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The spin-delocalization substituent parameter $\sigma_{JJ}^{\bullet}$. Part 10. The spin-delocalizing abilities of the *para*-trifluorovinyl and *para*-acetoxy groups. Synthesis of *para*-trifluorovinyl-, *para*-vinyl- and *para*-acetoxy-α,β,β-trifluorostyrenes

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Abstract

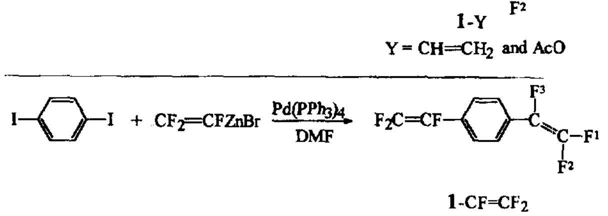
para-Trifluorovinyl α,β,β-trifluorostyrene (**1-CF=CF$_2$**), *p*-acetoxy α,β,β-trifluorostyrene (**1-AcO**) and *p*-vinyl α,β,β-trifluorostyrene (**1-CH=CH$_2$**) have been synthesized. The rate constants (k) for the thermal cyclodimerization of **1-CF=CF$_2$** and **1-AcO** have been measured over the temperature range 90–130 °C for **1-CF=CF$_2$** and 110–160 °C for **1-AcO**. The σ_{mb} polar substituent constants of the *p*-CF=CF$_2$, *p*-CH=CH$_2$ and *p*-AcO groups calculated from the ^{19}F NMR chemical shifts are: for *p*-CF=CF$_2$, 0.40; for *p*-CH=CH$_2$, 0.03; and for *p*-AcO, -0.14, and the $\sigma_{JJ}^{\bullet}$ spin-delocalization substituent constants of the *p*-CF=CF$_2$ and *p*-AcO groups are 0.86 and 0.35, respectively, i.e., the former is a highly effective spin-stabilizer while the latter is moderately effective. Owing to the occurrence of a small amount of side-reaction, the $\sigma_{JJ}^{\bullet}$ value of the *p*-CH=CH$_2$ group could not be accurately measured, but it was very roughly estimated to be in the range of 0.50–0.66.

Keywords: Trifluorovinyl group; Acetoxy group; Spin-delocalization substituent constant $\sigma_{JJ}^{\bullet}$; Polar substituent constants σ_{mb}; *p*-Substituted α,β,β-trifluorostyrenes; Cycloaddition; NMR spectroscopy; Mass spectroscopy

1. Introduction

Recently, on the basis of ^{19}F NMR data for Y-substituted α,β,β-trifluorostyrenes (**1-Y**) and the rate constants of their thermal cyclodimerization reactions, as shown by Eq. (1), we have set up a self-consistent and thoroughly cross-checked scale of spin-delocalization substituent constants, σ_{jj}^{*} [1], which has been successfully applied to the correlation analysis of radical addition reactions [2], hydrogen-atom abstraction reactions [3], the UV spectra of some representative aromatic compounds [4], the fluorescence spectra of substituted styrenes [5] and the EPR spectroscopy of phenyl nitroxides [6]. The present work reports the evaluation of the $\sigma_{JJ}^{\bullet}$ and σ_{mb} values for two interesting and important substituents, namely, trifluorovinyl (–CF=CF$_2$) and acetoxy (–AcO). The former is of interest because (1) it is a vinyl- or phenyl-type substituent ($\sigma_{JJ}^{\bullet}$ of the phenyl group = 0.47) and is expected to be a highly effective spin-delocalizing group, and because (2) an α-fluorine atom is known to be weakly spin-stabilizing rather than 'spin-destabilizing' [7]. Hence, it would be meaningful to compare the stabilizing ability of –CF=CF$_2$ with that of –CH=CH$_2$, if possible. The acetoxy group is an important substituent and it is of interest to compare its spin-delocalizing ability with that of its isomeric group, i.e., the methoxy carbony (–COOMe, $\sigma_{JJ}^{\bullet} = 0.33$) because the acetoxy group is an electron-pair donor ($\sigma_p = -0.31$, $\sigma^+ = -0.19$, $\sigma_{mb} = -0.14$) while the methoxycarbonyl group is a moderately strong electron-pair acceptor ($\sigma_p = 0.45$, $\sigma^+ = 0.49$, $\sigma_{mb} = 0.48$).

