

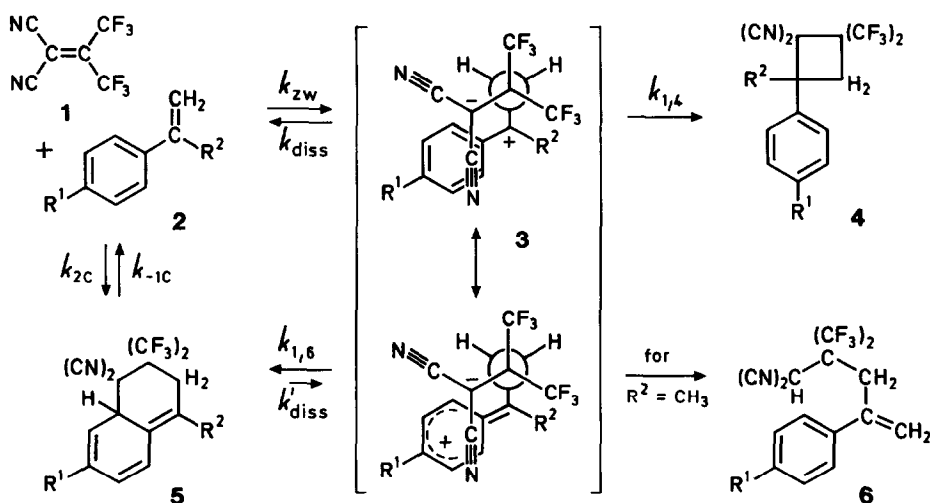
2,2-BIS(TRIFLUOROMETHYL)ETHYLENE-1,1-DICARBONITRILE AND STYRENES THE CONCERTEDNESS OF THE [2 + 4] CYCLOADDITION ¹

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Summary: The effects of substituents and solvent variation on the rate constants are in harmony with a concerted cycloaddition.

In the preceding communication we described reactions of 2,2-bis(trifluoromethyl)ethylene-1,1-dicarbonitrile (BTF; **1**) with styrenes **2**. By rapid reversible Diels-Alder additions we obtained the nonaromatic tetrahydronaphthalenes **5**, whereas slower irreversible reactions led to cyclobutanes **4** or ene products **6**. The cyclobutanes **4** are most likely formed via the 1,4-dipolar intermediates **3**. This zwitterion **3** could also furnish the ene products **6** by protonation/deprotonation; a concerted pathway, $1 + 2$ ($R = \text{CH}_3$) \rightarrow **6**, is likewise plausible.



Interestingly, the same zwitterion **3** might give rise to the Diels-Alder adduct **5** by 1,6 cyclization. *Gauche* conformations of the zwitterion **3** - favored over the anti conformation by Coulombic attraction - are required for the 1,4 and the 1,6 cyclization. In the [2+2] cycloaddition of TCNE with enol ethers, experimental evidence for the initial formation of *gauche* zwitterions came from the high dependence of the rate on solvent polarity ⁵ as well as from the steric course of intercepting the zwitterion by alcohols ⁶.

With **3** as a common intermediate on the pathway to **4** and **5**, the overall rate constants would consist of the rate constant of zwitterion formation, k_{zw} , multiplied by a partition coefficient, $k_{1,4}/(k_{diss} + k_{1,4})$ and $k_{1,6}/(k_{diss} + k_{1,6})$, respectively. The highest point in the energy profiles would be the transition state of zwitterion formation, and donor substituents in the styrene should mainly affect k_{zw} . Whether the Diels-Alder reaction furnishing **5** follows such a stepwise mechanism ⁷ or the concerted pathway (k_{2c}), is the subject of this Letter.

