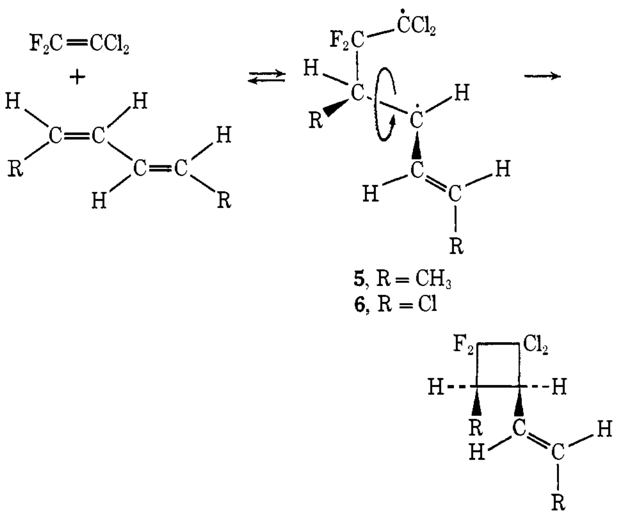
Table II. Ratios of Rate Constants Derived from the Data of Table I

	Ring closure / rotation	Ring closure / dissociation	Dissociation / rotation
Cis zwitterion **1**	k_2/k_r = 4.6	k_2/k_{-1} = 1.1	k_{-1}/k_r = 4.2
Trans zwitterion **2**	k_4/k_{-r} = 5.3	k_4/k_{-3} = 0.88	k_{-3}/k_{-r} = 6.0



5, R = CH_3
6, R = Cl

is revealing. For **5** at 80°, rotation about the marked double bond is ten times faster than cyclization.[3] The rotational equilibrium is nearly attained for **6** at 150°, while cyclization is 4.4 times faster than dissociation.[3] Thus, it is the rotation which is slowed down in the intermediates **1** and **2** of the TCNE cycloadditions due to the Coulomb attraction of the charged centers. Probably most of the zwitterions **1** and **2** are created in conformations with the smallest distance separating the charged centers.

The rate ratios of Table II refer to acetonitrile. In nonpolar solvents the rotation is suppressed even more by the higher Coulombic force which leads to larger ratios of cyclization *vs.* rotation, *e.g.* 50 for **1** and **2** in benzene.[1,4]

Further support for zwitterionic intermediates in TCNE cycloadditions to enol ethers comes from the dependence of rate on solvent polarity and on structure of the enol ether, as well as from the trapping reaction with alcohol.

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(3) P. D. Bartlett, C. J. Dempster, L. K. Montgomery, K. E. Schueller, and G. E. H. Wallbillich, *J. Amer. Chem. Soc.*, **91**, 405 (1969); P. D. Bartlett and G. E. H. Wallbillich, *ibid.*, **91**, 409 (1969).

(4) It may be emphasized that the ratio of ring closure to dissociation for the trans zwitterion **2** stems from experiments with *cis*-1-butenyl ether and *vice versa.* The smaller percentage of the material which isomerizes through rotation in *nonpolar* solvents does not allow the quantitative evaluation of the ratio of ring closure to dissociation here.

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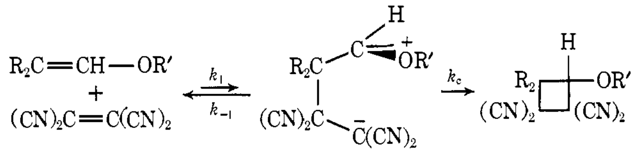
Tetracyanoethylene and Enol Ethers. Dependence of Cycloaddition Rate on Solvent Polarity