The synthetic routes to **1-CH=CH$_2$**, **1-AcO** and **1-CF=CF$_2$** are indicated by Scheme 1. Unfortunately, the



Scheme 1.

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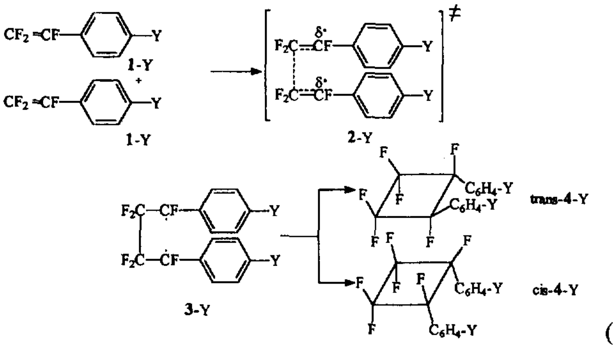
Table 1
^{19}F NMR data for **1-CF=CF$_2$**, **1-AcO** and **1-CH=CH$_2$** in n-hexane and the corresponding σ_{mb} values

Compound	Chemical shifts (ppm)			Coupling constants (Hz)			σ_{mb}
	F^1	F^2	F^3	J_{12}	J_{23}	J_{13}	
1-CF=CF$_2$	22.13	39.22	101.34	66	108	33	0.40
1-AcO	24.87	40.07	100.73	76	120	34	−0.14
1-CH=CH$_2$ [8b]	23.86	38.53	100.80	71	109	33	0.03

cyclodimerization of **1-CH=CH$_2$** was found to be accompanied by a small amount of side-reaction (probably polymerization), and the $\sigma_{JJ}^{\bullet}$ value of the vinyl group could not be accurately measured. However, it was estimated to be very roughly in the range 0.50–0.66.



(1)

2. Results and discussion

2.1. Polar substituent σ_{mb}

For α,β,β-trifluorostyrenes, 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 the **1-Y** compounds [6]. On the basis of this observation, we have used Eq. (2) to set up a polar substituent constant scale of σ_{mb} which reflects the degree of polarization of the π-bond of Y-substituted styrenes, where $\Delta\delta_{3-1} = (\delta_{3-1})_Y - (\delta_{3-1})_H$. The tailor-made polar substituent parameters σ_{mb} are expected to reflect the ability of a given substituent to polarize the π-bond of, for example, Y-substituted styrenes or phenylacetylenes in the ground state. From the ^{19}F NMR spectral values of compounds **1-CF=CF$_2$**, **1-CH=CH$_2$** and **1-AcO** listed in Table 1, the σ_{mb} values of the p-CF=CF$_2$, p-CH=CH$_2$ and p-AcO groups can be evaluated as 0.40, 0.03 and −0.14, respectively [1]. The σ_{mb} value for CF=CF$_2$, i.e.

$$\sigma_{mb} = 0.16\Delta\delta_{3-1} - 0.09 \qquad (2)$$

shows that the CF=CF$_2$ group is a moderately strong electron-pair withdrawing group, obviously a consequence of the presence of three highly electronegative fluorines. The vinyl group is known to be an electron-pair sink, its σ_{mb} value probably reflecting the net balance between two types of effects, i.e. the p–π repulsive force of the fluorine atoms versus the electronegativity of the CF=CF$_2$ group as a whole.

2.2. Spin-delocalization constants $\sigma_{JJ}^{\bullet}$

As in our previous work [1], we use a dual-parameter equation (Eq. (3)) for the evaluation of the $\sigma_{JJ}^{\bullet}$ constants.

$$\log(k_Y/k_H) = \rho_{mb}\sigma_{mb} + \rho^{\bullet}\sigma^{\bullet} \qquad (3)$$

As shown by Eq. (3), the rate constants (k) are evaluated from rate measurements for the thermal cyclodimerization reactions of compounds **1-Y** at five temperatures. Method A, as described previously in detail in Ref. [1c], was used for the calculation of the $\sigma_{JJ}^{\bullet}$ values of the substituents p-CF=CF$_2$ and p-AcO. The dimerization rate constants of **1-CF=CF$_2$** and **1-AcO**, together with the $\sigma_{JJ}^{\bullet}$ values of p-CF=CF$_2$ and p-AcO are listed in Table 2.

For the CH=CH$_2$ group, the rate constant of the dimerization reaction of **1-CH=CH$_2$** could not be measured accurately by UV spectroscopy because of the occurrence of some side-reaction, probably polymerization.

