMe	0.58	0.53	0.53	0.58	0.52	0.55±0.03
p-MeSO	0.53	0.46	0.48	0.48	0.54	0.50±0.03
p-Ph	0.49	0.49	0.44	0.45	0.46	0.47±0.02
p-CN	0.40	0.41	0.40	0.45	0.42	0.42±0.02
p-MeSO$_2$	0.38	0.36	0.39	0.43	0.48	0.41±0.05
p-COOH	0.43	0.41	0.36	0.34	0.39	0.39±0.04
p-CONH$_2$	0.39	0.40	0.38	0.40	0.34	0.38±0.02
p-NO$_2$	0.37	0.37	0.36	0.38	0.33	0.36±0.02
p-COOMe	0.31	0.32	0.32	0.37	0.34	0.33±0.02
p-SiMe$_3$	0.33	0.31	0.30	0.31	0.29	0.31±0.01
p-Pr^c	0.38	0.31	0.25	0.25	0.16	0.27±0.08
p-Bu^t	0.23	0.26	0.29	0.23	0.28	0.26±0.03
p-OMe	0.30	0.28	0.19	0.22	0.16	0.23±0.06
p-Br	0.24	0.23	0.22	0.25	0.25	0.24±0.01
p-Cl	0.24	0.22	0.20	0.22	0.23	0.22±0.01
p-Me	0.17	0.16	0.13	0.15	0.14	0.15±0.01
p-Et	0.18	0.17	0.12	0.16	0.12	0.15±0.03
p-CF$_3$	−0.02	−0.03	−0.001	−0.03	0.02	−0.01±0.02
p-F	0.03	−0.01	−0.05	−0.004	−0.06	−0.02±0.03
m-Me	0.007	0.01	−0.01	−0.004	−0.06	−0.001±0.008
m-Br	0.15	0.16	0.09	0.10	0.10	0.12±0.03
m-Bu^t	0.10	0.10	0.09	0.15	0.11	0.11±0.02
m-CN	0.07	0.09	0.15	0.10	0.13	0.11±0.02
m-OMe	0.11	0.09	0.08	0.11	0.06	0.09±0.02
m-COOMe	0.09	0.08	0.13	0.10	0.13	0.11±0.02
m-F	0.04	0.03	0.03	0.04	0.01	0.03±0.01
m-NO$_2$	−0.05	−0.01	0.02	0.02	0.03	0.002±0.03
m-Cl	−0.04	−0.04	−0.09	−0.05	−0.06	−0.06±0.02
m-CF$_3$	−0.06	−0.08	−0.08	−0.07	−0.06	−0.07±0.01

If for each table (2, 3 and 4), we cross-correlate the $\sigma^{\bullet}_{JJ}$ values for each temperature with each other (Table 5), we find that the degree of correlation (*vide supra*) is good. In other words, for each method of calculation, the rate data collected at the five temperatures form a self-consistent whole; they conform to one pattern, i.e. one $\sigma^{\bullet}_{JJ}$ scale.

Finally, we correlated the average $\sigma^{\bullet}_{JJ}$ values derived from the three different methods, as shown in Table 6. Clearly, there are no significant differences among all of these three methods, i.e. regardless of the approach that has been taken, basically the same $\sigma^{\bullet}$ scale is obtained. It is particularly noteworthy that our $\sigma^{\bullet}_{JJ}$ scale is not sensitive to the exact ρ_{mb} value chosen, provided that the value is within a certain range, e.g. -0.20 to -0.40.

As mentioned above, both the rate constants and the ^{19}F NMR data are prerequisites for the evaluation of the $\sigma^{\bullet}_{JJ}$ values. The cyclodimerization rate constants of compounds **1** and **2** at five temperatures are listed in Table 7, whereas the corresponding Arrhenius and activation parameters are summarized in Table 8. The ^{19}F NMR data together with the σ_{mb} values for **1** and **2** are given in Table 9*. Our σ_{mb} values for the three sulfur-containing groups MeSO$_2$−, MeSO− and MeS− are 0.64, 0.19 and −0.18, whereas the corresponding σ_P values are 0.73, 0.17 and 0.06, and the σ^0_R values are 0.16, 0.00 and −0.16 [7]. Clearly, the MeS group can decrease the degree of ground-state polarization of the π-bond of trifluorostyrenes and help to increase the rate of cyclodimerization by its polar effect, whereas the two other groups, especially MeSO$_2$−, will have opposite effects.

The main interest, however, lies in the values and relative magnitudes (in parentheses) of the $\sigma^{\bullet}$ values. For the three groups MeSO$_2$−, MeSO− and MeS−, the $\sigma^{\bullet}_{JJ}$ values are 0.41 [7] (1.0), 0.50 (1.2) and 0.62 (1.5), whereas Arnold's $\sigma^{\bullet}_{\alpha}$ values are 0.005 (1.0), 0.018 (3.6) and 0.063 (12.6), and Creary's $\sigma^{\bullet}_{C}$ values are 0.18

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*The σ_{mb} and $\sigma^{\bullet}_{JJ}$ values for the MeSO$_2$− group given in ref. 1 are in error. They should be revised from 0.55 to 0.64 and from 0.38±0.03 to 0.41±0.04, respectively.

