

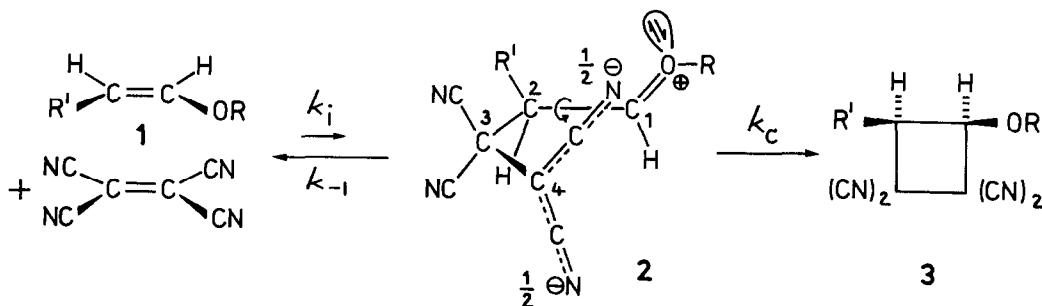
TETRACYANOETHYLENE AND ENOL ETHERS. RATES OF 2+2 → 4 CYCLOADDITIONS
AND STRUCTURAL VARIATION OF THE ENOL ETHER

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Cycloadditions of the type 2+2 → 4 (1) can take place step-wise through a diradical or a zwitterionic intermediate, or concertedly as a $[\pi 2_s + \pi 2_a]$ process (2). Williams, Wiley and McKusick (3) discovered the 2+2 → 4 cycloadditions of tetracyanoethylene (TCNE) to electron-rich double bonds. Common alkenes do not react with TCNE except for relatively slow additions to some exocyclic or strained double bonds and some 1,3-dienes (4,5). Enol ethers offer the optimum for cyclobutane formation while TCNE and enamines furnish zwitterionic adducts at -40° which do not cyclize, but eliminate hydrogen cyanide at 20° (6). Also chlorotricyanoethylene reacts with enamines by tricyanovinylating of the β -carbon atom (7).



Although the TCNE cycloadditions to electron-rich double bonds are regarded as the example par excellence for reaction via a zwitterionic intermediate, the mechanistic evidence for this pathway was meager. Only recently has the evidence accumulated. Some rotation within the zwitterion 2 gives rise to a non-stereospecific part of the reaction which increases with solvent polarity (5,8). Geometrical isomerization of the excess of cis- and trans-1-alkenyl alkyl ether (1) established the reversibility of zwitterion formation (8). From the high dependence of the cycloaddition rate constant on solvent polarity the dipole moments of the transition states have been evaluated (9); they are 2/3 of the ones calculated for the oriented zwitterion 2. The zwitterionic intermediate can be trapped by alcohol (10). It is shown here that the structure of the enol ether influen-

ces the addition rate constant in a manner to be expected for zwitterion formation in the rate-determining step. Bartlett and Kramer (5) measured rates of TCNE cycloadditions to 4-substituted styrenes and observed a 480-fold rate increase in going from 4-cyclopropyl to 4-methoxy.

On mixing TCNE and an enol ether in solution, the color of the charge-transfer (CT) complex is immediately produced. In the presence of at least 10 equivalents of enol ether the optical density of the CT complex is proportional to the TCNE concentration and the photometry of the CT complex band allows the evaluation of pseudo-first order rate constants. Division by the molar concentration of the enol ether provides the overall second order rate constant k_2 of the 2+2 cycloaddition which is the constant k_1 of zwitterion formation multiplied by the partition coefficient (8), $k_c / (k_c + k_{-1})$.

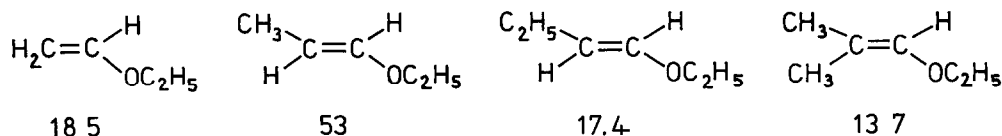
The numerical data below the formulae refer to $10^3 k_2$ ($l \cdot mol^{-1} sec^{-1}$) in ethyl acetate at 25° . All cycloadducts were isolated, analyzed, and spectroscopically characterized.