Considering the $\sigma_{JJ}^{\bullet}$ values of the phenyl (0.47) and vinyl (0.50–0.66) groups, the $\sigma_{JJ}^{\bullet}$ value of the trifluorovinyl group may also be expected to be around or above 0.50, because they all possess unsaturated bond(s) in conjugation with the reaction centre CF=CF$_2$. It has been established previously that an α-fluorine atom on the methyl radical is weakly stabilizing [7], i.e., the stability order of methyl radicals is CF$_2$H$^{\bullet}$ > CFH$_2^{\bullet}$ > CH$_3^{\bullet}$. Therefore, one may expect that the imaginary resonance structure (Scheme 2) **II-Z** (Z = F) carries more weight than does **II-Z** (Z = H), i.e., the substituent CZ=CZ$_2$ (Z = F) is expected to be more spin-delocalizing than the substituent CZ=CZ$_2$ (Z = H). Our value of 0.86 for the $\sigma_{JJ}^{\bullet}$ value of CF=CF$_2$ is certainly in accord with the aforesaid speculation.

Although both the AcO and MeO substituents possess an oxygen atom linked to the phenylene ring, the former is a more effective spin-delocalizing group ($\sigma_{JJ}^{\bullet} = 0.35$) than the latter ($\sigma_{JJ}^{\bullet} = 0.23$). This might be rationalized by considering the canonical structures in Scheme 3, i.e., for AcO, which has an extra structure **VI-C**. Finally, it is interesting to note that the two substituents, i.e., AcO ($\sigma_{JJ}^{\bullet} = 0.35$) and COOMe ($\sigma_{JJ}^{\bullet} = 0.35$), have similar abilities to delocalize the spin,

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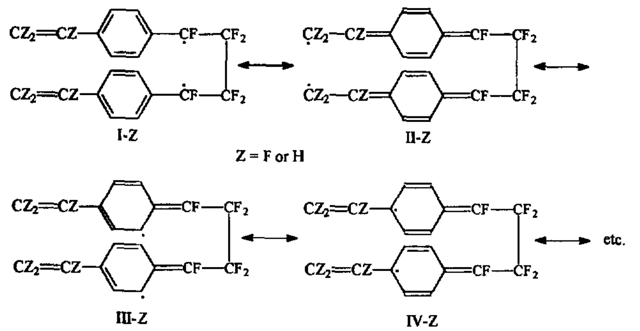
[1] Value of σ_{mb} for **1-CH=CH$_2$** taken from Ph.D. dissertation of Y.Q. Shi.

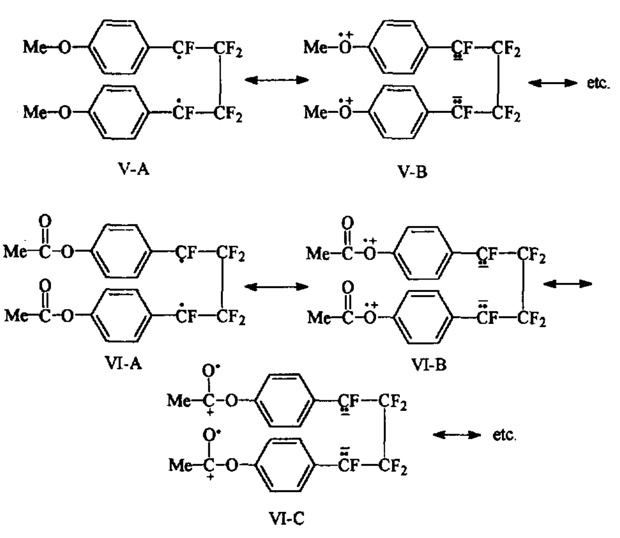
Table 2
Thermal cyclodimerization rate constants of **1-CF=CF$_2$** and **1-AcO**, their corresponding $\sigma_{JJ}^{\bullet}$ values at five different temperatures and the averaged $\sigma_{JJ}^{\bullet}$ value

Temp. (°C)	Compound **1-CF=CF$_2$**		Compound **1-AcO**	
	Rate constant ($\times 10^{-5}$)	$\sigma_{JJ}^{\bullet}$	Rate constant ($\times 10^{-5}$)	$\sigma_{JJ}^{\bullet}$
90	1.08 ± 0.04			
100	2.14 ± 0.05			
110	4.02 ± 0.07	0.86	1.64 ± 0.18	0.27
120	8.2 ± 0.3	0.89	3.71 ± 0.01	0.33
130	15.3 ± 0.2			
140	26.8 [a]	0.82	12.1 ± 0.1	0.31
150	46.8 [a]	0.87	26.6 ± 0.8	0.42
160	79.6 [a]	0.85	44.4 ± 1.3	0.42
average $\sigma_{JJ}^{\bullet}$		0.86 ± 0.02		0.35 ± 0.07

[a] Extrapolated from the rate constants at temperatures in the range 90–130 °C.



