$$(3)$$

10a, R = (EtO)$_2$PO
 b, R = Me$_3$Si
 c, R = CH$_3$CO

LDA in THF gave rise to exclusive formation of enolate 8 which, in addition to being alkylated with methyl iodide (8 → 9[5], 76%), was trapped with DEPCl (8 → 10a, 75%), TMSCl (8 → 10b, 74%), and CH$_3$COCl (8 → 10c, 72%).

The above data clearly establishes the ability to generate kinetic enolates of diketones such as 1 and 7 without complications due to intermolecular and intramolecular processes. However, in sharp contrast to the results reported in eq 1–3, diketone 11,[8] which possesses acidic hydrogens at C(4) and C(8) and is not capable of undergoing γ-dienolate formation due to the presence of the C(10) methyl group, undergoes exclusive deprotonation at C(4) under kinetically controlled conditions (eq 4) em-


$$(4)$$
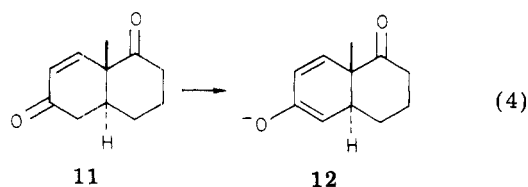
ploying the procedure described above. Alkylation of cross-conjugated enolate 12 with methyl iodide gave rise to exclusive formation of pure diketone 13[5] in 72% isolated yield. Trapping of 12 with DEPCl, TMSCl, and CH$_3$COCl produced dienes 14a–c in the yields specified.

14a, R = (EtO)$_2$PO [73%]
 b, R = Me$_3$Si [65%]
 c, R = CH$_3$CO [71%]
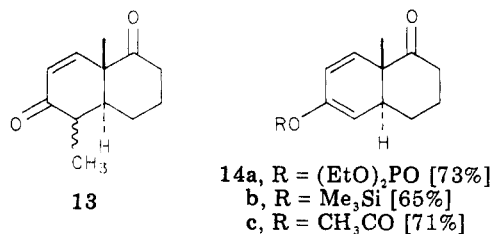
While it is not clear what factors are responsible for the

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(8) Diketone 11 was prepared from the known keto ketal iii[9] via the

iii
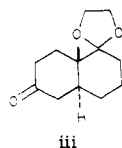
following sequence of reactions: (a) C$_6$H$_5$SeCl/EtOAc; (b) H$_2$O$_2$/CH$_2$Cl$_2$/Pyr; (c) H$_3$O$^+$/THF.
(9) Bauduin, G.; Pietrasanta, Y. *Tetrahedron* 1973, 29, 4225.

differences observed during the kinetically controlled deprotonation of substrates 1, 7, and 11, the ability to generate a specific enolate and carry out useful chemistry in the presence of an additional carbonyl unit, without prior protection, can be extremely useful during elaboration of complex molecules.

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Rates and Mechanism of (2 + 2) Cycloaddition Reactions of Tetracyanoethylene to Thioenol Ethers

Summary: The high influence of solvent polarity on rate indicates the mechanistic analogy between tetracyanoethylene cycloadditions to thioenol ethers and those to enol ethers for which a pathway with zwitterionic intermediate was established previously, whereas the structure–rate relation reveals a higher sensitivity of thioenol ethers to steric effects.

Sir: The recent report of Okuyama, Nakada, Toyoshima, and Fueno[1] on the rates of tetracyanoethylene (TCNE) additions to thioenol ethers prompts us to publish our evidence for the zwitterionic pathway which is based on additional mechanistic criteria. After establishing zwitterionic intermediates in TCNE cycloadditions to enol ethers,[2] we applied the same mechanistic probes to the sulfur analogues.

