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[2+2] CYCLOADDITIONS OF 2,2-BIS(TRIFLUOROMETHYL)ETHYLENE-1,1-DICARBONITRILE WITH VINYL SULFIDES AND KETENE S,S-ACETALS[1]

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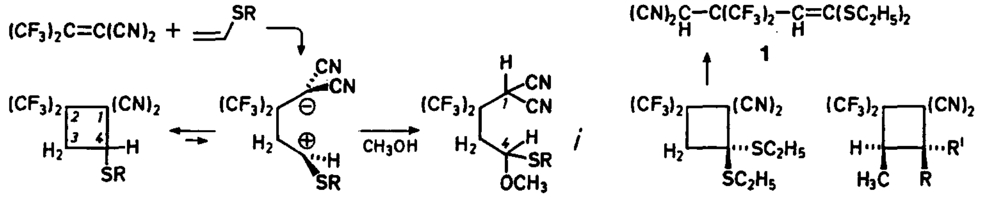
Summary: In its [2+2] cycloadditions to vinyl sulfides, the title olefin (BTF) exceeds tetracyanoethylene up to 8200-fold in rate, but is more sensitive to steric hindrance by β-substituents in the donor olefin; some vinyl sulfides react faster than vinyl ethers with BTF. The dependence of rate on solvent polarity is in harmony with zwitterionic intermediates.

Tetracyanoethylene (TCNE) forms cyclobutanes with enol ethers via zwitterionic intermediates[2], and thioenol ethers analogously combine with the acceptor olefin[3]. Pursuing the study of dipolar [2+2] cycloadditions, we have turned our attention to 2,2-bis(trifluoromethyl)ethylene-1,1-dicarbonitrile (BTF)[4] and demonstrated that cyclobutane formation with enol ethers takes place via 1,4-dipoles, too[5]. Here we compare BTF with TCNE in its cycloadditions to *thio*-substituted olefins.



2 **3** **4** **5**

1

6 R = SCH_3, R' = H

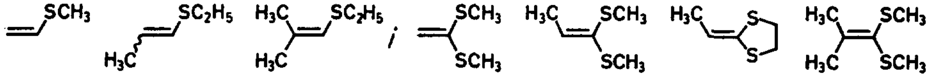
7 R = H, R' = SCH_3

Cyclobutanes **2**[6] were formed from BTF and vinyl sulfides in rapid reactions (10 s - 5 min at 0°C) and good yields (72 - 95% after high vac. distillation); **2**, R = *t*Bu, was described by Middleton in his pioneer paper[4]. The anisochronism of the CF_3 groups and the ABX pattern of the ring protons speak against β-substitution products of the vinyl sulfides. *E.g.*, the ^{19}F NMR spectrum ($CDCl_3$) of **2**, R = CH_3, shows two q at δ -68.6 and -70.1 with J = 10.6 Hz whereas the proton signals of 3-H_2 occur as two dd at 2.62 and 2.89 with $J_{3,3}$ = 15 Hz; the t of 4-H at 4.27 indicates equal couplings with 3-H_2 (10.2 Hz).

The ring closure of the zwitterion, **3** → **2**, is reversible as observed for the cycloadducts from BTF and vinyl ether[5]. When cyclobutanes **2** were kept in methanol at room temperature for several days, zwitterions **3** were trapped as O,S-acetals **4**, likewise distillable in high vacuum. The O,S-dimethyl acetal **4**, R = CH_3 (73%, oil, bp 70°C/0.4 Torr), displays δ_H 2.05 for SCH_3, 3.42 for OCH_3, and 5.48 for the s of 1-H.

In a similar [2+2] addition, ketene S,S-diethylacetal and BTF furnished cyclobutane **5** (s of 3-H_2 at δ_H 2.95) within fractions of a second. Distillation of **5** at 10^{-4} Torr furnished the substituted ketene dithioacetal **1** (mp 36.5 - 37.5°C) which probably originates from the open-chain zwitterion by prototropy. The s at δ_F -67.7 for two CF_3 groups reveals the symmetry of **1**; the s of the vinyl-H occurs at δ_H 5.73, and the s of 1-H at 6.86 is exchanged by CH_3OD.