We measured the overall rate constants for the [2+4] cycloadditions of BTF (k_2) to six styrenes (**2**, $R^2 = H$, $R^1 = tBu, CH_3, H, F, Cl, Br$) in benzene at 25°C. The decreasing extinction of the yellow charge transfer complex of **1** + **2** was monitored photometrically. The application of 20 - 100 equiv of **2** made the CT extinction (E_t) proportional to the BTF concentration, and the cycloaddition became pseudo-first-order: $k_{1\psi} = k_2[2]_{av}$, $[2]_{av}$ being the styrene concentration at half consumption of BTF. The graphic evaluation used the rate law of reversible first order reactions ⁸ with E_e being the extinction at equilibrium:

$$k_{exp} = (k_{1\psi} + k_{-1}) = \ln [(E_0 - E_e)/(E_t - E_e)] \cdot 1/t$$

$$k_{1\psi} = k_{exp}(E_0 - E_e)/E_0 = k_2[2]_{av}$$

Rate constants and equilibrium constants ($K = k_2/k_{-1}$) are compared in Table 1 with those for Diels-Alder reactions of tetracyanoethylene (TCNE) and *p*-substituted styrenes measured by Nakahara et al. ^{9,10}. The cycloaddition rates (k_2) for BTF are 2 - 15 times higher than for TCNE. In its [2+2] cycloadditions to butyl vinyl ether and methyl vinyl sulfide, the rate ratio BTF/TCNE reaches 2400 and 8200, but BTF shows much higher sensitivity to steric hindrance ¹¹. The cycloreversion rates (k_{-1}) in Table 1 differ less: BTF/TCNE 0.94 - 1.9.

Table 1. Rate and equilibrium constants for Diels-Alder reactions of BTF and *p*-substituted styrenes (benzene, 25°C) and of TCNE and *p*-substituted styrenes (chloroform, 25°C)

R ¹	10 ³ k ₂ (M ⁻¹ s ⁻¹)		10 ³ k ₋₁ (s ⁻¹)		K (M ⁻¹)	
	BTF	TCNE	BTF	TCNE	BTF	TCNE
OMe		750		120		6.1
<i>t</i> Bu	31		1.6		19	
Me	26	12	1.4	1.5	19	7.9
H	2.4	0.18	0.50	0.25	4.9	0.71
F	1.9		1.4		1.4	
Cl	0.60	0.040	0.54	0.37	1.1	0.11
Br	0.41	0.045	0.42	0.26	0.98	0.18

4-*tert*-Butylstyrene consumes BTF 75 times faster than 4-bromostyrene. The log k_2 values for the cycloadditions of BTF to six styrenes correlate well with Hammett equations both for σ ($r = -0.987$) and for σ^+ (Fig. 1, $r = -0.979$). Slopes of $\rho_{BTF} = -4.2$ and $\rho^+_{BTF} = 4.1$, respectively, indicate considerable stabilization of positive charge by aryl in the transition state. The correspon-

ding rate data for TCNE and styrenes^{9,10} include the fast [2+4] cycloaddition to 4-methoxystyrene. 4-Methoxy allows to differentiate between σ and σ^+ scale; the $\log k_2$ are linearly related to σ^+ with $\rho^+_{\text{TCNE}} = -4.7$. Do these ρ^+ -values distinguish the concerted Diels-Alder mechanism from the pathway via a zwitterionic intermediate?

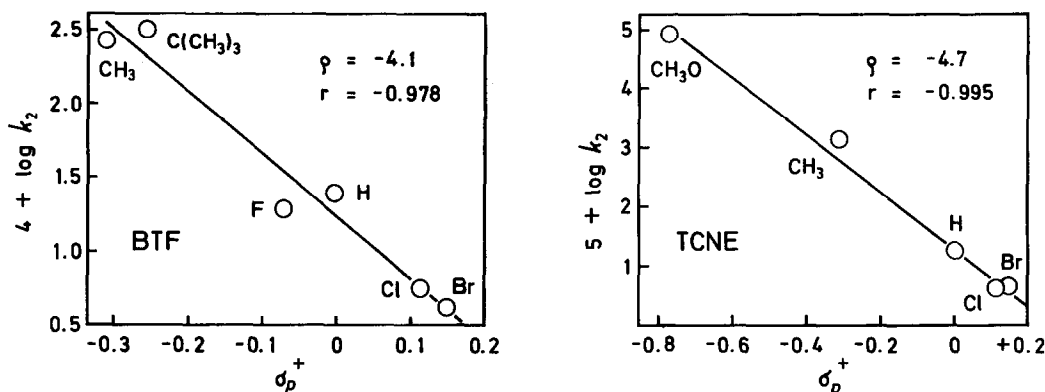


Figure 1. Hammett plot for Diels-Alder reactions of styrenes with BTF (left) and TCNE (right)