Scheme 2. Resonance structures for the intermediates in the cyclodimerization of **1-CF=CF$_2$** and **1-CH=CH$_2$**.



Scheme 3. Resonance structures for the intermediates in the cyclodimerization of **1-MeO** and **1-AcO**.

although they possess opposite polar (electron-pair) properties.

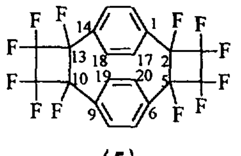
2.3. Kinetic experiments

2.3. For compound 1-CF=CF$_2$

Although previous experiments were run in the temperature range 110–160 °C, the experiments on **1-CF=CF$_2$** were performed over the temperature range 90–130 °C because the dimerization rate of **1-CF=CF$_2$** is much faster than those of the other **1-Y** compounds. The rate constants for **1-CF=CF$_2$** given in Table 1 for 140–160 °C were obtained by extrapolation from the rate constants measured at 90–130 °C.

With two identical reaction centres (CF=CF$_2$) in the molecule, the reaction probability of **1-CF=CF$_2$** is four-times the probability for the other **1-Y** compounds which possess only one reaction centre. In other words, there is a statistical factor of four for the dimerization of **1-CF=CF$_2$** in comparison with all the other trifluorostyrenes, i.e., $k = k_{\text{ob}}/4$, where k_{ob} is the observed rate constant based on the concentration of **1-CF=CF$_2$** and k is the true rate constant.

The dimerization reaction of **1-CF=CF$_2$** was confirmed by the identification of very small amounts of the dimerization products *trans*-1,2-bis(*p*-trifluoroethenylphenyl)-hexafluorocyclobutane (*trans*-**4-CF=CF$_2$**) and *cis*-1,2-bis-(*p*-trifluoroethenylphenyl)hexafluorocyclobutane (*cis*-**4-CF=CF$_2$**). Another product, i.e., 2,3,3,4,4,5,10,11,11,12,12,13-dodecafluoro-(1,14:6,9)-diethano[2,2]paracyclophane (**5**) was isolated in trace amounts. The former two products (*trans*-**4-CF=CF$_2$** and *cis*-**4-CF=CF$_2$**) were identified by MS and NMR spectroscopy, and product **5** was identified by NMR spectroscopy (see Experimental details).



(**5**)

2.3.2. For compound 1-AcO

The thermal cyclodimerization rate constant of **1-AcO** was measured by UV spectroscopy over the usual temperature range (110–160 °C).

As the UV absorption of **1-AcO** (monomer, $\lambda_{\max} = 249.0$ nm) is far from its dimer ($\lambda_{\max} = 230.0$ nm), the concentration of **1-AcO** in the cyclodimerization reaction at specific time intervals could be monitored accurately by UV absorp-

Table 3
Arrhenius activation energies (E), and activation parameters $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$, for the cyclodimerization of **1-CF=CF$_2$** and **1-AcO**

Temp. (°C)	Compound **1-CF=CF$_2$**[a]			Compound **1-AcO**[b]		
	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)	$\Delta G^{\neq}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)	$\Delta G^{\neq}$ (kcal mol^{-1})
90	18.58 ± 1.74	−30.50 ± 4.80	29.65 ± 1.74			
100	18.56 ± 1.74	−30.61 ± 4.67	29.98 ± 1.74			
110	18.54 ± 1.74	−30.76 ± 4.55	30.32 ± 1.74	20.79 ± 2.23	−26.75 ± 5.80	31.04 ± 2.23
120	18.52 ± 1.74	−30.68 ± 4.43	30.58 ± 1.74	20.77 ± 2.23	−26.60 ± 5.70	31.23 ± 2.23
130	18.50 ± 1.74	−30.71 ± 4.32	30.88 ± 1.74			
140	18.48 ± 1.74	−30.80 ± 4.22	31.20 ± 1.74	20.75 ± 2.23	−26.96 ± 5.40	31.89 ± 2.23
150	18.46 ± 1.74	−30.84 ± 4.12	31.51 ± 1.74	20.73 ± 2.23	−26.68 ± 5.30	32.02 ± 2.23
160	18.44 ± 1.74	−30.89 ± 4.02	31.82 ± 1.74	20.71 ± 2.23	−26.89 ± 5.20	32.36 ± 2.23