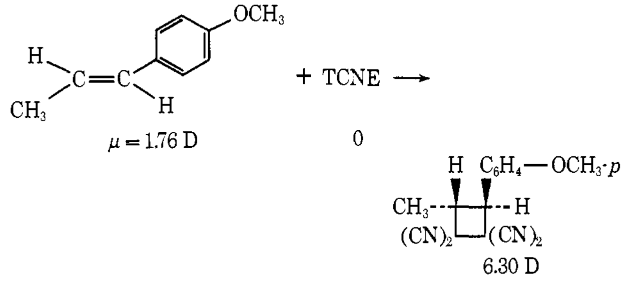
Sir:

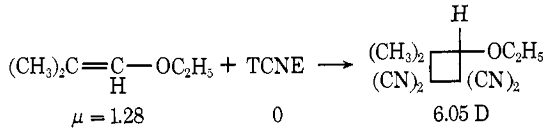
The kinetics of tetracyanoethylene (TCNE) cycloadditions to enol ethers (at least 10 equiv) have been measured photometrically by the color of the charge-transfer complex which is produced instantly. The overall k_2 values are the rate constants of zwitterion formation times the partition coefficient $k_c/(k_{-1} + k_c)$.[1]



The solvent influence on the cycloaddition rate constant (Figure 1) is of an unusual magnitude as evidenced by k(acetonitrile)/k(cyclohexane) = 29,000 for anethole,[2] 10,800 for 1-ethoxyisobutene, and 2600 for butyl vinyl ether, as well as k(acetonitrile)/k(CCl_4) = 17,000 for 2,3-dihydro-4*H*-pyrane. These ratios correspond to a $\Delta\Delta G^{\neq}$ of up to 5.5 kcal/mol for the increase of solvation energy during activation. This is a much higher solvent dependence than reported for the reaction of chlorotricyanoethylene with 4-methoxystyrene.[3]

The formation of the zwitterionic intermediate—its energy trough is surrounded by barriers of equal height (Figure 2)[1]—is assumed to be rate determining. In replacing a nonpolar by a polar solvent, the rate constant k_1 (and probably the overall constant k_2) profits from a decrease of activation energy by $\Delta E_2 - \Delta E_1$.





How can one distinguish between the zwitterionic mechanism and a hypothetical concerted cycloaddition with equal bond formation in the transition state? The dipole moments of reactants and adducts, measured in benzene, reveal a substantial increase of charge separation and suggest an acceleration by polar solvents.

Based on an electrostatic model of Kirkwood,[4] Laidler and Eyring[5] developed eq 1 for the solvent

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(1) See the preceding communication: R. Huisgen and G. Steiner, *J. Amer. Chem. Soc.*, **95**, 5055 (1973). A partition coefficient of 0.5 was found for TCNE + *cis*- and *trans*-1-butenyl ethyl ether in acetonitrile at 20°.

(2) Dr. D. W. Wiley, E. I. du Pont de Nemours Co., has measured k(acetonitrile)/k(cyclohexane) = 63,000 for the system TCNE + *p*-methoxystyrene (private communication).

(3) k(acetonitrile)/k(cyclohexane) = 200; J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, **84**, 2216 (1962).

(4) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934). See also C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier, New York, N. Y., 1952.

(5) K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940); S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1944, p 419. See also E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms," Academic Press, New York, N. Y., 1966, p 59.

Table I. Calculated Dipole Moments of the Transition States and the Zwitterions for the Cycloaddition of TCNE to Four Enol Ethers

	Butyl vinyl ether	1-Ethoxy-isobutene	2,3-Dihydro-4*H*-pyrane	Anethole
R as in eq 3	11.8	13.2	14.8	19.6
μ(enol ether), D	1.25	1.28	1.33	1.96
Molar vol (enol ether), cm^3	129	129	91.4	150
Molar vol (transition state), cm^3	236	236	198	257
r(enol ether), Å	3.7	3.7	3.3	3.9
$r_\pm$(transition state), Å	4.5	4.5	4.3	4.7
$\mu_\pm$(transition state), D	10.3	11.0	10.7	14.0
Charge distance zwitterion, Å	3.0	3.0	3.5	4.0
Charge moment, D	14	14	14	19
Calcd μ zwitterion, D	17	17	17	21