BTF cycloadditions to ethyl *cis*- and *trans*-propenyl sulfide afforded the *cis,trans* isomeric cyclobutanes **6** (mp 47 - 48°C) and **7** (mp 54.5-55.5°C) in 76% and 82% yield. The stereochemical leakage due to rotation in the zwitterion was smaller than observed for the corresponding enol ethers [5], *e.g.*, the *cis* donor olefin gave rise to **6**/**7** = 97:3 in pentane and 94:6 in acetonitrile.



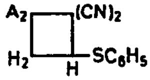
BTF *(C_6H_6)*	*4 900*	*0.66*	*(< 0.034)* [8]	*> 10 000*	*61*	*13 000*	*(< 0.0024)* [8]
TCNE *(EtOAc)*	*24*	*13*	*0.14*				

The decline of the CT complex color allowed photometric rate measurements. The second-order rate constant essentially refers to the formation of the zwitterion [7] and the structure-rate effects reflect stabilizations of the cationic portion of the intermediate 1,4-dipole. The numerical data below the formulae are values of 10^3k_2 ($M^{-1}s^{-1}$) in benzene at 20°C.

Ketene S,S-acetals outrun thioenol ethers in reactivity by at least one order of magnitude. Noteworthy is the 200-fold higher reaction rate of a bridged vs. an open-chain S,S-acetal. Bridging enforces a geometry which allows *optimum* stabilization of the intermediate by the +M effect of sulfur.

Methyl groups at the β position of vinyl sulfides or ketene S,S-acetals diminish the rate of dipole formation even more than in cycloadditions of BTF with vinyl ethers [7]. In fact, two β-methyl groups suppress [2+2] additions *totally*: (Ethylthio)isobutene or bis(methylthio)isobutene transfer a hydride ion on BTF, instead [8]. Dimethoxyisobutene is the only β,β-dimethylated donor olefin studied so far which undergoes a [2+2] cycloaddition with BTF [5].

R:	$C(CH_3)_3$	$CH(CH_3)_2$	CH_3	$(CH_2)_2CH_3$	$CH_2C_6H_5$	C_6H_5
BTF *(C_6H_6)*	*29 000*	*19 000*	*4 900*	*2 000*	*450*	*93*
TCNE *(EtOAc)*	*72*	*71*	*24*	*67*	*19*	*0.63*

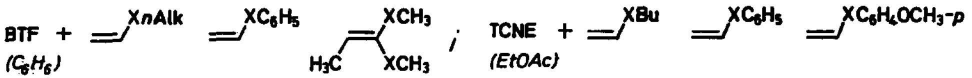


ΔH_r in CH_2Cl_2 at 25°C

A = CF_3 -26.0 kcal mol^{-1}

A = CN -21.0 " "

Alkyl groups attached to the *heteroatom* of vinyl sulfides attenuate k_2 with increasing σ_I values, Taft's inductive substituent constants. The substituent influence is higher for BTF than for TCNE. The comparison of the two acceptor olefins reveals that BTF exceeds TCNE 24- to 400-fold in k_2. The superiority reaches a factor of 8200 ($\Delta\Delta G^{\neq}$ 5.3 kcal mol^{-1}) for methyl vinyl sulfide when measured in the same solvent (benzene, 25°C): 10^3k_2 for BTF *4900*, for TCNE *0.60*. The rationalization given for vinyl ethers [7] applies here unchanged. Similarly as observed for butyl vinyl ether [7], the [2+2] cycloaddition to phenyl vinyl sulfide is for BTF more exothermic by 4.8 kcal mol^{-1} than for TCNE [9].



BTF + (C_6H_6)	XnAlk	XC_6H_5	H_3C, XCH_3, XCH_3	TCNE + (EtOAc)	XBu	XC_6H_5	$XC_6H_4OCH_3$-p
X = S	*2 000*	*93*	*61*		*77.3*	*0.63*	*44.7* [10]
X = O	*2 700*	*1.41*	*> 24 000*		*20.0*	*0.0043*	*0.024* [10]
k_s/k_o	0.7	66	< 0.003		3.9	146	1 900

An astounding phenomenon is common to BTF and TCNE: vinyl sulfides match or even surpass vinyl ethers in cycloaddition rate. In the 10^3k_2 values above, this is most conspicuous for TCNE + $H_2C{=}CH\text{-}XAr$ [3,10]; steric effects are less disturbing for TCNE than for BTF. However, $k_o >> k_s$ holds for methylketene acetals. The "double-bond rule" is responsible for the widespread misconception that oxonium is favored over sulfonium. *Ab initio* calculations intimate comparable energies for the fully developed ions [11,12]. Since $H_2C{=}CH\text{-}OH$ is more stable than $H_2C{=}CH\text{-}SH$, the following isodesmic reaction (MP4/6-31G*//6-31G*)[13], pertinent to our zwitterion formation, is exothermic:

$$H_2C{=}CH\text{-}SH + H_2C^+\text{-}OH \rightarrow H_2C{=}CH\text{-}OH + H_2C^+\text{-}SH \quad \Delta H = -5.6 \text{ kcal mol}^{-1}$$