[a] $E = 19.36 \pm 1.74$ kcal mol^{-1}; $\ln A = 15.33 \pm 2.29$.
[b] $E = 21.64 \pm 2.23$ kcal mol^{-1}; $\ln A = 17.41 \pm 2.7$.

tion spectroscopy. Results from UV spectra and GC methods have previously been proven to be the same [1b,8].

2.4. *The activation parameters $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$*

The activation energy E of compounds **1-CF=CF$_2$** and **1-AcO** were obtained by application of the Arrhenius equation. The logarithm of the rate constant and the reciprocal of the absolute temperature are well correlated, for **1-CF=CF$_2$** by the equation $\log k = 6.657 - 4226/T$, $r = 0.9996$, $F = 3405.9$, $n = 5$, $\varphi = 0.0383$, and for **1-AcO** by the equation $\log k = 7.560 - 4725/T$, $r = 0.9987$, $F = 45.63$, $n = 5$, $\varphi = 0.321$. Other activation parameters, i.e., $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$, are also listed in Table 3.

3. Experimental details

^{19}F NMR spectra were obtained at 56 MHz on a Varian EM360A spectrometer or at 188 MHz on a Varian XL-200 spectrometer with trifluoroacetic acid as the external standard. UV–vis absorption spectra were taken on a Perkin-Elmer 559 spectrometer or a Perkin-Elmer Lamda 2 spectrometer. Mass spectra (MS) were taken on a Finnigan 402 spectrometer or a Hewlett Packard model 5989A spectrometer. GC analysis were undertaken on a Hewlett Packard 5890 gas chromatograph.

3.1. *Synthesis of **1-CF=CF$_2$***

To a 250 ml three-necked flask, 10 g of *p*-diiodobenzene, 1.75 g of Pd(PPh$_3$)$_4$ and 100 ml of a DMF solution of CF$_2$=CFZnBr (0.75 M) were added [9]. The temperature was maintained at 70 °C for 6 h and the solution then diluted with HCl solution, extracted with petroleum ether and purified by column chromatography using petroleum ether as eluent when 6.0 g (83.1% yield) of **1-CF=CF$_2$** was obtained. ^{19}F NMR (hexane): see Table 1. MS (EI, 70 eV, m/z, relative intensity): 238 (100.0) [$C_{10}H_4F_6$] = M$^+$; 219 (6.58) [$C_{10}H_4F_5$] = [M − F]$^+$; 187 (26.69) [$C_9H_3F_4$] = [M − CF$_2$H]$^+$; 169 (52.12) [$C_9H_4F_3$] = [M − CF$_3$]$^+$; 149 (3.57) [$C_9H_3F_2$] = [M − 1 − CF$_4$]$^+$; 138 (7.59) [$C_8H_4F_2$] = [M − C$_2$F$_4$]$^+$. HRMS [found (calculated)]: 238.0195 (238.132). UV (in 95% ethanol): $\lambda_{max} = 268.0$ nm.

3.2. *Synthesis of **1-CH=CH$_2$***

3.2.1. *Preparation of p-bromobenzyl bromide [10]*

To a 250 ml three-necked flask, 27.7 g of *p*-bromotoluene, 28.8 g of NBS and 60 ml of CCl$_4$ were added. The mixture was refluxed and the reaction was monitored by TLC. When the reaction was over, the white solid was filtered and washed with CCl$_4$. The organic layers were combined, washed with brine and dried over Na$_2$SO$_4$ when 38.8 g (95.8% yield) of *p*-bromobenzyl bromide was obtained.

3.2.2. *Preparation of p-bromobenzyltriphenylphosphine bromide [11]*

A mixture consisting of 38.8 g of *p*-bromobenzyl bromide, 41.6 g of PPh$_3$ and 100 ml of CHCl$_3$ was added to a 250 ml round-bottomed flask and refluxed for 5 h. The solvent was removed by rotary evaporation and ethyl ether added to the flask when 71.0 g (89.4% yield) of a white solid was obtained.