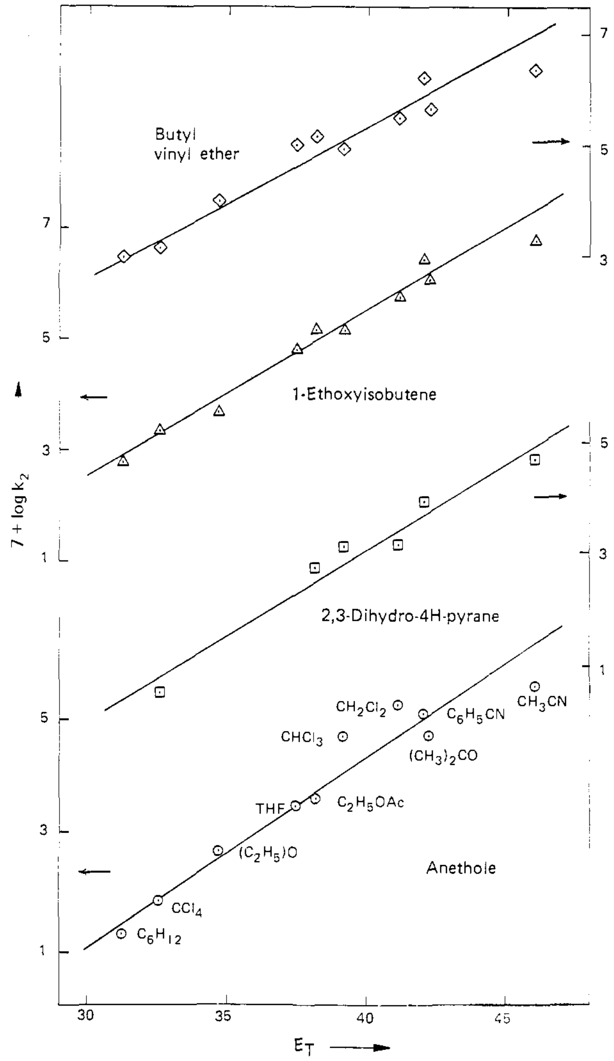

Figure 1. Rate constants k_2 for [2 + 2] cycloadditions of TCNE to anethole, 2,3-dihydropyrane, and 1-ethoxyisobutene at 25° and to butyl vinyl ether at 20° in various solvents plotted against the parameter E_T (K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963); C. Reichardt, "Lösungsmitteleffekte in der organischen Chemie," Verlag Chemie, Weinheim, 1969) of solvent polarity.

$$\ln k = \ln k_0 - \frac{1}{k_B T}\left(\frac{\epsilon - 1}{2\epsilon + 1}\right)\left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_\pm^2}{r_\pm^3}\right) \quad (1)$$

dependence of the rate constant of two spherical dipolar molecules A and B; k_0 refers to vacuum and k to a solvent with the dielectric constant ϵ. Equation 1

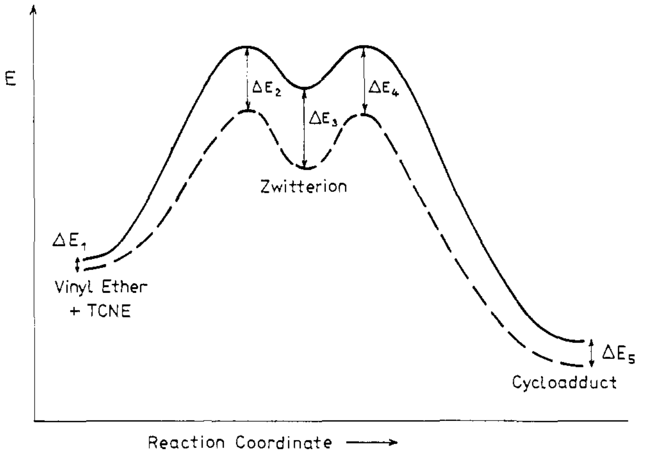

Figure 2. Schematic energy profile for the cycloaddition of TCNE to an enol ether in nonpolar (solid line) and highly polar (broken line) solvent.

permits one to evaluate $\mu_\pm$, the dipole moment of the transition state, from the known solvent dependence of k_2.