We studied spectrophotometrically the kinetics of (2 + 2) cycloadditions of TCNE to *cis*- and *trans*-propenyl ethyl sulfides (1 and 2)[3] in ten solvents of widely varying polarity
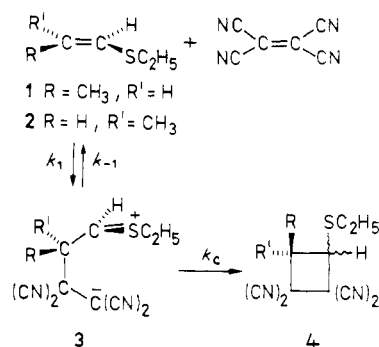
as judged by their E_T values, an empirical measure of solvent polarity.[4] The extinction of the violet or deep blue charge-transfer complexes (λ_{max} 500–600 nm) is proportional to the TCNE concentration when 10–30 equiv of thioenol ether are used. A low and constant concentration

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(1) T. Okuyama, M. Nakada, K. Toyoshima, and T. Fueno, *J. Org. Chem.*, 43, 4546 (1978).
(2) Review: R. Huisgen, *Acc. Chem. Res.*, 10, 117 (1977).
(3) Satisfactory C, H, N, and S analyses were obtained for all new cycloadducts.
(4) C. Reichardt, "Lösungsmitteleffekte in der organischen Chemie", Verlag Chemie, Weinheim, W. Germany, 1969, pp 141–149, 162.
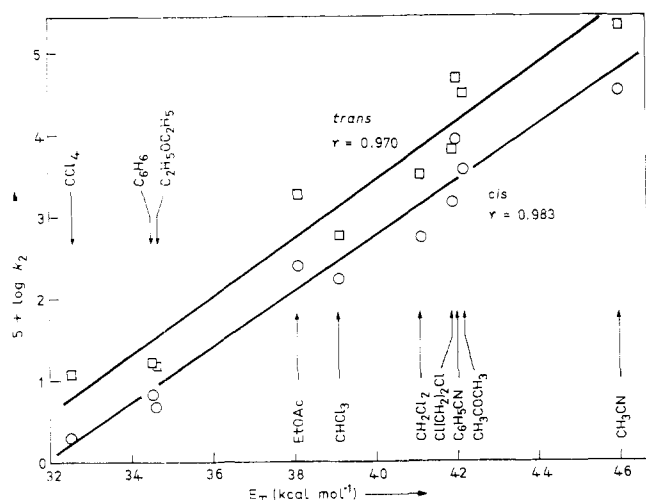
Figure 1. Rate constants k_2 for TCNE cycloadditions to ethyl *cis*- and *trans*-propenyl sulfide in various solvents at 25 °C in a logarithmic plot against E_T.

of **1** and **2** (0.075–0.085 M) kept polarity changes of the medium by the thioenol ether at low levels.[5]

The overall second-order rate constants k_2 display a spectacular increase with solvent polarity (Figure 1). The addition to **1** and **2** is in acetonitrile 17 100 and 16 800 times faster than in CCl_4, compared with k_2(acetonitrile)/k_2 (CCl_4) = 2900 for isobutenyl ethyl ether, 17 000 for 3,4-dihydro-2*H*-pyrane, and 7600 for anethole.[6] The increase of k_2 corresponds to $\Delta\Delta G^\ddagger = 5.8$ kcal mol^{-1}, which is due to the rising dielectric constant of the solvent and the $\Delta\Delta G$ of solvation during the activation process. The data harmonize with the formation of the zwitterion **3**. The experimental k_2 value contains besides k_1 a partition coefficient of the intermediate **3** for cyclization and dissociation,[7] $k_c/(k_{-1} + k_c)$; its solvent dependence is probably small compared with that of k_1, but may well be responsible for variations of the net trans,cis rate ratios (2.4–8.2), which disclose no obvious relation to solvent polarity.

The cycloaddition constants on structural variation of the thioenol ether[3] are compared in Table I with those of corresponding O ethers.[8]

(a) Surprisingly, the k_2 values of S and O ethers are of similar magnitude. The argument that sulfonium zwitterions of type **3** are not as good as oxonium zwitterions is somewhat fallacious, because the ground-state energies likewise influence $\Delta G^\ddagger$.

(b) Steric effects of β-alkylation are greater for S than for O ethers. The rate constant of vinyl ethyl *ether* is increased two- to threefold by *trans*- or *cis*-β-methyl, whereas β,β-dimethyl causes a decrease by a factor of 0.7. The same substituents decrease the rate of vinyl ethyl *sulfide* 5-, 19-, and 450-fold. Thus, the acceleration of addition to O ethers due to the electron release by CH_3 is superseded in the S ethers by steric hindrance, which is especially evident in the k_2 of *cis*-1-alkenyl ethyl sulfides: vinyl/*cis*-propenyl/*cis*-1-butenyl = 1:0.052:0.0043.