TABLE 4. Method C: $\sigma^{\bullet}_{JJ}$ values at different temperatures based on the ρ_{mb} value of −0.30

Y	Temperature (°C)					Averaged $\sigma^{\bullet}_{JJ}$ values
	110	120	140	150	160	
H	0	0	0	0	0	0
p-NMe_2	1.23	1.16	1.00	0.96	0.91	1.05 ± 0.14
p-MeS	0.54	0.58	0.59	0.73	0.71	0.63 ± 0.08
p-COMe	0.55	0.50	0.50	0.55	0.49	0.52 ± 0.03
p-MeSO	0.52	0.45	0.47	0.47	0.54	0.49 ± 0.04
p-Ph	0.49	0.49	0.44	0.45	0.46	0.47 ± 0.02
p-CN	0.36	0.37	0.36	0.41	0.39	0.38 ± 0.02
p-$MeSO_2$	0.35	0.32	0.36	0.39	0.45	0.37 ± 0.05
p-COOH	0.41	0.39	0.34	0.32	0.37	0.37 ± 0.04
p-$CONH_2$	0.38	0.39	0.37	0.39	0.33	0.37 ± 0.02
p-NO_2	0.33	0.33	0.32	0.34	0.29	0.32 ± 0.02
p-COOMe	0.29	0.30	0.30	0.35	0.32	0.31 ± 0.02
p-$SiMe_3$	0.32	0.30	0.29	0.30	0.28	0.30 ± 0.01
p-Pr^c	0.40	0.33	0.27	0.27	0.28	0.30 ± 0.06
p-Bu^t	0.24	0.27	0.30	0.24	0.29	0.27 ± 0.03
p-OMe	0.34	0.32	0.23	0.26	0.20	0.27 ± 0.06
p-Br	0.23	0.22	0.21	0.24	0.23	0.23 ± 0.01
p-Cl	0.23	0.21	0.19	0.21	0.22	0.21 ± 0.01
p-Me	0.18	0.17	0.14	0.16	0.15	0.16 ± 0.02
p-Et	0.20	0.19	0.14	0.18	0.14	0.17 ± 0.03
p-CF_3	−0.04	−0.05	−0.03	−0.05	−0.003	−0.03 ± 0.02
p-F	0.04	−0.002	−0.04	0.01	−0.05	−0.01 ± 0.04
m-Me	0.017	0.02	0	0.014	0	0.01 ± 0.01
m-Br	0.13	0.14	0.07	0.08	0.08	0.10 ± 0.03
m-Bu^t	0.11	0.11	0.10	0.16	0.12	0.12 ± 0.02
m-CN	0.03	0.06	0.11	0.06	0.09	0.07 ± 0.03
m-OMe	0.12	0.10	0.09	0.12	0.08	0.10 ± 0.02
m-COOMe	0.08	0.07	0.12	0.09	0.12	0.10 ± 0.02
m-F	0.03	0.02	0.02	0.03	−0.001	0.02 ± 0.01
m-NO_2	−0.09	−0.04	−0.01	−0.02	−0.003	−0.03 ± 0.03
m-Cl	−0.05	−0.04	−0.09	−0.05	−0.06	−0.06 ± 0.02
m-CF_3	−0.08	−0.10	−0.10	−0.09	−0.08	−0.09 ± 0.01

TABLE 5. Correlation coefficients (values of *r*) for the cross-correlation between the $\sigma^{\bullet}_{JJ}$ values at different temperatures as well as the averaged $\sigma^{\bullet}_{JJ}$ value for Method B for 32 substituents[a]

	110 °C	120 °C	140 °C	150 °C	160 °C	Averaged value
110 °C	1.000	0.993	0.980	0.943	0.945	0.987
120 °C		1.000	0.990	0.969	0.968	0.994
140 °C			1.000	0.970	0.985	0.995
150 °C				1.000	0.981	0.988
160 °C					1.000	0.989
Averaged value						1.000

[a] Similar results were obtained for Method A and Method C.

TABLE 6. Correlation between pairs of different methods[a]

Correlation method	Correlation coefficient (*r*)
A with C	0.9997
A with B	0.9963
B with C	0.9956

[a] Thirty-two averaged $\sigma^{\bullet}_{JJ}$ values were used for each method.

(1.0), 0.18 (1.0) and 0.43 (2.4), respectively. Obviously, the $\sigma^{\bullet}_{\alpha}$ and $\sigma^{\bullet}_{C}$ values for the first two groups differ from the $\sigma^{\bullet}_{JJ}$ values in opposite ways. Although the trustworthiness of the $\sigma^{\bullet}_{JJ}$ scale has been shown very recently, we suggest that all the above-mentioned $\sigma^{\bullet}$ values should be tested in future by rigorously measured rate constants of an exceedingly clean radical reaction (cf. refs. 1 and 8).