Fortunately, log k_2 showed a fairly linear dependence on $(\epsilon - 1)/(2\epsilon + 1)$ of the solvent;[6] eq 2 defines the

$$R = \Delta \log k_2/\Delta[(\epsilon - 1)/(2\epsilon + 1)] \quad (2)$$

slopes R of the straight lines as a measure of the sensitivity to the change of solvent polarity.

The molar volumes, obtained from the densities, provided the radii r of the idealized spherical molecules. The molar volume of the transition state was set equal to the sum of the reactants minus one double bond increment.[7] The zero dipole moment of TCNE furnishes eq 3 with subscript A referring to the enol ether.

$$\mu_\pm^2 = r_\pm^3\,[(\mu_A^2/r_A^3) + 2.303Rk_BT] \quad (3)$$

From eq 3 $\mu_\pm = 10.3 - 14.0$ D was calculated for the cycloadditions of TCNE to four model enol ethers (Table I). These dipole moments are larger than expected for the transition states of synchronous cycloadditions.

The stereochemical studies[8] suggest a preference of the zwitterionic intermediates for conformation **1** of low Coulomb potential. Values for μ(zwitterion) were estimated as the vector sum of the "charge moment"

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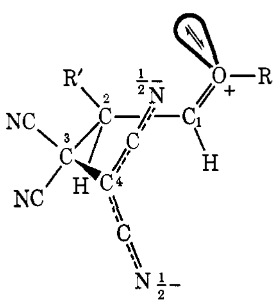
(6) The frequent failure of this correlation is mainly due to the specific solvation forces of protic solvents. Protic solvents were not used here (Figure 1).

(7) W. Biltz, *Justus Liebigs Ann. Chem.*, **453**, 259 (1927); *Z. Phys. Chem., Abt. A*, **151**, 13 (1930).

(8) R. Huisgen and G. Steiner, *J. Amer. Chem. Soc.*, **95**, 5054 (1973).



1

(point charges on oxygen and in the center of the line connecting the two anionic nitrogens) and the moments of the cyano groups at C-3 of **1**. The transition state moments, $\mu_{\pm}$, come out as two-thirds of the μ(zwitterion) in Table I. This seems reasonable because (a) the charge separation is not yet complete in the transition state of zwitterion formation and (b) optimal solvation (Kirkwood's concept[4]) is probably not achieved in the transition state.

Though the results are consistent with zwitterionic intermediates in the [2 + 2] cycloadditions of TCNE, the precision of $\mu_{\pm}$ should not be overestimated because the concept[4] is based on many simplifications.

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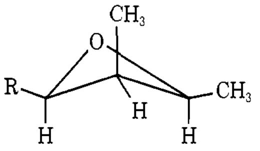
Paterno–Büchi Reactions of Aromatic Aldehydes with 2-Butenes and Their Implication on the Rate of Intersystem Crossing of Aromatic Aldehydes

Sir:

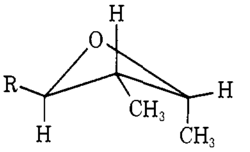
Arnold reported that benzophenone reacted with isomeric 2-butenes to give the same mixture of oxetanes suggesting that the Paterno–Büchi reaction of aromatic carbonyl compounds proceeded *via* the $^3n,\pi^*$.[1] We found that alkanals reacted photochemically with isomeric 2-butenes in a highly stereoselective manner suggesting that the Paterno–Büchi reaction of alkanals proceeded *via* predominantly the $^1n,\pi^*$.[2] This result indicated that the $^1n,\pi^*$ of aldehydes may react with olefins at a rate faster than that of intersystem crossing. The degree of stereoselectivity in the photochemical additions of aldehydes to isomeric 2-butenes may be thus used as a qualitative probe for the rates of intersystem crossing of their $^1n,\pi^*$. This communication deals with the reactions of benzaldehyde and its derivatives with isomeric 2-butenes and their implication on the rate of intersystem crossing in aromatic aldehydes.