$ \begin{array}{c} H \\ \diagup \\ H_2C=C \\ \diagdown \\ O-R \end{array} \quad 4 $							
R	$-C_6H_5$	$-CH_2CH_2Cl$	$-C_2H_5$	$-n-C_4H_9$	$-cyclo-C_6H_{11}$	$-C(CH_3)_3$	
$10^3 k_2$	0.0043	0.92	18.5	20	112	255	

$ \begin{array}{c} C_2H_5 \quad H \\ \diagdown \quad \diagup \\ C=C \\ \diagup \quad \diagdown \\ H \quad O-R \end{array} \quad 5 $					
R	$-CH_3$	$-C_2H_5$	$-CH(CH_3)_2$	$-C(CH_3)_3$	
$10^3 k_2$	4.2	17.4	57	140	

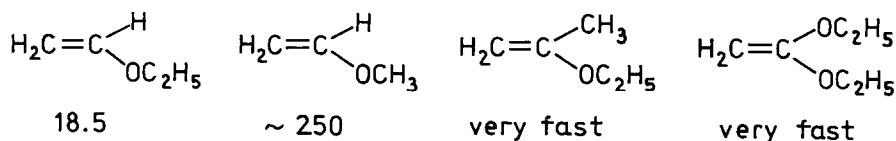
The cycloaddition constants of simple vinyl ethers 4 increase with the donor activity of the oxygen, the $\log k_2$ obey linear relations with the λ_{max} of the CT complex, i.e., with the ionization potentials of the vinyl ethers (11), as well as with Taft's polar substituent constants σ^* for R (12). The ionization energies and k_2 are both functions of the HOMO energies of 4. The correlation line between $\log k_2$ of the 1-butenyl ethers 5 and λ_{max} is different from the one of 4. A superposition of an electronic acceleration and a steric deceleration by

β -alkyl can be diagnosed from the following data.



The rate constants for TCNE additions to cis-trans isomeric 1-alkenyl alkyl ethers do not differ by much (Table 1) compared to the analogous 2+2 cycloadditions of ketenes, in which cis-alkenyl ethers react up to 180 times faster than do the trans isomers (13) as a consequence of the concerted mechanism [$\pi^2_s + \pi^2_a$]. Neither the variation of the alkoxy substituent nor the β -alkyl group changes $k_{2\text{cis}}/k_{2\text{trans}}$ dramatically except for the sterically crowded C-isopropyl group. The second part of Table 1 discloses for 1-propenyl methyl ether a 10^4 -fold increase of the addition constant in going from CCl_4 to acetonitrile as solvent; however, $k_{2\text{cis}}/k_{2\text{trans}}$ is barely affected. The ratio 1.21 in acetonitrile comes close to the true formation constants k_1 of the zwitterion because the partition coefficient $k_c/(k_c + k_{-1})$ is ca. 0.5 for the closely related cis- and trans-1-butenyl ethyl ether (8).

cis- and trans-1,2-Diethoxyethylene (Table 1) do not accept TCNE faster, but somewhat slower than 1-butenyl ethyl ether which is similar in its steric requirements. The donor activities of the two ethoxy groups seem to impair each other. SCF calculations (14) of mono- and 1,2-dihydroxyethylene confirm a higher electron density on the β -carbon atom of the monohydroxy compound. Probably, the loss of the conjugation energy of the second ethoxy function in forming the zwitterion 2 also plays a role.

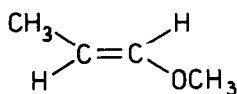


α -Substituents contribute to the stabilization of the carbonium oxonium charge of the zwitterion 2. The acceleration by methyl is larger than the one by phenyl due to steric hindrance of resonance in α -methoxystyrene. cis- β -Methoxystyrene ($10^3 k_2 = 0.0025$), however, reacts 100,000 times more slowly than the α -isomer; the bulk effect of the phenyl at the reacting β -carbon and the loss of phenyl conjugation in the zwitterion 2 are supposed to be responsible. This factor of 10^5 sheds light on the different roles of the enol ether α - and β -carbon in the rate-determining step of the cycloaddition. Ketene diethylacetal reacts with TCNE

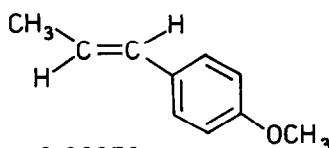
(unstable adduct) so fast that the CT color does not even become visible.