3.2.3. *Preparation of p-bromostyrene*

To a 500 ml triangular flask, 35.5 g of *p*-bromobenzyltriphenylphosphine bromide and 250 ml fo 40% formaldehyde were added. A concentrated sodium hydroxide solution containing 3.0 g of NaOH was then dropped slowly into the solution. The reaction mixture was allowed to stand overnight, extracted with petroleum, washed with brine, dried over CaCl$_2$ and concentrated by rotary evaporation. *para*-Bromostyrene (9.0 g) was obtained in 70.9% yield.

*3.2.4. Synthesis of **1-CH=CH$_2$***

To a 250 ml three-necked flask, 1.6 g of $Pd(PPh_3)_4$, 9.0 g of *p*-bromostyrene and 160 ml of a DMF solution of $CF_2{=}CFZnBr$ (0.75 M) were added. The mixture was maintained at 70 °C for 8 h. The product obtained was treated by the same procedure as for **1-CF=CF$_2$**. The product **1-CH=CH$_2$** (8.0 g) was obtained in 88.3% yield. MS (EI, 70 eV, *m/z*, relative intensity): 184 (M^+, 100.00); 183 (M^+-1, 22.92); 182 (M^+-2, 18.91); 185 (M^++1, 16.04); 133 (M^+-CF_2-1, 16.81); 103 ($M^+-CF{=}CF_2$, 15.36). Elemental analysis for $C_{10}H_7F_3$ [found (calculated)]: C, 64.72 (65.22); H, 3.46 (3.83); F, 30.25 (30.95)%.

*3.3. Synthesis of **1-AcO***

3.3.1. Preparation of p-acetoxybromobenzene

To a 250 ml three-necked flask, 25 g of *p*-bromophenol and 60 ml of pyridine were added and then 20 ml of acetyl chloride was added dropwise. After the reaction was complete, the mixture was diluted by ice-cooled dilute aqueous HCl, extracted with ethyl ether, washed with water, dried over $CaCl_2$ and concentrated by rotatory evaporation. The product *p*-$AcOC_6H_4Br$ was obtained in 90.0% yield (27.87 g). ^{1}H NMR (CCl_4) δ: 2.12 (s, 3H); 6.87 (s, 2H); 6.87 (s, 2H) ppm.

*3.3.2. Synthesis of **1-AcO***

To a 250 ml three-necked flask, 10 g of *p*-$AcOC_6H_4Br$, 1.4 g of $Pd(PPh_3)_4$ and 140 ml of a DMF solution of $CF_2{=}CFZnBr$ (0.75 M) were added. The temperature was maintained at 70 °C for 8 h. The reaction mixture was diluted with HCl solution, extracted with ether and purified by column chromatography with ethyl acetate petroleum ether (3:100) as eluent when 8.0 g of product was obtained in 64.0% yield [b.p. 184–186 °C (not corrected)]. Elemental analysis for $C_{10}H_7F_3O_2$ [found (calculated)]: C, 54.35 (55.56); H, 3.06 (3.26); F, 26.12 (26.37)%. ^{19}F NMR (hexane): see Table 1. ^{1}H NMR (CCl_4) δ: 2.24 (s, 3H); 7.19 (d, $J=10.0$ Hz, 2H); 7.54 (d, $J=10.0$ Hz, 2H) ppm. MS (EI, 70 eV, *m/z*, relative intensity): 216 (30.64) $[C_{10}H_7F_3O_2]=M^+$; 217 (19.11) $[C_{10}H_8F_3O_2]=[M+1]^+$; 174 (100.0) $[C_8H_5F_3O]=[M-CH_3CHO]^+$; 145 (12.50) $[C_9H_5O_2]=[M-2-CF_3]^+$; 43 (38.79) $[C_2H_3O]=[CH_3CO]^+$. UV (in 95% ethanol): $\lambda_{max}=249.0$ nm.

3.4. Typical kinetic experiment

The cycloaddition reactions of **1-CF=CF$_2$**, **1-AcO** and **1-CH=CH$_2$** were performed in sealed tubes as described previously [1]. In a thick-walled tube of 2.5 mm i.d. was placed 0.2 ml of a n-hexane solution of the reactants and internal references for GC measurements for **1-CF=CF$_2$**. For UV measurements of **1-AcO** and **1-CH=CH$_2$**, no internal reference was needed. The sealed tube was twice degassed (0.05 Torr) at liquid nitrogen temperature, and replaced by high purity nitrogen treated with Ag and Pd molecular sieves three times. The reactions were conducted at five temperatures and the products were quenched in Dry Ice at specified time intervals. In experiments with **1-CH=CH$_2$** some turbidity of the solution was observed, and for this reason the rate constant values thus obtained were not considered to be highly reliable. The $\sigma_{JJ}^{\bullet}$ value calculated therefrom was considered to be an approximate value only.