Polar solvents facilitate [2+2] cycloadditions of BTF with enol ethers; this observation argues strongly for a zwitterionic intermediate [2]. Similarly, phenyl vinyl sulfide and BTF react 1600 times faster in acetonitrile than in cyclohexane. Again, this ratio supports the notion of *considerable* charge separation in the activation step. Moreover, log k_2 for BTF + phenyl vinyl sulfide increases in 17 solvents roughly with the empirical polarity parameter E_T (Fig. 1).

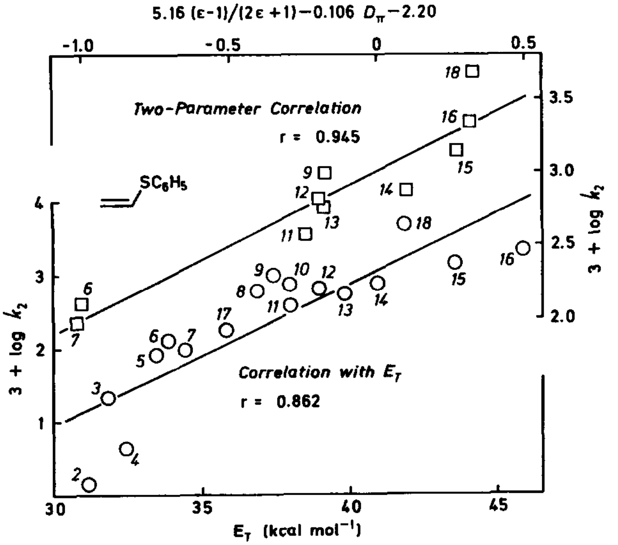


Figure 1. Plot of log k_2 for the [2+2] cycloaddition of BTF to phenyl vinyl sulfide in various solvents at 20°C versus E_T and a combination of Kirkwood's polarity function and D_π (see text). The key to the solvent numbers is offered in Fig. 1 of the preceding communication [7]; *17* trichloroethylene, *18* nitrobenzene.

The general equation (1) relates rate constants $k_{obs,1}$ and $k_{obs,2}$ in solvents 1 and 2 to the free enthalpies of transition states (TS) and starting materials (SM). As shown, the rate ratio $k_{obs,1}/k_{obs,2}$ depends upon the free transfer enthalpies $\delta\Delta G_{1\rightarrow2}$ from solvent 1 into solvent 2.

$$\ln (k_{obs,1}/k_{obs,2}) = (\delta\Delta G^{TS}{}_{1\rightarrow2} - \delta\Delta G^{SM}{}_{1\rightarrow2})/RT \quad (1)$$

Our earlier discussion of solvent effects on [2+2] cycloaddition rates was focussed on charge separation, *i.e.*, increase of dipole moment in the activation process, and its consequences on dielectric constant ϵ and electrostriction of solvent molecules. However, the dissipation of charge is not the only kind of solvent interaction. Although TCNE has no dipole moment, its π or σ complexation with nucleophilic solvents is a rate decreasing factor which we neglected previously. Konovalov et al. [14] measured solvation energies of TCNE + partner and demonstrated the importance of $\delta\Delta H^{SM}$ for Diels-Alder reactions and [2+2] cycloadditions of TCNE and other acceptor olefins. The desolvation is dominant in the reaction TCNE + diphenyldiazomethane, and its log k_2 served Oshima, Arikata, and Nagai [15] for defining D_π as a parameter of nucleophilic solvation.

We correlated the log k_2 of our test reaction with the polarity function $(\epsilon-1)/(2\epsilon+1)$ *and* D_π, the latter being available only for 10 of the solvents used. The result on the upper abscissa of Fig. 1 reveals that D_π enters with the coefficient -0.106 instead of -1.0 for TCNE + diphenyldiazomethane. *We conclude that transsolvation of BTF does not contribute significantly to the solvent/rate effects.*

REFERENCES AND NOTES

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