Table 1. Rate Constants $10^3 k_2$ ($l \cdot mol^{-1} sec^{-1}$) of TCNE Cycloadditions to cis-trans Isomeric Enol Ethers at 25°

				$\frac{k_2 \text{ cis}}{k_2 \text{ trans}}$
		<i>cis</i>	<i>trans</i>	
a. Variation of the enol ether in ethyl acetate				
R	OR'			
C ₂ H ₅	OCH ₃	55	42	1.31
C ₂ H ₅	OC ₂ H ₅	15	17	0.88
C ₂ H ₅	OCH(CH ₃) ₂	28	57	0.49
C ₂ H ₅	OC(CH ₃) ₃	80	140	0.57
CH ₃	OC ₂ H ₅	40	53	0.75
C ₂ H ₅	OC ₂ H ₅	15	17	0.88
n-C ₄ H ₉	OC ₂ H ₅	11	15	0.73
CH(CH ₃) ₂	OC ₂ H ₅	0.060	1.52	0.04
OC ₂ H ₅	OC ₂ H ₅	1.7	8.8	0.19
b. Solvent dependence for propenyl methyl ether (R = R' = CH₃)				
Carbon tetrachloride		0.048	0.046	1.04
Ethyl acetate		16	13	1.23
Acetonitrile		496	408	1.21



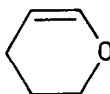
13.2



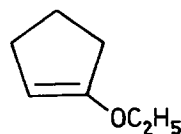
0.00050



2.26

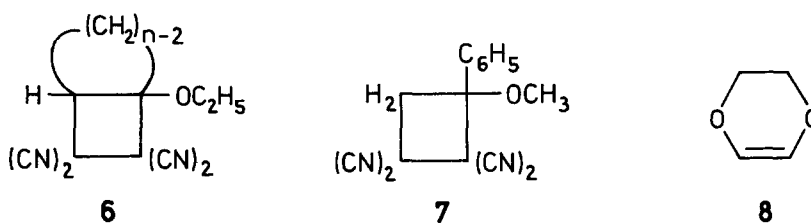


0.077



very fast

Insertion of a benzene nucleus between methoxy group and ethylenic carbon of trans-1-propenyl methyl ether dampens the donor activity of the oxygen function; anethole adds TCNE 26,000-fold more slowly. The addition constant of 2,3-dihydrofuran resembles that of the open-chain cis-1-propenyl methyl ether, while that of the six-membered analogue, 2,3-dihydro-4H-pyran, is smaller by a factor of 300 (15). The high reactivity of 1-ethoxycyclopentene and 1-ethoxycyclohexene accords with that of 2-ethoxypropene.



The 2+2 cycloadditions of TCNE to enol ethers are normally complete and most of them provide virtually quantitative yields of the colorless cyclobutane derivatives. In a few cases, the cycloreversion becomes noticeable. Of all the mentioned adducts only 6, $n = 5, 6$, and 7 are partially dissociated in solution as evidenced by the appearance of the CT color. On adding cis-1-propenyl ethyl ether to the violet solution of 7 in chloroform at 50°, the CT complex color faded and 97% of the 1-ethoxy-2-methyl-3,3,4,4-tetracyanocyclobutane was isolated. Thus, the less reactive propenyl ether produces the more stable product. In contrast to cis-1,2-diethoxy-ethylene, 1,4-dioxene (8) does not yield a cycloadduct, but forms only a violet CT complex (λ_{max} 525 nm in CHCl_3).

Are the CT complexes intermediates of the 2+2 cycloadditions of TCNE? We must leave the question open. No correlation of CT complex stabilities and cycloaddition constants was found by Bartlett (5) in the investigation of TCNE and *p*-substituted styrenes. Equilibrium constants of complex formation from enol ethers and TCNE are too small to be measured by the usual techniques, the optical density of the deep violet complex of 8 and TCNE is proportional up to high excess concentrations of 8 (16).

The intermediate 2 is a substituted tetramethylene. Salem and Rowland (17) recently described the tetramethylene structure by a wave function consisting of one term each for the singlet biradical and the zwitterionic structure, the ratio of the coefficients depends on the nature of the substituents. The intermediate of

the TCNE cycloadditions discussed here complies fully with the limiting case of the tetramethylene zwitterion, and to find evidence of hybrids between biradical and zwitterion remains a challenge to organic chemists.

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- (14) We express our thanks to Dr. G. Szeimies, Munich, for carrying out MINDO/2 calculations.
- (15) This phenomenon is mainly due to the relief of angle and conformational strain in the 5-membered ring. Reactions of cyclopentene via 4- to 6-membered cyclic transition states are faster than the ones of cyclohexene. See e.g. E.W. Garbisch, S.M. Schildcrout, D.B. Patterson, and C.M. Sprecher, J.Amer.Chem.Soc., 87, 2932 (1965).
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