*3.4.1. Preparation of trans-1,2-bis(p-trifluoroethenylphenyl)hexafluorocyclobutane (trans-**4-CF=CF$_2$**) and cis-1,2-bis(p-trifluoroethenylphenyl)hexafluorocyclobutane (cis-**4-CF=CF$_2$**) and the isolation of (2,3,3,4,4,5,10,11,11,12,12,13)-dodecafluoro-(1,14:6,9)-diethano[2,2]paracyclophane (**5**)*

trans-1,2-Bis(*p*-trifluoroethenylphenyl)hexafluorocyclobutane (*trans*-**4-CF=CF$_2$**, *cis*-1,2-bis(*p*-trifluoroethenylphenyl)hexafluorocyclobutane (*cis*-**4-CF=CF$_2$** and (2,3,3,4,4,5,10,11,11,12,12,13)-dodecafluoro-(1,14:6,9)-diethano[2,2]paracyclophane (**5**) were prepared by the cyclodimerization reaction of **1-CF=CF$_2$** conducted in a sealed tube at 160 °C for 30 h. Separation was effected by thin layer chromatography, the eluent being petroleum ether (30–60 °C). The first two compounds were identified by MS and NMR spectroscopy. Compound **5** was obtained only in trace amounts and was identified by NMR spectroscopy.

trans-1,2-Bis(*p*-trifluoroethenylphenyl)hexafluorocyclobutane (*trans*-**4-CF=CF$_2$**): ^{19}F NMR ($CDCl_3$) δ: 100.89 (d–d, $J_1=111.72$ Hz, $J_2=33.10$ Hz, 2F); 87.12 (s, 2F); 48.03 (s, 4F); 35.11 (d–d, $J_1=107.58$ Hz, $J_2=62.06$ Hz, 2F); 20.01 (d–d, $J_1=62.02$ Hz, $J_2=33.10$ Hz, 2F) ppm. ^{1}H NMR ($CDCl_3$) δ: 7.57 (s, 8H) ppm. MS (EI, 70 eV, *m/z*, relative intensity): 313 (6.42) $[M+1-CF_4-C_6H_4]^+$; 163 (5.40) $[C_4F_6+1]^+$; 97 (56.67) $[CF_2{=}CF_2-3]^+$ or $[F-C_6H_4+2]^+$; 83 (58.84) $[CF{=}CF_2+2]^+$; 81 (46.89) $[CF{=}CF_2]^+$; 69 (83.77) $[CF_3]^+$.

cis-1,2-Bis(*p*-trifluoroethenylphenyl)hexafluorocyclobutane (*cis*-**4-CF=CF$_2$**): ^{19}F NMR ($CDCl_3$) δ: 101.21 (d–d, $J_1=33.10$ Hz, $J_2=107.58$ Hz, 2F); 89.04 (s, 2F); 47.96 (AB spin system, $J_{AB}=223.45$ Hz, 4F); 34.79 (d–d, $J_1=62.07$ Hz, $J_2=107.59$ Hz, 2F); 19.92 (d–d, $J_1=33.10$ Hz, $J_2=62.01$ Hz, 2F) ppm. ^{1}H NMR ($CDCl_3$) δ: 7.31 (s, 4H); 7.34 (s, 4H) ppm. MS (EI, 70 eV, *m/z*, relative intensity): 277 (11.48) $[CF_2{=}CF-C_6H_4-CF_2-CF_3+1]^+$; 149 (15.87) $[C_6H_5-CF_3+3]^+$; 81 (51.02) $[CF{=}CF_2]^+$; 69 (100.00) $[CF_3]^+$.

(2,3,3,4,4,5,10,11,11,12,12,13)-Dodecafluoro-(1,14:6,9)-diethano[2,2]paracyclophane (**5**): ^{19}F NMR ($CDCl_3$) δ: 87.07 (s, 4F); 47.90 (s, 8F) ppm. ^{1}H NMR ($CDCl_3$) δ: 7.26 (s) ppm.

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