According to preparative and kinetic experience, the rate of [2+2] cycloadditions of BTF or TCNE to styrenes responds stronger to the substituent influence than the rate of Diels-Alder reactions. E.g., styrene and halostyrenes do not afford [2+2] cycloadducts with TCNE, whereas donor-substituted styrenes react fast. Bartlett¹² analyzed [2+2] cycloaddition rates of TCNE to 4-donor-substituted styrenes (CH_3O , CH_3S , $\text{C}_6\text{H}_5\text{O}$, cyclopropyl) with the Yukawa-Tsuno equation; $\rho = -7.1$ was interpreted with the formation of the zwitterion - analogous to **3** - in the rate-determining step. This ρ value is distinctly higher than -4.7 and -4.1 reported above and excludes **3** as the common intermediate of [2+2] and [2+4] cycloadditions.

Do ρ values of -4.1 and -4.7 not militate against a concerted pathway? The rates of "normal" Diels-Alder reactions should be inversely proportional to the energy distance of HO (1,3-diene) and LU (dienophile). Sustmann¹³ who successfully applied PMO Theory to concerted Diels-Alder reactions explained the dramatic rate effects observed for dienophiles with exceptionally low LUs. The EA values of maleic anhydride (-1.3 eV) and TCNE (-2.8 eV; cf. BTF: -3.1 eV) are reflected in the Diels-Alder rate constants with 1-substituted butadienes measured by Sauer et al.¹⁴: maleic anhydride $\rho^+ = -1.4$, TCNE $\rho^+ = -5.4$.

We compared the rate constants of two Diels-Alder reactions, BTF + styrene and BTF + 2,3-dimethylbutadiene, in nine solvents (Table 2). The k_2 values for styrene (loss of aromatic resonance) are only by a factor of 100 smaller than those of the open-chain diene, a good argument for an early transition state. With ranges of ≈ 10 the solvent influence is small and is not well described by the polarity parameter E_T . Complexing of BTF is highest for ethyl acetate (lowest k_2)

and lowest for chlorinated hydrocarbons (highest k_2). Nakahara et al.⁹ measured the rates for TCNE + styrene in four chlorinated hydrocarbons and likewise observed a small solvent effect.

Table 2. Rate constants, $10^3 k_2$ ($M^{-1}s^{-1}$) for Diels-Alder additions of BTF to styrene (A) and 2,3-dimethylbutadiene (B) at 25°C

No.	Solvent	A	B
1	AcOEt	1.2	100
2	<i>c</i> -C ₆ H ₁₂	0.93	110
3	CCl ₄	1.6	170
4	C ₂ H ₅ CN	2.8	260
5	C ₆ H ₆	2.4	330
6	CH ₃ CN	4.0	390
7	CHCl ₃	6.9	750
8	CH ₂ Cl ₂	6.1	850
9	<i>o</i> -C ₆ H ₄ Cl ₂	9.1	1100

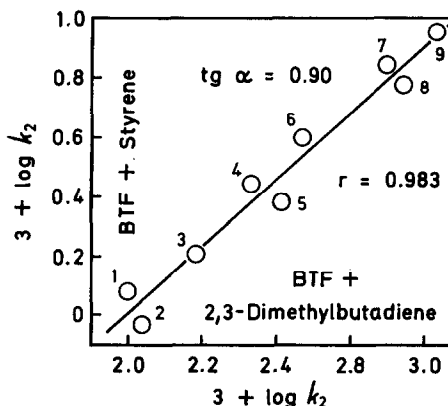


Figure 2. Correlation of $\log k_2$ for two Diels-Alder reactions of BTF (solvent key Table 2)

The $\log k_2$ of the two cycloadditions (Table 2) correlate well with each other (Fig. 2), and the slope of 0.90 is tantamount to a nearly identical response to solvent variation. This convergence argues for the same mechanism, in all likelihood the concerted one; the experimental k_2 for styrenes is the k_{2c} of the formula scheme.

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