(c) Greater trans,cis rate ratios (3.8–30) of 1-alkenyl sulfides compared with alkenyl ethers (1.1–1.5) are a consequence of this steric effect. The screening of the

(5) Increasing concentrations of enol ether (3,4-dihydro-2*H*-pyrane) increased the polarity of dibutyl ether and decreased the polarity of acetonitrile, thereby alluding to a concentration dependence of the rate constants: see R. Huisgen and R. Schug, *J. Chem. Soc., Chem. Commun.*, 59 (1975).
(6) G. Steiner and R. Huisgen, *J. Am. Chem. Soc.*, **95**, 5056 (1973).
(7) R. Huisgen and H. Graf, *J. Org. Chem.*, following paper in this issue.
(8) R. Huisgen and G. Steiner, *Tetrahedron Lett.*, 3763 (1973).

Table I. Rate Constants for TCNE Cycloadditions to Thioenol Ethers in Ethyl Acetate at 25 °C

RR′C=CHSR″			config-uration	$10^3 k_2$, M^{-1} s^{-1}	enol ether, $10^3 k_2$, M^{-1} s^{-1}
R	R′	R″			
H	H	CH_3		24	
H	H	C_2H_5		63	19
H	H	$n\text{-}C_4H_9$		77	20
H	H	$CH(CH_3)_2$		71	112^a
H	H	$C(CH_3)_3$		72	255
H	H	C_6H_5		0.63	0.0045
CH_3	H	CH_3	cis	2.74	16
CH_3	H	CH_3	trans	15	13
CH_3	H	C_2H_5	cis	3.3	40
CH_3	H	C_2H_5	trans	12.6	53
CH_3	H	$n\text{-}C_3H_7$	cis	2.7	32
CH_3	H	$n\text{-}C_3H_7$	trans	18	48
CH_3	H	$CH(CH_3)_2$	cis	1.8	
CH_3	H	$CH(CH_3)_2$	trans	13.4	
C_2H_5	H	C_2H_5	cis	0.27	15
C_2H_5	H	C_2H_5	trans	8.1	17
CH_3	CH_3	C_2H_5		0.14	15

^{a} Cyclohexyl vinyl ether.

reacting β-carbon atom may contribute to it as well as steric inhibition of resonance in the sulfonium zwitterion of type **3**.

(d) Branching of the *O*-alkyl increases the k_2 of cycloaddition by increasing electron release; this effect is compensated by the larger steric requirements of *S*-alkyl.

(e) Fueno et al.[1] observed a higher ρ value for the TCNE cycloadditions to aryl vinyl sulfides (−5.5) than for aryl vinyl ethers (−3.1). The a priori expectation of the opposite effect underlines that the diverse substituent effects of OR and SR are not fully understood.

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Stereochemistry of Tetracyanoethylene Cycloadditions to Thioenol Ethers

Summary: In the cyclobutane formation from ethyl *cis*-propenyl sulfide and *cis*-1-butenyl ethyl sulfide with tetracyanoethylene, the nonstereospecific portion of the cycloadduct rises with increasing solvent polarity in accordance with a zwitterionic intermediate, whereas cis → trans isomerization of the excess of thioenol ether signals the reversibility of zwitterion formation.

Sir: Cis and trans isomers of ethyl propenyl sulfide and 1-butenyl ethyl sulfide were separated by preparative VPC; steric purity: **1**, 99.6%; **2**, 99.5%; **3**, 99.2%; **4**, 98.8%. We
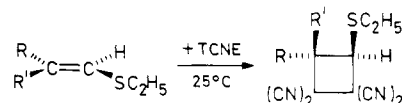
1 R = H , R′ = CH_3 , *cis* 5
2 R = H , R′ = C_2H_5 , *cis* 6
3 R = CH_3 , R′ = H , *trans* 7
4 R = C_2H_5 , R′ = H , *trans* 8

reacted 0.022–0.063 M thioenol ether with 0.025–0.072 M tetracyanoethylene (TCNE), i.e., a ~10% excess of the