The substituent effects of sulfur-containing groups on an α-spin have been discussed by previous workers (cf. refs. 3 and 4). We prefer to visualize these effects in terms of two simple and well-known resonance schemes involving n-pair type resonance (Scheme 1) and π-pair type resonance (Scheme 2). The dashed line in these schemes represents either shared or unshared electron pairs.

TABLE 7. Rate constants for the thermal dimerization of compounds **1** and **2** at different temperatures

Compound	110 °C	120 °C	140 °C	150 °C	160 °C
	$k\times10^5$	$k\times10^5$	$k\times10^{4a}$	$k\times10^4$	$k\times10^4$
1	2.24±0.02	3.72±0.16	1.38	2.30±0.01	4.46±0.00
2	1.12±0.09	2.06±0.09	0.80	1.42±0.02	2.67±0.13

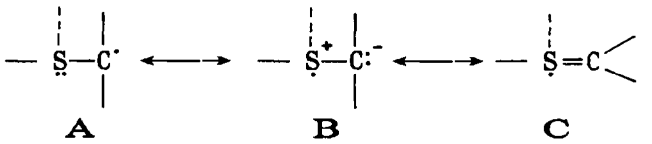
[a] Calculated from a correlation of the other rate constants with the temperatures.

TABLE 8. The Arrhenius and activation parameters for the cyclodimerization of compounds **1** and **2**

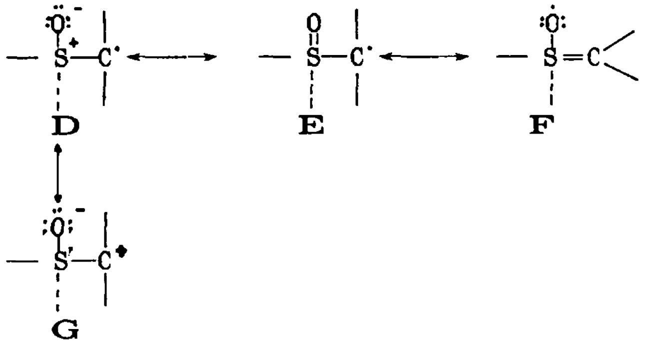
Compound	Temperature (°C)	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	$\Delta G^{\ddagger}$ (kcal mol^{-1})	
1	110	18.97±2.27	−30.87±5.9	30.80	$E=19.73\pm2.27$
	120	18.95±2.27	−31.23±5.8	31.23	(kcal mol^{-1})
	140	18.91±2.27	−31.15±5.5	31.78	$\ln A=15.11\pm2.8$
	150	18.89±2.27	−31.31±5.4	32.14	
	160	18.87±2.27	−31.12±5.2	32.35	$r=0.9984$
2	110	20.25±1.75	−28.91±4.6	31.33	$E=21.01\pm1.75$
	120	20.23±1.75	−29.14±4.4	31.81	(kcal mol^{-1})
	140	20.19±1.75	−29.14±4.2	32.23	$\ln A=16.12\pm2.2$
	150	20.17±1.75	−29.25±4.1	32.55	
	160	20.15±1.75	−29.19±4.0	32.70	$r=0.9987$

TABLE 9. The chemical shifts and coupling constants for compounds **1** and **2**

Compound	Chemical shifts (ppm)			Coupling constants (Hz)			σ_{mb}
	F^1	F^2	F^3	J_{12}	J_{23}	J_{13}	
1	22.93	37.48	100.83	76	38	120	0.19
2	20.90	35.47	101.60	70	40	120	0.64



Scheme 1.



Scheme 2.

Apparently, although the MeS— group can delocalize the spin only via Scheme 1, with perhaps a heavily weighted contribution from structure C, it becomes a very effective α-spin-stabilizer. On the other hand, the $MeSO_2$— group remains a good spin-stabilizer, even though it can only operate via Scheme 2, by analogy with substituents such as CH_3CO— ($\sigma_{JJ}^{\bullet}=0.54$). Finally, we may note that the MeSO— group is a better spin-stabilizing group than the $MeSO_2$— group. This observation might be related to the fact that the MeSO— group, which carries with it both an n-pair and a π-pair, can delocalize spin via both schemes.

Experimental

The syntheses of *para*-methylsulfinyl-trifluorostyrene (**1**) and *para*-methylsulfonyl α,β,β-trifluorostyrene (**2**) have been reported elsewhere [1]. ^{19}F NMR data (with chemical shifts in ppm from external TFA and positive for upfield shifts) were recorded on a Varian EM-360L spectrometer (60 MHz for ^{1}H and 56.4 MHz for ^{19}F).

The rate constants for the dimerizations of **1** and **2** in THF over the temperature range 110–160 °C were measured by previously described methods [9]; however, tetrahydrofuran was used as the solvent instead of n-hexane in which the solubility of **1** and **2** is too low.

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