Photochemical additions of benzaldehyde (**1a**), *p*-methoxybenzaldehyde (**1b**), *m*-methoxybenzaldehyde (**1c**), 3,4-methylenedioxybenzaldehyde (**1d**), and 2-naphthaldehyde (**1e**) to isomeric 2-butenes were investigated. The reactions were carried out with a Hanovia 450-W Hg arc with a Pyrex filter, and the quantum yield determinations were carried out with an apparatus previously described.[3] The oxetane fractions were isolated by chromatography over alumina. The by-products were alcohols and glycols.[4] Photochemical addition of an aldehyde to 2-butenes may yield four isomeric oxetanes (A–D). *cis*-2-Butene would give oxetanes A and B while *trans*-2-butene would give oxetanes C and D if the additions proceeded stereospecifically. The relative proportions of isomeric oxetanes were analyzed by the areas of low field aliphatic protons in the nmr spectra for **1a–c**. The assignment of isomeric structures was based upon (1) the cis vicinal C–H signals occur at a lower field than the isomeric trans vicinal C–H signals and (2) the cis vicinal C–H signals have higher coupling constants than those of the trans isomers.[2,5,6] The relative amounts of some of the oxetanes formed from **1e** (A and B from *trans*-2-butene and C and D from *cis*-2-butene) were so small such that the low field aliphatic proton signals in the nmr were no longer useful for their quantitative analysis, and they were determined from the integrated areas of the methyl signals in the nmr using 100-Hz scans. Due to the low solubility of **1d** in nonpolar solvents at low temperatures and the poor quantum efficiency of its reactions with 2-butenes, the reactions of **1d** with 2-butenes could not be investigated with the same degree of reliability as the reactions of other aldehydes. The relative amounts of oxetanes formed from **1d** were also estimated from the methyl signals in the nmr. The major source of experimental errors or uncertainties in this work is from the integration of the nmr signals. In all reactions carried out in neat 2-butenes, the unreacted 2-butene was recovered and analyzed for its isomeric composition. It was found that the starting 2-butene had not been appreciably isomerized (<5%). The results are summarized in Table I.

RCHO
1a,R = phenyl
b,R = *p*-methoxyphenyl
c,R = *m*-methoxyphenyl
d,R = 3,4-methylenedioxyphenyl
e,R = 2-naphthyl
f,R = methyl



A



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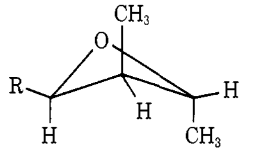
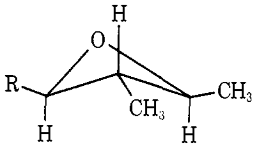


C



D

The nmr and ir spectra of the oxetane fractions isolated from the irradiations of **1a**, **1b**, or **1c** in neat *cis*- and *trans*-2-butenes were indistinguishable from each other. The results clearly indicated that the reactions proceeded *via* a long-lived biradical inter-

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[1] D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964).

[2] N. C. Yang and W. Eisenhardt, *J. Amer. Chem. Soc.*, **93**, 1277 (1971).

[3] D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

[4] N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Lett.*, 3657 (1964).

[5] Satisfactory elemental analyses and ir spectra for the oxetane fractions were obtained.

[6] J. J. Beereboom and M. S. von Wittenau, *J. Org. Chem.*, 30, 1231 (1965).